DALTON
FULL PAPER

Unexpected formation of gallium–gallium single bonds by irradiation of the hydride $[(Me_3C)_2GaH]_3$

Werner Uhl,* Lars Cuypers, Gertraud Geiseler, Klaus Harms and Bernhard Neumüller

Fachbereich Chemie der Philipps Universität Marburg, Hans-Meerwein-Straße,
D-35032 Marburg, Germany. E-mail: uhl@chemie.uni-marburg.de

Received 17th April 2001, Accepted 11th June 2001
First published as an Advance Article on the web 31st July 2001

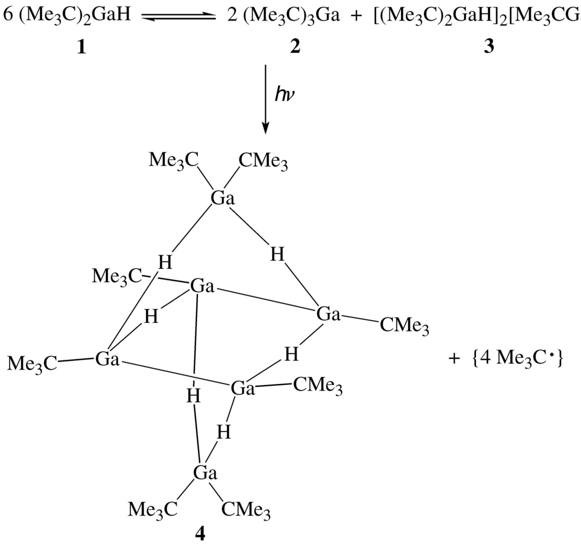
Di(*tert*-butyl)gallium hydride **1** dismutates partially in solution forming tri(*tert*-butyl)gallium **2** and the sesquihydride $[(Me_3C)_2GaH]_2[H_2GaCMe_3]_2$ (**3**). The loss of *tert*-butyl radicals upon irradiation of this mixture with day light or an UV lamp gave the hexagallium compound $(Me_3CGaGaCMe_3)_2(\mu\text{-}H)_2[\mu\text{-}H_2Ga(CMe_3)_2]_2$ (**4**), which possesses two Ga–Ga single bonds. These Ga_2 groups are bridged by two hydrogen atoms to give a six-membered Ga_4H_2 heterocycle. Couples of opposite gallium atoms of this heterocycle are bridged *via* Ga–H–Ga 3c–2e bonds by two $H_2Ga(CMe_3)_2$ ligands, which are situated above and below the molecular plane. Compound **4** may be described as a *hypho*-hexagallane(14) cluster compound.

Introduction

The compound $[(Me_3Si)_2CH]_2Ga–Ga[CH(SiMe_3)_2]_2$ containing a Ga–Ga single bond was the first stable organoelement digallane(4) derivative reported in the literature.[1] It possesses a surprisingly high thermal stability and was obtained by our group about 12 years ago when we treated the dioxane adduct of Ga_2Br_4[2] with the bulky alkyllithium compound $LiCH(SiMe_3)_2$.[3] During the last decade the synthesis of such digallanes(4) developed into a broad field of activities, and many derivatives were synthesized by similar methods or by the reduction of diaryl- or dialkyl-gallium halides with alkali metals.[4] However, these compounds merit particular interest not only because of their singular structures, but also owing to their fascinating chemical reactivity, which led to the observation of five different types of reaction and the isolation of many unprecedented products.[5] Here we report on the unexpected formation of a Ga–Ga single bond by the homolytic cleavage of Ga–C bonds.

Results and discussion

Recently, we published the synthesis and crystal structure of di(*tert*-butyl)gallium hydride **1**.[6] In contrast to other, dimeric dialkylgallium hydrides[7,8] compound **1** forms a trimer in the solid state *via* three 3c–2e Ga–H–Ga bonds. However, upon dissolution in non co-ordinating organic solvents dismutation occurred, and the characteristic resonances of tri(*tert*-butyl)gallium **2** and the sesquihydride $[(Me_3C)_2GaH]_2[H_2GaCMe_3]_2$ (**3**) were detected beside the signals of **1** in the ^1H and ^{13}C NMR spectra.[6] This dismutation reaction is reversible, and **1** could be isolated from solution by cooling and crystallization. However, storing such solutions in day light at room temperature led to slow decomposition and the formation of only one new product, (**4**, $(Me_3CGaGaCMe_3)_2(\mu\text{-}H)_2[\mu\text{-}H_2Ga(CMe_3)_2]_2$). A faster reaction was observed on irradiation with an UV lamp (366 nm) in *n*-hexane as solvent, which led to the complete consumption of the mixture of **1**, **2** and **3** over a period of 24 hours, eqn. (1). The new component was almost insoluble under these conditions and precipitated as a colourless solid in 83% yield. The ^1H NMR spectrum of **4** showed two resonances of chemically different *tert*-butyl groups in a 1 to 1 intensity ratio and two resonances for hydrogen atoms attached to gallium at δ 3.53 and 2.73 in a 1 to 2 ratio. A very broad absorption at 1638 cm^{-1} in the IR spectrum verified the occurrence of bridging hydrido ligands. Compound **4** is quite stable and decomposes at 158 °C forming elemental gallium.



(1)

The constitution of compound **4** was elucidated by a crystal structure determination (Fig. 1). A singular product had been formed which contains Ga–H and two Ga–Ga single bonds. These Ga_2 couples are connected by two bridging hydrogen atoms *via* 3c–2e bonds to give a six-membered Ga_4H_2 heterocycle in a *twist* conformation (torsion angles starting with H1–Ga2–Ga2′–H1′ counter clockwise 54.5°, −19.5°, −26.3°, 56.5°, −26.3°, −19.5°). The heterocycle is bridged by two $[H_2Ga(CMe_3)_2]^-$ groups, each hydrogen atom of which is attached to one gallium atom of the ring. These anions are situated above and below the molecular plane and co-ordinate to opposite gallium atoms. The structure of the molecular center may be described alternatively as a distorted octahedron of six gallium atoms, two edges of which are Ga–Ga single bonds, while six further edges are bridged by hydrogen atoms. Four edges remain unoccupied. The point group of the whole molecule is D_2. All gallium atoms are co-ordinatively saturated and have co-ordination numbers of four with distorted tetrahedral co-ordination spheres. The Ga–Ga single bonds are

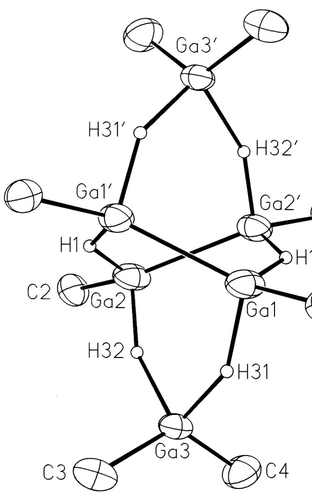


Fig. 1 Molecular structure of **4**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups are omitted. Important bond lengths (pm) and angles (°): Ga1–Ga1′ 263.8(2), Ga2–Ga2′ 264.2(2), Ga1–C1 201.7(8), Ga2–C2 201.0(8), Ga3–C3 200(1), Ga3–C4 196.9(9); Ga1′–H1–Ga2 140(2), Ga1–Ga1′–H1 98(2), Ga2′–Ga2–H1 101(3), Ga1–H31–Ga3 152(2), Ga2–H32–Ga3 156(2); the atoms Ga1′ and Ga2′ were generated by $-x + 1, y, -z + 3/2$.

longer (263.8 pm) than usually observed for digallane(4)[1,4] or digallate(5)[9] derivatives (<255 pm), which may be caused by the co-ordinative saturation of the gallium atoms, electrostatic repulsion and some steric stress in the cage. The Ga1′–H1–Ga2 bridge of the six-membered heterocycle is not symmetric [Ga2–H1 143(8) pm, Ga1′–H1 167(8) pm]. A similar argument holds for the Ga–H–Ga bridges to the H_2GaR_2 ligands, which have alternating short and long Ga–H distances to the atoms of the Ga–Ga bond [165(6) and 176(5) pm] or to the atom Ga3 [164(5) and 175(5) pm]. The shortest Ga–H distance is in the range of terminal Ga–H bonds,[6–8,10] the longer ones correspond to normal values of Ga–H–Ga bridges.[6–8] The Ga · · · Ga distances of these bridges are quite different (292.1 pm, Ga1 · · · Ga2′, and 331 pm on average for Ga1 · · · Ga3 and Ga2 · · · Ga3). Smaller ones (261 and 258 pm, respectively) were observed for the compounds $Me_2Ga(\mu\text{-}H)_2GaMe_2$[7] and Ga_2H_6,[8] however, both derivatives possess two hydrogen bridges between their gallium atoms. As expected, the Ga–C distances to the Ga(II) atoms of the Ga–Ga single bonds (201.4 pm on average) are longer than those of the H_2GaR_2 group (198.4 pm on average).

The mechanism of the unexpected formation of **4** is not clear. The homolytic cleavage of Ga–C bonds of the starting compound $(Me_3C)_2GaH$ (**1**) may be initiated by irradiation, and the radical intermediates may dimerize *via* Ga–Ga bond formation. Clearly, the monomeric product $Me_3C(H)Ga–Ga(H)CMe_3$ is not shielded enough to be stable and isolable. It gives a dimer *via* two Ga–H–Ga 3c–2e bonds and is further stabilized by two bridging $[(Me_3C)_2]_2GaH$ groups. Interestingly, tri(*tert*-butyl)gallane gave the same product (**4**) upon irradiation. Owing to its particular constitution and number of electrons compound **4** may be assigned to the *hypho*-class of cluster compounds. The corresponding boron hydride B_6H_{14} is known from quantum-chemical calculations only.[11] One of the calculated minimum structures is quite similar, although not identical to that of **4**, and has a six-membered B_4H_2 heterocycle in the molecular center with neighboring boron atoms bridged by BH_4 ligands, instead of opposite ones as in **4**. Thus, the synthesis and characterization of **4** may mark the starting point of a new type of cluster chemistry with the heavier elements of the third main-group.

Experimental

All procedures were carried out under purified argon. *n*-Hexane and cyclopentane were dried over $LiAlH_4$, pentafluorobenzene was stored over molecular sieves. Di(*tert*-butyl)gallium hydride **1** was obtained according to the literature procedure.[6]

Synthesis

Compound 4. Di(*tert*-butyl)gallium hydride **1** (1.622 g, 8.78 mmol) was dissolved in 25 mL of *n*-hexane. The solution was irradiated with an UV lamp (366 nm, 6 W) through the glass wall of the reaction flask for 24 h. A colourless solid precipitated, which was filtered off and was washed with 20 mL of *n*-hexane. Spectroscopically pure **4** remained. Owing to its low solubility in non co-ordinating organic solvents, only small quantities of **4** may be recrystallized from cyclopentane or pentafluorobenzene for further purification. Yield: 1.066 g (83%). Mp (argon, sealed capillary): 158 °C (decomp.) (Found: Ga, 47.5%; $C_{32}H_{78}Ga_6$ requires Ga, 47.1%). δ_H (C_6D_6, 300 MHz) 3.53 (s, 2 H, H1), 2.73 (s, 4 H, H31/H32), 1.35 and 1.28 (each s, 36 H, CMe_3). δ_C (C_6D_6, 75.5 MHz) 32.6 and 32.0 ($C\mathit{Me}_3$); GaC not detected. $\tilde{\nu}_{max}/cm^{-1}$ (CsBr, paraffin) 1638br,vs νGaH; 1460vs, 1377vs paraffin; 1363sh, 1316m, 1188w, 1161s δCH_3; 1009s, 969m, 939m, 836m, 808s δC_3C; 719m, 695s δGaH; 602m, 556w, 548w, 521w νGaC; 437w, 385w δC_3C. λ_{max}/nm (*n*-hexane) ($\varepsilon/M^{-1}\ cm^{-1}$): 210 (14000), 260 (1600) and 300 (sh, 500).

Crystal structure determination of 4

Single crystals of **4** were obtained on cooling a pentafluorobenzene solution to 8 °C. The crystallographic data were collected with a STOE IPDS diffractometer system. $C_{32}H_{78}Ga_6$, monoclinic, $a = 1441.26(8)$ pm, $b = 1732.8(2)$ pm, $c = 1835.9(1)$ pm, $\beta = 101.582(7)°$, $U = 4491.6(6) \times 10^{-30}\ m^3$, $T = 193(2)$ K, space group $C2/c$ (no. 15[12]), $Z = 4$, $D_{calcd} = 1.303\ g\ cm^{-3}$, $\mu(\text{Mo-K}\alpha) = 3.564\ mm^{-1}$, $T_{min} = 0.332$, $T_{max} = 0.509$, numerical absorption correction, crystal dimensions 0.39 × 0.24 × 0.21 mm, 2θ range $4.0 \le 2\theta \le 51.8°$, index ranges $-17 \le h \le 17$, $-21 \le k \le 21$, $-22 \le l \le 22$, 4192 unique, number of parameters 258. The structure was solved by direct methods and refined with the program SHELXL-97[13] by a full-matrix least-squares method based on F^2. $R1$ (2269 reflections $I > 2\sigma(I)) = 0.0576$; w$R2$ (all data) = 0.1624, max./min. residual electron density = $0.875/-1.379 \times 10^{30}\ e\ m^{-3}$. The molecules of **4** are located on a twofold crystallographic rotation axis perpendicular to the Ga–Ga single bonds. The hydrogen atoms of the methyl groups were refined on ideal positions by employing the riding model while those attached to gallium were located in a Fourier map and refined freely. Two *tert*-butyl groups (C2, C3) showed disorder; their methyl groups were refined on split positions (occupation factors 0.74/0.26 and 0.55/0.45, respectively).

CCDC reference number 161949.

See http://www.rsc.org/suppdata/dt/b1/b103409j/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous financial support.

References

1 W. Uhl, M. Layh and T. Hildenbrand, *J. Organomet. Chem.*, 1989, **364**, 289.
2 R. W. H. Small and I. J. Worrall, *Acta Crystallogr., Sect. B*, 1982, **38**, 250; J. C. Beamish, R. W. H. Small and I. J. Worrall, *Inorg. Chem.*, 1979, **18**, 220.
3 P. J. Davidson, D. H. Harris and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1976, 2268.
4 Alkyl- and aryl-compounds only; excluding cluster derivatives: R. D. Schluter, A. H. Cowley, D. A. Atwood, R. A. Jones, M. R. Bond and C. J. Carrano, *J. Am. Chem. Soc.*, 1993, **115**, 2070; X. He, R. A. Bartlett, M. M. Olmstead, K. Ruhlandt-Senge, B. E. Sturgeon

and P. P. Power, *Angew. Chem.*, 1993, **105**, 761; X. He, R. A. Bartlett, M. M. Olmstead, K. Ruhlandt-Senge, B. E. Sturgeon and P. P. Power, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 717; R. J. Wehmschulte and P. P. Power, *Angew. Chem.*, 1998, **110**, 3344; R. J. Wehmschulte and P. P. Power, *Angew. Chem., Int. Ed.*, 1998, **37**, 3152; X.-W. Li, P. Wei, B. C. Beck, Y. Xie, H. F. Schaefer III, J. Su and G. H. Robinson, *Chem. Commun.*, 2000, 453; A. K. Saxena, H. Zhang, J. A. Maguire, N. S. Hosmane and A. H. Cowley, *Angew. Chem.*, 1995, **107**, 378; A. K. Saxena, H. Zhang, J. A. Maguire, N. S. Hosmane and A. H. Cowley, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 332; A. H. Cowley, A. Decken and C. A. Olazábal, *J. Organomet. Chem.*, 1996, **524**, 271; N. Wiberg, K. Amelunxen, H. Nöth, H. Schwenk, W. Kaim, A. Klein and T. Scheiring, *Angew. Chem.*, 1997, **109**, 1258; N. Wiberg, K. Amelunxen, H. Nöth, H. Schwenk, W. Kaim, A. Klein and T. Scheiring, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1213; G. Linti and W. Köstler, *Angew. Chem.*, 1996, **108**, 593; G. Linti and W. Köstler, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 550; X.-W. Li, W. T. Pennington and G. H. Robinson, *J. Am. Chem. Soc.*, 1995, **117**, 7578; X.-W. Li, Y. Xie, P. R. Schreiner, K. D. Gripper, R. C. Crittendon, C. F. Campana, H. F. Schaefer and G. H. Robinson, *Organometallics*, 1996, **15**, 3798; G. H. Robinson, *Chem. Commun.*, 2000, 2175; B. Twamley and P. P. Power, *Angew. Chem.*, 2000, **112**, 3643; B. Twamley and P. P. Power, *Angew. Chem., Int. Ed.*, 2000, **39**, 3500.

5 W. Uhl, *Coord. Chem. Rev.*, 1997, **163**, 1; W. Uhl, *Chem. Soc. Rev.*, 2000, **29**, 259; W. Uhl, L. Cuypers, K. Schüler, T. Spies, C. Strohmann and K. Lehmen, *Z. Anorg. Allg. Chem.*, 2000, **626**, 1526.

6 W. Uhl, L. Cuypers, R. Graupner, J. Molter, A. Vester and B. Neumüller, *Z. Anorg. Allg. Chem.*, 2001, **627**, 607.

7 P. L. Baxter, A. J. Downs, M. J. Goode, D. W. H. Rankin and H. E. Robertson, *J. Chem. Soc., Dalton Trans.*, 1990, 2873; P. L. Baxter, A. J. Downs, M. J. Goode, D. W. H. Rankin and H. E. Robertson, *J. Chem. Soc., Chem. Commun.*, 1986, 805; $Me_2Ga(\mu\text{-}H)_2BH_2$: S. Konietzny, H. Fleischer, S. Parsons and C. R. Pulham, *J. Chem. Soc., Dalton Trans.*, 2001, 304.

8 C. R. Pulham, A. J. Downs, M. J. Goode, D. W. H. Rankin and H. E. Robertson, *J. Am. Chem. Soc.*, 1991, **113**, 5149; $HGa(BH_4)_2$: A. J. Downs, T. M. Greene, L. A. Harman, P. F. Souter, P. T. Brain, C. R. Pulham, D. W. H. Rankin, H. E. Robertson, M. Hofmann and P. von Ragué Schleyer, *Inorg. Chem.*, 1995, **34**, 1799; $H_2Ga(BH_4)$: A. J. Downs, S. Parsons, C. R. Pulham and P. F. Souter, *Angew. Chem.*, 1997, **109**, 910; A. J. Downs, S. Parsons, C. R. Pulham and P. F. Souter, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 890; C. R. Pulham, P. T. Brain, A. J. Downs, D. W. H. Rankin and H. E. Robertson, *J. Chem. Soc., Chem. Commun.*, 1990, 177.

9 W. Uhl and T. Spies, *Z. Anorg. Allg. Chem.*, 2000, **626**, 1059.

10 Some recent examples: P. T. Brain, H. E. Brown, A. J. Downs, T. M. Greene, E. Johnsen, S. Parsons, D. W. H. Rankin, B. A. Smart and C. Y. Tang, *J. Chem. Soc., Dalton Trans.*, 1998, 3685; E. Johnsen, A. J. Downs, T. M. Greene, P. F. Souter, K. Aarset, E. M. Page, D. A. Rice, A. N. Richardson, P. T. Brain, D. W. H. Rankin and C. R. Pulham, *Inorg. Chem.*, 2000, **39**, 719; B. Luo, V. G. Young, Jr. and W. L. Gladfelter, *Inorg. Chem.*, 2000, **39**, 1705; J. F. Janik, R. L. Wells, V. G. Young, Jr., A. L. Rheingold and I. A. Guzei, *J. Am. Chem. Soc.*, 1998, **120**, 532.

11 M. L. McKee, *J. Phys. Chem.*, 1990, **94**, 435; H. Horn, R. Ahlrichs and C. Kölmel, *Chem. Phys. Lett.*, 1988, **150**, 263; M. Bühl, P. von Ragué Schleyer and M. L. McKee, *Heteroatom Chem.*, 1991, **2**, 499; E. Fontain, *Heteroatom Chem.*, 1994, **5**, 61.

12 T. Hahn (Editor), *International Tables for Crystallography, Space-Group Symmetry*, Kluwer Academic Publishers, Dordrecht, Boston, London, 1989, vol. A.

13 SHELXTL-Plus, Release. 4.1; Siemens Analytical X-RAY Instruments Inc., Madison, WI, 1990; G. M. Sheldrick, SHELXL-97, Program for the Refinement of Structures, Universität Göttingen, 1997.