The reactions of dialkylgallium hydrides with *tert*-butylethynylbenzenes—a systematic investigation into the course of hydrogallation reactions

Werner Uhl,* Michael Claesener, Sima Haddadpour, Beate Jasper and Alexander Hepp

Received 26th September 2006, Accepted 13th November 2006 First published as an Advance Article on the web 23rd November 2006 DOI: 10.1039/b614003c

The reactions of bis- and tris(*tert*-butylethynyl)benzenes with dialkylgallium hydrides afforded two different types of products. 1,4-Di(*tert*-butylethynyl)benzene and dialkylgallium hydrides R_2GaH bearing relatively small substituents (R = Et, nPr) gave the expected addition products with each $C \equiv C$ triple bond inserted into a Ga–H bond. The intact GaR₂ groups are attached to those carbon atoms which are in α -position to the benzene rings, and intermolecular Ga–C interactions led to the formation of one-dimensional coordination polymers. In contrast secondary reactions with the release of the corresponding trialkylgallium derivatives GaR₃ (R = Et, nPr, iPr, CH_2tBu , tBu) were observed for all hydrogallation reactions involving the trisalkyne 1,3,5-tris(*tert*-butylethynyl)benzene. A similar reaction was observed upon treatment of the 1,4-bisalkyne with a dialkylgallium hydride bearing a relatively bulky substituent (R = neopentyl). Cyclophane type molecules are formed in all these cases with two or three gallium atoms in the bridging positions between both benzene rings.

Introduction

Hydroalumination and hydrogallation reactions are well-known procedures for the reduction of unsaturated organic compounds such as alkenes or alkynes.^{1,2} In many cases the structures of the organometallic products were derived from the constitution of hydrolysis products only, and molecules were postulated in which intact ER₂ groups were attached to the carbon atoms of the reduced C2 moieties. In some recent investigations on hydroalumination or hydrogallation reactions with alkynes we found that the reaction courses are more complicated than those suggested in the literature and that unprecedented molecular structures resulted. The simple addition products, $R' - (R_2 E)C = C(H) - R''$ (E = Al, Ga), were isolated only when trimethylsilyl substituted alkynes³ or sterically highly encumbered dialkylaluminium hydrides⁴ were employed. In other cases very fast condensation reactions occurred with the release of the corresponding trialkylelement derivatives, and the simple addition products could not be detected even as intermediates by NMR spectroscopy. Accordingly, the hydroalumination of dialkylaluminium alkynides yielded carbaalanes, which established a new class of compounds and possess clusters formed by aluminium and carbon atoms [e.g. an Al₈C₅ cluster in (AlMe)₈(CCH₂C₆H₅)₅(H)].⁵ Gallium alkynides gave heteroadamantane type molecules, $(GaR)_6(CCH_2R')_4$, containing coordinatively unsaturated gallium atoms and a localized bonding situation.⁶ Compounds possessing two or more coordinatively unsaturated aluminium atoms are very effective chelating Lewisacids.⁷ We were able to generate such a compound by the twofold hydroalumination of di(tert-butyl)butadiyne only recently.8 A persistent butadienyl cation resulted in that case (1, Scheme 1) because



of the very effective coordination of the hydride counterion by two aluminium atoms.

Owing to experiences gained in our group in recent investigations hydrogallation reactions proved to be more selective than

Institut für Anorganische und Analytische Chemie, Universität Münster, D-48149, Münster, Germany. E-mail: uhlw@uni-muenster.de

hydroalumination reactions. The last ones often gave inseparable mixtures of products. The increased selectivity of the insertion into Ga-H bonds may be caused by their lower polarity and slower reaction rates. Thus, we are able to apply a broader variability of dialkylgallium hydrides and to conduct systematic investigations into the influence of steric interactions on the course of these reactions. Recently, we observed that di(neopentyl)gallium hydride reacted with 1,3,5-tris(tert-butylethynyl)benzene or 1,4di(tert-butylethynyl)benzene by the release of trineopentylgallium and the formation of novel cyclophane-type cage molecules with three or two gallium atoms in the bridging positions (2 and 3, respectively, an example is shown in Scheme 1).9,10 These reactions may comprise the addition of Ga-H bonds to the triple bonds in a first step followed by a fast substituent exchange. Thus, they require the approach of two independent molecules to initiate the secondary exchange reaction. Accordingly, very bulky substituents blocked that pathway, and stable addition products without any condensation reaction were obtained with the aluminium hydride H-Al[CH(SiMe₃)₂]₂.⁴ However, that simple and at a first glance reasonable description of the reaction mechanism proved to be inadequate or at least incomplete after we unexpectedly observed the formation of a persistent addition product (4, Scheme 1) upon the reaction of 1,4-(Me₃C–C=C)₂C₆H₄ with the gallium hydride Et₂GaH.¹⁰ Despite the rather ineffective steric shielding by ethyl groups condensation with the release of triethylgallium could not be detected even as a minor side-reaction. Owing to the importance of that particular reaction type, which belongs to text book knowledge, we conducted further experiments by a systematic variation of the substituents attached to gallium in order to get a concise insight into the reaction courses and to gain additional information for an understanding of the different reaction patterns.

Results and discussion

Experimental work

Hydroalumination reactions usually proceed spontaneously below room temperature, while hydrogallation reactions are slow, and complete transformations require refluxing *n*-hexane over periods of up to 16 h. The formation of the corresponding trialkylgallium compounds GaR₃ was observed in all reactions of the trisalkynyl starting compound 1,3,5-tris(tert-butylethynyl)benzene with different dialkylgallium hydrides R_2Ga-H (R = Et, *nPr*, *iPr*, neopentyl, tBu), eqn (1). The reaction of dineopentylgallium hydride has been published before,9 nevertheless it is included in eqn (1) to facilitate a complete survey. It proved to be almost impossible to isolate the GaR₃ derivatives quantitatively and to determine their respective yields. Some are relatively volatile and were removed partially with the solvent under vacuum. In other cases they were enclosed in the residue remaining after evaporation of the solvents and could not be removed completely from the other products even by thorough evacuation. The formation of the trialkylgallium compounds in reasonable quantities was derived from the NMR spectra of the raw products. The pure compounds 2a to 2e could be obtained only by repeated recrystallization from hydrocarbon solvents. This procedure diminished the yield of the hydrogallation products, although they were formed almost quantitatively in most reactions. The constitution



of the finally isolated crystalline compounds was determined by NMR spectroscopy, in particular by considering the characteristic integration ratios of their resonances, and by crystal structure determinations. A schematic drawing of the molecular structures is given in eqn (1). In all cases [3,3,3]-cyclophane type molecules (2) resulted, in which two benzene rings were bridged by three CGaC moieties. Also di(*tert*-butyl)gallium hydride afforded the product in a reasonable yield, although it exists as an equilibrium mixture in solution with three constituents, di(*tert*butyl)gallium hydride, tri(*tert*-butyl)gallium and the sesquihydride [Me₃CGaH₂]₂[(Me₃C)₂GaH]₂. Dimethylgallium hydride could not be applied. It decomposed under the conditions required for these reactions (boiling *n*-hexane) by the precipitation of elemental gallium. Lower temperatures did not give any transformation even after prolonged reaction times.

A more complicated behaviour with the formation of different products was observed for the similar reactions of the bisalkyne 1,4-di(*tert*-butyl)ethynylbenzene under the same reaction conditions as described before. The products obtained with dineopentyl-gallium and diethylgallium hydride have been published before.¹⁰ The release of a trialkylgallium derivative as an indication for the occurrence of a condensation process could only be detected in the reaction of the sterically shielded dineopentylgallium hydride, eqn (2),which yielded a [3,3]-cyclophane (**3a**) similar to compounds **2**. Smaller substituents attached to the gallium atoms (R = Et and *n*Pr) gave another type of product. The respective trialkylgallium



compounds could not be detected in the NMR spectra of the reaction mixtures, hence, condensation reactions similar to eqn (1) could clearly be excluded. Instead the simple addition products (4) were isolated and identified by crystal structure determination and the characteristic integration ratios of their ¹H NMR spectra. They are stable in solution at room temperature without any indication of the release of trace quantities of the trialkyl compounds. Condensation reactions could not be detected even in boiling *n*-hexane or in hot benzene (50 $^{\circ}$ C) after prolonged reaction times over several days. Di(isopropyl)gallium hydride afforded a mixture of at least two products which could not be separated by repeated attempts at recrystallization from different solvents (n-pentane, n-hexane, cyclopentane, pentafluorobenzene). The ratio of the products could not be changed by prolonged heating, and triisopropylgallium was not detected in the ¹H NMR spectra. However, that particular trialkylgallium compound is very volatile and may be removed with the solvent upon concentration under vacuum. Nevertheless, the formation of a mixture of the simple addition product and the cyclophane derivative indicating an intermediate behaviour between small and bulky substituents seems to be rather improbable, because in such a case we would expect a changing product ratio with increasing heating time. The reaction of di(*tert*-butyl)gallium hydride with the bisalkyne gave a relatively pure product in a rather selective reaction. The signals of the phenyl and ethenyl protons in the ¹H NMR spectrum verify the successful hydrogallation of the C \equiv C triple bonds, however, two resonances of equal intensities were detected for two chemically different *tert*-butyl groups. This result does not fit to either of the structures discussed so far. Up to now we do not have any reasonable suggestion for its structure, and we did not succeed in

growing single crystals for an unambiguous identification of that product.

Spectroscopic findings

The NMR data of the [3,3,3]-cyclophane molecules (2) are quite similar and almost indistinguishable with respect to the resonances of the molecular skeleton. Also, the NMR data of the only [3,3]-cyclophane type molecule obtained so far (3a) fit quite well into this scheme which allows a relatively short summary. The integration ratios clearly exclude the occurrence of simple addition products in these cases and verify instead the formation of condensation products. The phenyl protons and the hydrogen atoms attached to the C=C double bonds gave two singlets of equal intensity (or a ratio of 2 to 1 for 3a) in a narrow range at about $\delta = 6.2$. With the exception of the ethyl compound 2a the resonances of the alkenyl protons are shifted to higher field. While the differences between both chemical shifts are usually below 0.14 ppm, a relatively broad gap of 0.47 ppm was observed for the *tert*-butyl compound 2e. Those carbon atoms of the C=C double bonds, which are attached to the gallium atoms, resonate at $\delta = 154$, while the remaining carbon atoms have chemical shifts of $\delta = 155$ on average. The *ipso*-carbon atoms of the phenyl rings occur at about $\delta = 145$. This assignment partially deviates from the one given in references 9 and 10. The chemical shifts of the inner carbon atoms of the alkyl groups attached to gallium depend on the number of methyl groups in these substituents. A continuous deshielding was observed on going from $R = Et (2a, \delta = 4.8)$ to $R = CMe_3$ (2e, $\delta = 29.2$). All IR spectra of the [3,3,3]-cyclophanes (2) show two relatively intense absorptions at about 1580 and 1560 cm⁻¹ characteristic of stretching vibrations of the benzene rings and the C=C double bonds. Compound 3a has slightly different absorptions at 1602 and 1592 cm⁻¹ and a further one at 1497 cm⁻¹.

Interestingly both persistent addition products (4a and 4b), which do not form cages and have intact GaR_2 groups attached to their alkenyl groups, show chemical shifts in their NMR spectra, which are almost entirely identical to those of the cyclophane type compounds (2 and 3). Hence, the chemical shifts do not allow for a secure differentiation between both structural types, and the characteristic integration ratios of the ¹H NMR spectra are the only reliable criterion for an unambiguous spectroscopic identification.

Molecular structures

Three new molecular structures were determined by X-ray diffraction methods (**2a**, **2b** and **4b**), they are depicted in Fig. 1 to 3. Three further structures have been published before (**2d**, **3a** and **4a**),^{9,10} however, owing to their close relationship to the structures discussed here, they were included in the discussion and the calculation of average values. Cyclophane-type molecules (**2** and **3**) and the products of the simple addition of R₂Ga– H to the triple bonds of the alkynes (**4**) without secondary reactions establish the different structural motifs resulting from the hydrogallation of *tert*-butylethynyl benzenes. These reactions are highly regio- and stereoselective. In all cases the hydrogen atoms and the gallium atoms attached to a particular C=C double bond adopted a *cis*-arrangement, and the gallium atoms



Fig. 1 Molecular structure of 2a. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups and hydrogen atoms are omitted for clarity. Important bond lengths (pm) and angles (°): Ga(1)–C(1) 195.8(3), Ga(1)–C(4) 195.8(3), Ga(2)–C(2) 196.5(3), Ga(2)–C(5) 197.1(3), Ga(3)–C(3) 196.5(3), Ga(3)–C(6) 196.2(3), C(1)–C(11) 133.7(4), C(2)–C(21) 134.4(4), C(3)–C(31) 135.3(4), C(4)–C(41) 134.4(4), C(5)–C(51) 134.4(4), C(6)–C(61) 134.2(4); C(1)–Ga(1)–C(4) 123.3(1), C(2)–Ga(2)–C(5) 123.8(1), C(3)–Ga(3)–C(6) 123.6(1), C(1)–C(11)–C(12) 131.8(3), C(2)–C(21)–C(22) 131.4(3), C(3)–C(31)–C(32) 131.8(3), C(4)–C(41)–C(42) 132.4(3), C(5)–C(51) 133.7(3), C(6)–C(61)–C(62) 131.9(3).

attacked exclusively those carbon atoms which are in α -position on the benzene rings. That position may be preferred because it allows some mesomeric stabilization of the negative charge induced by the electronegativity difference between carbon and gallium.

The cyclophane-type molecules have two benzene rings bridged by two or three C-Ga-C groups. The different numbers of bridging groups do not cause any significant difference in structural parameters. The C=C double bond lengths are about 134 pm on average, which corresponds well to the standard value.¹¹ Also, the Ga-C distances in the cages are in the expected range of 197 pm. There is a small increase of the C-Ga-C angle in the cages $(\sim 123^{\circ})$ compared to the ideal value of sp² atoms, but this may be expected owing to some strain in the molecules. Relatively large angles of 131 to 134° were observed for the groups C=C-CMe₃. They may be caused by steric interactions between the tert-butyl groups arranged above one phenyl ring (three tert-butyl groups for the [3,3,3]-cyclophanes) and additionally by interactions between the tert-butyl groups and the aromatic systems. The benzene rings of one molecule are almost ideally coplanar, however they are slightly rotated with respect to each other with rotation angles of 14 to 16° (2a and 2b) or 3 to 4° for the neopentyl compounds 2d and 3a. The shortest distances between the carbon atoms of the benzene rings are 340 to 360 pm, which is in the normal range of van der Waals interactions.



Fig. 2 Molecular structure of **2b**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups are omitted for clarity. Important bond lengths (pm) and angles (°): Ga(1)–C(1) 197.1(3), Ga(1)–C(2) 197.1(3), C(1)–C(11) 133.5(4), C(2)–C(21) 134.3(4); C(1)–Ga(1)–C(2) 123.1(1), C(1)–C(11)–C(12) 132.2(3), C(2)–C(21)–C(22) 131.4(3); Ga1' generated by -y + 1, x - y, z; Ga1" by -x + y + 1, -x + 1, z.



Fig. 3 Molecular structure of **4b**. The thermal ellipsoids are drawn at the 40% probability level. CH_3 and CH_2 groups are omitted for clarity. Important bond lengths (pm) and angles (°): Ga(1)–C(1) 203.5(7), C(1)–C(11) 134.3(9), Ga(2)–C(2) 205.6(7), C(2)–C(21) 133.4(9), Ga(1)–C(2) 251.9(7), Ga(2)–C(1) 256.2(7), Ga(1) ··· Ga(2) 298.9(1); Ga(1)–C(1)–C(13) 111.5(5), Ga(2)–C(2)–C(23) 112.4(5), C(1)–C(11)–C(12) 133.3(7), C(2)–C(21)–C(22) 134.5(6); Ga1', C1' to C15' were generated by -x, y, -z + 0.5; Ga2', C2' to C25' by -x, -y + 2, -z; Ga1", C1", Ga2" and C2" indicate the next atoms in the chain.

The compounds **4a** and **4b** contain two intact GaR_2 groups (R = Et, *n*Pr) attached to their double bonds. Both structures are quite similar and have two crystallographically independent molecules.

One is located on a twofold rotational axis (GaR₂ groups on the same side of the inner ring) and one encloses a center of symmetry (GaR_2 groups on different sides). Despite these differences the structural parameters are very similar. The C=C bond lengths (about 134 pm) and the angles $C=C-C(Me_3)$ (134°) correspond to the values discussed before. The angles Ga-C-C including the ipso carbon atoms of the benzene rings are smaller than those of the cyclophane molecules (113 versus 119°) which might reflect some strain in the cyclophane cages. An interesting intermolecular interaction causes a lengthening of the Ga-C distances to the alkenyl groups by about 7 pm compared to those observed for the cyclophane-type molecules (197 versus 204 pm). Each gallium atom of 4a and 4b has a relatively close contact to a negatively charged a-carbon atom (attached to Ga) of an alkenyl group of a neighboring molecule with distances of 255 pm on average. By these interactions folded Ga₂C₂ heterocycles (folding angle 36°) with strongly differing Ga-C distances result leading to onedimensional coordination polymers possessing alternating C_{2v} and C_{2h} molecules in the chain.

Conclusion

The systematic investigations into hydrogallation reactions with alkylethynylbenzenes summarized in this article enable a better understanding of the different reaction patterns. In general, the simple addition products $R_2Ga-(R')C=C(H)-R''$ were obtained in rare cases only, instead condensation with the spontaneous release of trialkylgallium derivatives seem to establish the more common reaction courses. The final structural motifs of the products reported here depend on the number of alkynyl groups attached to the inner benzene rings and on the streric shielding of the dialkylgallium hydrides. 1,3,5-Tris(tert-butylethynyl)benzene gave exclusively the cyclophanetype molecules (2) by the release of GaR_3 . While in these cases the simple addition products bearing intact GaR₂ groups could not be detected even by NMR spectroscopy, stable compounds of that type were obtained with the corresponding 1,4-bisalkyne upon hydrogallation with sterically less shielded dialkylgallium hydrides.

The simple addition products form one-dimensional coordination polymers in the solid state via relatively short intermolecular distances between gallium and carbon atoms of alkenyl groups. This singular structure may offer the key for an understanding of the different reaction behavior. Ga2C2 heterocycles result which include exclusively carbon atoms of C=C double bonds, while the alkyl substituents are in terminal positions. From that particular situation a substituent exchange cannot occur. Thus, if the formation of those rings is strongly favoured compared to a transition state having an alkyl carbon atom in the bridging position, the addition products remain stable as in the case of some 1,4-alkenylbenzene derivatives. However, when the close approach of the gallium atoms via two alkenyl bridges is prevented or at least hindered by steric shielding as in the case of the 1,3,5-trisalkynes, the exchange may be initiated by the occurrence of alkyl bridges. Two points are of interest in future investigations. Sterically more shielded dialkylgallium hydrides bearing for instance bis(trimethylsilyl)methyl groups should prevent the condensation reactions. However, despite many efforts we were not able to synthesize that compound, although the corresponding aluminium compound is well-known.⁴ Furthermore, it would be of particular interest to conduct such hydrogallation reactions with monoalkynes. Up to now we have not really been successful in that direction. However, in view of the mechanism derived from the results reported here it should be worth revisiting these investigations.

Experimental

All procedures were carried out under purified argon. *n*-Hexane, *n*-pentane, and cyclopentane were dried over LiAlH₄, diethyl ether over Na–benzophenone. The starting compounds $nPr_2GaCl_{,1^2}$ Et₂GaH,¹³ *i*Pr₂GaH,¹³ *t*Bu₂GaH,¹⁴ 1,4-(Me₃C–C≡C)₂C₆H₄,¹⁰ and 1,3,5-(Me₃C–C≡C)₃C₆H₃⁹ were obtained according to literature procedures. LiH (Aldrich) was applied as purchased. The synthesis of di(*n*-propyl)gallium hydride is described below. The assignment of the NMR spectra is based on HSQC, HMBC, ROESY and DEPT135 data.

Synthesis of di(n-propyl)gallium hydride

Di(*n*-propyl)gallium chloride (4.00 ml, 4.94 g, 25.8 mmol) was dissolved in 25 ml of diethyl ether and added to a suspension of lithium hydride (1.4 g, 177 mmol, excess) in 50 ml of diethyl ether. The mixture was heated under reflux for 48 h. After filtration and evaporation of the solvent the waxy residue was thoroughly evacuated (6 d, $<10^{-3}$ Torr, 45 °C) to completely remove diethyl ether. Yield: 3.00 g (71%) of colorless solid Li[H₂GanPr₂] as an intermediate, which was not recrystallized for purification, but directly employed for the generation of the R₂GaH compounds. ¹H NMR (C₆D₆, 200 MHz): $\delta = 2.34$ (br., 2 H, s, GaH), 1.76 (4 H, pseudo-sextet, ³J_{HH} = 7 Hz, CH₂CH₂CH₃), 1.24 (6 H, t, ³J_{HH} = 7 Hz, Me of *n*Pr), 0.67 (br., 4 H, t, ³J_{HH} = 7 Hz, GaCH₂). ¹³C NMR (C₆D₆, 50 MHz): $\delta = 22.2$ (CH₂CH₂CH₃), 19.9 (Me of *n*Pr), 14.0 (GaC).

Li[H₂GanPr₂] (3.00 g, 18.2 mmol) was suspended in 60 ml of n-pentane. Cl-GanPr₂ (2.82 ml, 3.48 g, 18,2 mmol) was added, and the mixture was heated under reflux for 17 h. The product was isolated as a light yellowish, highly viscous liquid after filtration and evaporation of the solvent in vacuum. Decomposition occurred above room temperature, so that purification by distillation failed. However, the purity of the product as determined by NMR spectroscopy is sufficiently high enough for its application in secondary reactions. Yield: 3.88 g (68%). ¹H NMR (C_6D_6 , 200 MHz): δ = 3.11 (br., 1 H, s, GaH), 1.64 (4 H, pseudo-sextet, ${}^{3}J_{\text{HH}} = 7.2 \text{ Hz}, \text{CH}_{2}\text{CH}_{2}\text{CH}_{3}$), 1.04 (6 H, t, ${}^{3}J_{\text{HH}} = 7.2 \text{ Hz}$, Me of *n*Pr), 0.84 (4 H, t, ${}^{3}J_{HH} = 7.2$ Hz, GaCH₂). ${}^{13}C$ NMR (C₆D₆, 50 MHz): $\delta = 21.0 (CH_2CH_2CH_3)$, 19.1 (Me of *n*Pr), 16.5 (GaC). IR (CsBr plates, paraffin, cm⁻¹): 1658 br., vs vGaH; 1455 s paraffin; 1412 m δ CH; 1375 s paraffin; 1330 s, 1276 m δ CH₃; 1210 vw, 1190 w, 1181 w, 1160 w, 1057 s, 1017 w, 986 s vCC, phenyl; 843 br., m δ GaH; 796 m, 694 br., s, 664 s, 633 m, 564 m, 525 m δ CC, *v*GaC. Molar mass (in benzene by cryoscopy, $0.06 \text{ mol } l^{-1}$): Found: 430 g mol⁻¹; Calc. 470.1 g mol⁻¹ for the trimer, 313.4 g mol⁻¹ for the dimer. MS (EI, 70 eV): m/z (%) (three or two most intensive peaks only, complete isotopic patterns as expected) = 469, 471, 473(1.2, 3.9, 2.3; M⁺ of the trimer + H); 155, 157 (100, 67.7; M⁺ of the monomer).

Reactions of the alkynes with dialkylgallium hydrides—general procedure

A solution of the dialkylgallium hydride in *n*-hexane (2 to 6 mmol in 25 ml) was added to a solution of the respective bis- or trisalkyne in the same solvent (about 1 to 2 mmol in 25 ml) at room temperature. While usually the exact stoichiometric ratios of the starting compounds were applied, an excess of 5% of the hydride was employed in all reactions of di(*n*-propyl)gallium hydride. The solutions were heated under reflux for 16 h and filtered because small quantities of colorless, unknown solids preciptated in some cases. The filtrates were concentrated under vacuum at room temperature to a few ml. In some cases the products precipitated directly, while in others cooling to down to -80 °C was required to get the solid products. Compound 4b could be recrystallized with some difficulties from *n*-pentane only. Owing to the NMR spectroscopic characterization of the raw products the compounds were formed almost quantitatively. However, precipitation from the solutions as solids or the complete removal of the trialkylgallium derivatives proved to be difficult. Thus, very low yields of the pure products were obtained in a few cases.

Characterization of the [3,3,3]-cyclophane 2a (R = Et). Yield: 44%. Decomp. (argon, sealed capillary): above 220 °C. ¹H NMR (C₆D₆, 400 MHz): δ = 6.26 (6 H, s, C=C–H), 6.24 (6 H, s, C₆H₃), 1.36 (9 H, t, ³J_{HH} = 8 Hz, Me of ethyl), 1.13 (54 H, s, CMe₃), 0.97 (6 H, q, ³J_{HH} = 8 Hz, CH₂ of ethyl). ¹³C NMR (C₆D₆, 100 MHz): δ = 155.3 (Ga–C=*C*-H), 153.9 (Ga–*C*=C–H), 144.7 (*ipso*-C of phenyl), 121.5 (*ortho*-C of phenyl), 36.7 (*C*Me₃), 31.8 (*CMe*₃), 10.5 (Me of ethyl), 4.8 (br., CH₂ of ethyl). IR (CsBr plates, paraffin, cm⁻¹): 1582 s, 1558 vs *v*C=C, phenyl; 1455 vs, 1377 vs paraffin; 1306 m δ CH₃; 1225 m, 1202 m, 1170 w, 1155 w, 1138 sh, 1088 vw, 1058 vw, 1038 w, 1028 w, 989 m, 937m, 912 m, 897 m *v*CC, δ CH₃, phenyl; 721 s paraffin; 706 m, 660 w, 600 w, 573 w, 560 vw, 523 w, 453 w *v*GaC.

Characterization of the [3,3,3]-cyclophane 2b ($\mathbf{R} = n\mathbf{Pr}$). Yield: 57%. Decomp. (argon, sealed capillary): above 210 °C. ¹H NMR $(C_6D_6, 400 \text{ MHz}): \delta = 6.31 (6 \text{ H}, \text{ s}, C_6H_3), 6.25 (6 \text{ H}, \text{ s}, C=C-H),$ 1.83 (6 H, pseudo-sextet, ${}^{3}J_{HH} = 7.6$ Hz, CH₂CH₂CH₃), 1.14 (9 H, t, ${}^{3}J_{HH} = 7.6$ Hz, Me of propyl), 1.13 (54 H, s, CMe₃), 1.05 (6 H, pseudo-triplet, ${}^{3}J_{HH} = 7.6$ Hz, GaCH₂). ${}^{13}C$ NMR (C₆D₆, 100 MHz): $\delta = 155.6$ (Ga–C=C–H), 154.7 (Ga–C=C–H), 145.1 (ipso-C of phenyl), 121.1 (ortho-C of phenyl), 36.8 (CMe₃), 31.9 (CMe₃), 20.5 (CH₂CH₂CH₃), 20.0 (Me of propyl), 15.9 (Ga–CH₂). IR (CsBr plates, paraffin, cm^{-1}): 1582 s, 1564 s vC=C, phenyl; 1455 vs, 1377 vs paraffin; 1325 w, 1310 w, 1287 vw, 1272 vw δ CH₃; 1226 s, 1202 s, 1165 w, 1150 w, 1135 w, 1059 m, 1037 w, 1025 w, 989 m, 939 w, 913 m, 898 w, 883 w vCC, δ CH₃, phenyl; 724 m paraffin; 706 s, 647 w, 534 w, 458 w vGaC. MS (EI, 70 eV): m/z (%) (three most intensive peaks only, complete isotopic patterns as expected) = $979, 981, 983 (0.4, 0.7, 0.6; M^+ + H), 935, 937, 939$ $(3.7, 8.1, 6.5; M^+ - Pr).$

Characterization of the [3,3,3]-cyclophane 2c (R = *i***Pr).** Yield: 61%. Decomp. (argon, sealed capillary): above 210 °C. ¹H NMR (C₆D₆, 400 MHz): δ = 6.35 (6 H, s, C₆H₃), 6.21 (6 H, s, C=C–H), 1.64 (3 H, septet, ³J_{HH} = 7.6 Hz, CHMe₂), 1.44 (18 H, d, ³J_{HH} = 7.6 Hz, Me of isopropyl), 1.12 (54 H, s, CMe₃). ¹³C NMR (C₆D₆, 100 MHz): δ = 155.0 (Ga–C=C–H), 153.7 (Ga–C=C–H), 145.0 (*ipso*-C of phenyl), 122.1 (*ortho*-C of phenyl), 36.9 (CMe₃), 32.0 (CMe₃), 21.4 (Me of isopropyl), 17.9 (GaCH). IR (CsBr plates, paraffin, cm⁻¹): 1674 m, 1590 sh, 1568 vs ν C=C, phenyl; 1455 vs, 1377 vs paraffin; 1310 w, 1256 w, 1246 w δ CH₃; 1225 m, 1202 s, 1153 w, 1122 w, 1025 m, 970 s, 911 m, 873 m, 837 w ν CC, δ CH₃, phenyl; 723 m paraffin; 709 s, 595 s, 539 s, 457 m, 433 m ν GaC.

Characterization of the [3,3,3]-cyclophane 2e (R = *t***Bu). Yield: 10% of pure 2e** after twofold recrystallization; the complete removal of the by-product tri(*tert*-butyl)gallium was extremely difficult. Decomp. (argon, sealed capillary): above 210 °C. ¹H NMR (C₆D₆, 400 MHz): $\delta = 6.41$ (6 H, s, C₆H₃), 5.94 (6 H, s, C=C-H), 1.42 (27 H, s, GaCMe₃), 1.12 (54 H, s, C=C-CMe₃). ¹³C NMR (C₆D₆, 100 MHz): $\delta = 152.4$ (Ga-*C*=C-H), 152.3 (Ga-C=*C*-H), 145.7 (*ipso*-C of phenyl), 122.6 (*ortho*-C of phenyl), 36.9 (CMe₃ of ethenyl), 31.9 (CMe₃ of ethenyl), 30.9 (Ga-CMe₃), 28.7 (br., Ga-CMe₃). IR (CsBr plates, paraffin, cm⁻¹): 1578 vs, 1557 vs *v*C=C, phenyl; 1454 vs paraffin; 1402 m δ CH₃; 1377 s paraffin; 1366 s, 1330 vw, 1310 vw, 1274 vw, 1253 w δ CH₃; 1225 m, 1202 s, 1179 m, 1134 m, 1119 m, 1105 m, 1037 m, 1026 m, 989 m, 977 m, 910 m, 896 w, 879 w, 806 m *v*CC, δ CH₃, phenyl; 727 m paraffin; 718 m, 706 m, 640 w, 596 w, 560 w, 532 w, 459 m, 445 m *v*GaC.

Characterization of the addition product 4b ($\mathbf{R} = n\mathbf{Pr}$). Yield: 5% of pure **4b**; owing to its very high solubility in hydrocarbon solvents the recrystallization of 4b from *n*-pentane gave very low yields only. Mp (argon, sealed capillary): 130 °C. ¹H NMR (C₆D₆, 400 MHz): $\delta = 6.58$ (4 H, s, C₆H₃), 6.19 (2 H, s, C=C-H), 1.58 (8 H, pseudo-sextet, ${}^{3}J_{HH} = 7.4$ Hz, CH₂CH₂CH₃), 1.05 (18 H, s, C=C-CMe₃), 1.03 (12 H, t, ${}^{3}J_{HH} = 7.4$ Hz, Me of propyl), 0.66 (br., 8 H, t, ${}^{3}J_{HH} = 7.4$ Hz, GaCH₂). ${}^{13}C$ NMR (C₆D₆, 100 MHz): $\delta = 155.6$ (Ga–C=C–H), 154.3 (Ga–C=C–H), 142.2 (*ipso*-C of phenyl), 126.6 (ortho-C of phenyl), 37.1 (CMe₃), 31.6 (CMe₃), 20.8 (Ga-CH₂), 20.0 (Me of propyl), 19.8 (CH₂CH₂CH₃). IR (CsBr plates, paraffin, cm⁻¹): 1654 m, 1599 s, 1571 s, 1497 s vC=C, phenyl; 1454 vs paraffin; 1408 s δ CH₃; 1360 s paraffin; 1325 m, 1298 w, 1258 m δCH₃; 1229 m, 1202 s, 1187 m, 1155 m, 1101 m, 1059 s, 1020 m, 986 m, 939 w, 905 w, 864 w, 808 w, 785 w vCC, δ CH₃, phenyl; 731 m paraffin; 689 br., sh, 673 s, 654 br., s, 554 br., m, 457 w vGaC. MS (EI, 70 eV): m/z (%) (three most intensive peaks only, complete isotopic patterns as expected) = 551, 552, 553 (16, 6, 11; M⁺); 396, 397, 398 (1, 0.7, 0.8; M⁺ - Ga - isopropyl propene); 353, 354, 355 (100, 23, 68; M⁺ – Ga*i*Pr₂ – propene).

Crystal structure determinations of 2a, 2b and 4b

Single crystals of compound **2a** were obtained from a saturated solution in *n*-hexane upon cooling to -15 °C, crystals of **2b** by slow concentration of a solution in cyclopentane at room temperature, those of **4b** from *n*-pentane at -45 °C. The crystallographic data were collected with a Bruker Smart Apex diffractometer. The structures were solved by direct methods and refined with the program SHELXL-97¹⁵ by a full-matrix least-squares method based on F^2 . Crystal data, data collection parameters and structure refinement details are given in Table 1. Compound **2a** crystallizes with half an *n*-hexane molecule per formula unit. The crystals of **2b** enclose cyclopentane molecules, one of which is strongly disordered over a crystallographic $\overline{3}$ axis. The cyclophane molecules of compound **2b** are located on crystallographic threefold rotation axes.

Table 1 Crystal data, data collection parameters, and structure refinement details for 2a, 2b and 4b

	2a	2b	4b
Formula	C57H88Ga3	C ₇₅ H ₁₂₃ Ga ₃	C ₃₀ H ₅₂ Ga ₂
Crystal system	Triclinic	Trigonal	Monoclinic
Space group ¹⁶	<i>P</i> 1 (No. 2)	<i>P</i> 3 <i>c</i> 1 (No. 165)	C2/c (No. 15)
Z	2	4	8
a/Å	12.417(5)	17.6535(3)	27.889(8)
b/Å	15.300(5)	17.6535(3)	12.053(3)
c/Å	15.668(5)	25.9914(4)	19.249(5)
a (°)	104.047(5)	90	90
β (°)	107.164(5)	90	111.919(6)
γ (°)	94.608(5)	120	90
$V/10^{-30} \text{ m}^3$	2721.7(17)	7014.9(2)	6003(3)
T/K	153(2)	100(2)	153(2)
μ/mm^{-1}	1.507	1.619	1.810
Unique rflns (R_{int})	16302 (0.0463)	4456 (0.0739)	7286 (0.2431)
R1 (reflns $I > 2\sigma(I)$)	0.0577 (11376)	0.0424 (3096)	0.0857 (2993)
wR_2 (all data)	0.1386	0.1088	0.1841

CCDC reference numbers 621972 (2a), 621973 (2b) and 621974 (4b).

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b614003c

Acknowledgements

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

References

- 1 (a) E. Winterfeldt, Synthesis, 1975, 10, 617; (b) I. Marek and J.-F. Normant, Chem. Rev., 1996, 96, 3341; (c) J. J. Eisch, in Comprehensive Organic Synthesis, ed. B. M. Frost and J. Flemming, Pergamon, Oxford, 1991 vol. 8, p. 773.
- 2 (a) S. Nogai and H. Schmidbaur, Inorg. Chem., 2002, 41, 4770; (b) H. Schmidbaur and H. F. Klein, Angew. Chem., 1966, 78, 306; (c) H. Schmidbaur and H. F. Klein, Chem. Ber., 1967, 100, 1129; (d) J. Ohshita and H. Schmidbaur, J. Organomet. Chem., 1993, 453, 7; (e) H. Schumann, U. Hartmann and W. Wassermann, Polyhedron, 1990, 9,

353; (f) E. Johnsen, A. J. Downs, M. J. Goode, T. M. Greene, H. J. Himmel, M. Müller, S. Parsons and C. R. Pulham, Inorg. Chem., 2001, 40, 4755; (g) C. R. Pulham, A. J. Downs, M. J. Goode, D. W. H. Rankin and H. E. Robertson, J. Am. Chem. Soc., 1991, 113, 5419; (h) J. L. Atwood, S. G. Bott, C. Jones and C. L. Raston, Inorg. Chem., 1991, 30, 4868; (i) M. J. Henderson, C. H. L. Kennard, C. L. Raston and G. Smith, J. Chem. Soc., Chem. Commun., 1990, 1203; (j) W. Uhl, J. Molter and B. Neumüller, J. Organomet. Chem., 2001, 634, 193; (k) J. R. Jennings and K. Wade, J. Chem. Soc. A, 1967, 1222.

- 3 (a) W. Uhl and F. Breher, J. Organomet. Chem., 2000, 608, 54; (b) W. Uhl and M. Matar, J. Organomet. Chem., 2002, 664, 110.
- 4 W. Uhl and M. Matar, Z. Anorg. Allg. Chem., 2005, 631, 1177.
- 5 (a) W. Uhl and F. Breher, Angew. Chem., 1999, 111, 1578, (Angew. Chem., Int. Ed., 1999, 38, 1477); (b) W. Uhl, F. Breher, A. Lützen and W. Saak, Angew. Chem., 2000, 112, 414, (Angew. Chem., Int. Ed., 2000, 39, 406); (c) W. Uhl, F. Breher, J. Grunenberg, A. Lützen and W. Saak, Organometallics, 2000, 19, 4536; (d) W. Uhl, F. Breher, A. Mbonimana, J. Gauss, D. Haase, A. Lützen and W. Saak, Eur. J. Inorg. Chem., 2001, 3059; (e) W. Uhl, Inorganic Chemistry Highlights, ed. G. Meyer, D. Naumann and L. Wesemann, Wiley-VCH, Weinheim, 2002, p. 229; (f) Similar compounds: A. Stasch, M. Ferbinteanu, J. Prust, W. Zheng, F. Cimpoesu, H. W. Roesky, J. Magull, H.-G. Schmidt and M. Noltemeyer, J. Am. Chem. Soc., 2002, 124, 5441.
- 6 W. Uhl, L. Cuypers, B. Neumüller and F. Weller, Organometallics, 2002, 21, 2365.
- 7 (a) W. Uhl, F. Hannemann, W. Saak and R. Wartchow, Eur. J. Inorg. Chem., 1998, 921; (b) W. Uhl and F. Hannemann, J. Organomet. Chem., 1999, 579, 18.
- 8 W. Uhl, J. Grunenberg, A. Hepp, M. Matar and A. Vinogradov, Angew. Chem., 2006, 118, 4465, (Angew. Chem., Int. Ed., 2006, 45, 4358).
- 9 W. Uhl, F. Breher and S. Haddadpour, Organometallics, 2005, 24, 2210.
- 10 W. Uhl, S. Haddadpour and M. Matar, Organometallics, 2006, 25, 159.
- 11 J. March, Advanced Organic Chemistry, Wiley, New York, 3rd edition, 1985, p. 19.
- 12 nPr₂GaCl was synthesized from n-propyllithium and GaCl₃ in a molar ratio of 2 to 1 according to a procedure in: R. A. Kovar, H. Derr, D. Brandau and J. O. Callaway, *Inorg. Chem.*, 1979, **14**, 2809. 13 W. Uhl, L. Cuypers, G. Geiseler, K. Harms and W. Massa, *Z. Anorg.*
- Allg. Chem., 2002, 628, 1001.
- 14 W. Uhl, L. Cuypers, R. Graupner, J. Molter, A. Vester and B. Neumüller, Z. Anorg. Allg. Chem., 2001, 627, 607.
- 15 SHELXTL-Plus, REL. 4.1, Siemens Analytical X-RAY Instruments Inc., Madison, WI, 1990; G. M. Sheldrick, SHELXL-97, Program for the Refinment of Structures, Universität Göttingen, Germany, 1997.
- 16 International Tables for Crystallography, Space-Group Symmetry, ed. T. Hahn, Kluwer Academic Publishers, Dordrecht, Boston, London, 1989, vol. A.