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cis/trans Isomerism of Hydroalumination and Hydrogallation Products—Reflections on Stability and Rearrangement Mechanism

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Abstract: Treatment of (silylalkynyl)benzenes with $(Me_3C)_2Ga{-}H$ afforded stable *cis*-addition products, for example, $(Me_3C)_2Ga{-}C(SiMe_3){=}C(H){-}C_6H_5$ (**1**), while spontaneous *cis/trans* rearrangement was observed for sterically less shielded gallium hydrides. The corresponding *trans*-di(*tert*-butyl)gallium compounds (**13**, **14**) were obtained by the reaction of $C_6H_{6-n}[C(H){=}C(SiMe_3)GaCl_2]_n$ (**11**, **12**) with $LiCMe_3$. In contrast, spontaneous isomerization took place upon reaction of $(Me_3C)_2Al{-}H$ with phenyltrimethylsilylethyne. In this case the *cis* isomer (**17**) was detected only at low temperature, while the *trans* product (**18**) formed quantitatively above 0°C. Quantum-chemical calculations showed that the *trans* forms are thermodynamically favored, essentially caused by a better mesomeric interaction of the C=C double bonds with the phenyl groups, a smaller steric stress in the molecules, and a short bonding contact of the coordinatively unsaturated Al or Ga atoms to C−H bonds of the aromatic rings. The rotation about the C=C double bonds follows a zwitterionic mechanism, and the relatively small rotational barrier is further lowered by an interaction to a Lewis acidic lithium cation.

Keywords: aluminum · gallium · hydroalumination · hydrogallation · isomerization

Introduction

The hydroalumination of alkynes represents text book knowledge and has been applied in preparative chemistry for the effective reduction of unsaturated compounds.[1] Addition products of the type $R_2Al{-}C(R'){=}C(H){-}R''$ were postulated as intermediates. However, in most cases these compounds were not isolated and characterized, but consumed by hydrolysis. In recent investigations we found that only the reactions with trimethylsilylethynylbenzenes gave the stable addition products.[2] In many other cases condensation reactions took place to yield unprecedented organoaluminum compounds such as carbaalanes[3] or cyclophane-type molecules.[4] Carbocations resulted upon the hydroalumination of butadiynes.[5] The related hydrogallation reactions proved to be much more selective. Stable addition products were isolated from reactions with trimethylsilylethynylbenzenes in a broad variety.[6] They showed spontaneous *cis/trans* isomerization when small alkyl groups were attached to the gallium atoms, while the stable *cis*-addition products resulted only with di(*tert*-butyl)gallium hydride (**1**–**10**).[6] The *cis* products with the hydrogen and gallium atoms on the same side of the C=C double bond (Scheme 1) may represent the first step of these addition reactions by the reasonable assumption of a concerted reaction mechanism. Condensation occurred for alkynylgallium compounds with the formation of Ga_6C_4 heteroadamantane structures[7] and in most cases for *tert*-butylethynylbenzenes.[8] Interestingly, these last reactions gave the simple addition products with sterically less shielded compounds.[8] The reactions of trimethylsilylethynes with the dichloro compound $H{-}GaCl_2$[9] afforded highly functionalized alkenylgallium chlorides (for example, **11** and **12** in Scheme 1, below).[10] These compounds are excellent starting materials for the synthesis of secondary products by salt elimination and should allow the generation of particular configurations that are not accessible by direct hydrogallation.

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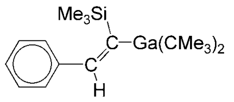
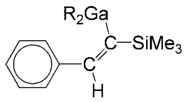
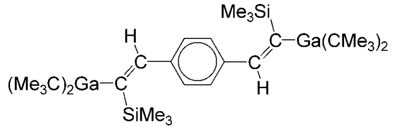


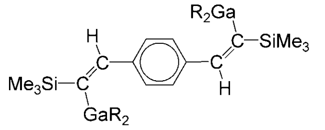
cis (*E*): **1**



trans (*Z*): R = Me (**2**)
R = Et (**3**)
R = *n*Pr (**4**)
R = CH_2CMe_3 (**5**)



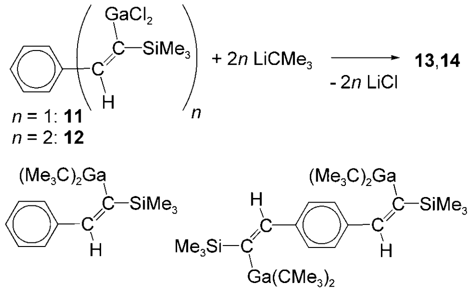
cis (*E*,*E*): **6**



trans (*Z*,*Z*): R = Et (**7**)
R = *n*Pr (**8**)
R = *i*Pr (**9**)
R = CH_2CMe_3 (**10**)

Results and Discussion

Synthesis of the alkenylgallium compounds 13 and 14: Reactions of trimethylsilylethynylbenzene and 1,4-bis(trimethylsilylethynyl)benzene with di(*tert*-butyl)gallium hydride[11] in boiling *n*-hexane afforded quantitatively the *cis*-alkenyl products **1** and **6**.[6] Rearrangement did not occur even after prolonged heating in *n*-hexane or benzene. In contrast, the addition of H−$GaCl_2$ yielded exclusively the dimeric *trans*-addition products (**11** and **12**).[10] Treatment of these compounds (Scheme 1) with stoichiometric quantities of *tert*-butyllithium in *n*-hexane gave almost quantitatively the alkenylgallium derivatives **13** and **14**. However, owing to their very high solubility in hydrocarbons they were isolated as colorless solids in only moderate yields of about 40% after recrystallization. NMR spectroscopic characterization gave clear evidence for the formation of the *trans* isomers (*Z* configuration). The NMR data summarized in Table 1 show that the chemical shifts of the vinylic hydrogen atoms, the *ipso*-carbon atoms of the phenyl groups, and the alkenyl carbon atoms attached to gallium and silicon depend more or less significantly on the respective configuration. The most reliable parameter is the $^3J_{Si\text{-}H}$ coupling constant across the C=C double bond. Hydrogen and silicon in *trans* positions (*E*) gave values of about 20 Hz, while about 11 Hz were detected for their *cis* arrangement (*Z*). Similar to the *cis*-addition products **1** and **6** both *trans* forms **13** and **14** proved to be stable in solution. Heating to 70 °C in benzene for one week did not result in any rearrangement or decomposition. The differing behavior of the corresponding di(*tert*-butyl)aluminum compounds is discussed below.

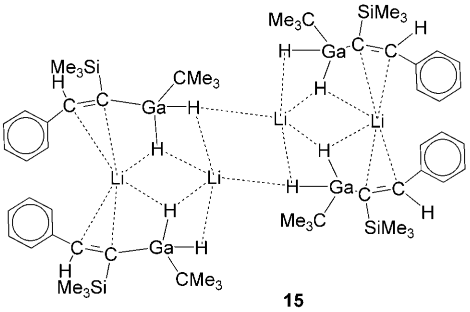


Scheme 1.

Table 1. Comparison of important NMR data of the *E*/*Z* isomers **1**, **13**, **6**, **14**, **17**, and **18**.

(R=CMe_3; R′=$SiMe_3$)	δC=C-*H*	δC=C-H	δ*C*=C-H	δ*ipso*-C	$^3J_{SiH}$
(*E*)-R_2Ga-(R′)C=C(H)-C_6H_5 (*cis*) (**1**)	7.52	150.7	162.8	142.4	19.9
(*Z*)-R_2Ga-(R′)C=C(H)-C_6H_5 (*trans*) (**13**)	7.92	150.8	168.5	147.2	11.1
(*E*,*E*)-[R_2Ga-(R′)C=C(H)]$_2C_6H_4$ (*cis*) (**6**)	7.46	150.5	163.1	141.4	19.6
(*Z*,*Z*)-[R_2Ga-(R′)C=C(H)]$_2C_6H_4$ (*trans*) (**14**)	7.83	149.9	168.0	145.5	11.6
(*Z*)-R_2Al-(R′)C=C(H)-C_6H_5 (*cis*) (**17**)	7.64	154.2	156.8	142.0	21.0
(*E*)-R_2Al-(R′)C=C(H)-C_6H_5 (*trans*) (**18**)	7.93	154.1	168.8	149.7	11.9

In some cases a byproduct (**15**) was isolated from the syntheses of the monoalkenyl compound **13** in up to 5% yield. A broad resonance in the ^1H NMR spectrum at $\delta =$ 2.92 ppm indicated the presence of hydrogen atoms attached to gallium. Compound **15** was identified by crystal-structure determination as the tetrameric lithium gallanate Li[Me_3C−GaH_2−C($SiMe_3$)=C(H)−C_6H_5]. Its formation may result from a threefold attack of *tert*-butyllithium and β-elimination. However, a specific reaction of **11** with three equivalents of *tert*-butyllithium failed. Treatment of the tetrachloro compound **12** with two equivalents of $LiCH(SiMe_3)_2$ gave a complicated mixture of products, from which the chlorogallium compound Cl−Ga[CH($SiMe_3$)$_2$]$_2$ (**16**) crystallized in trace quantities.



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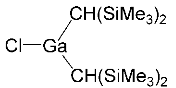

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Reactions of di(*tert*-butyl)aluminum hydride, spontaneous *cis*/*trans* isomerization: Similar to the hydrogallation reactions described before, the treatment of phenyltrimethylsilylethyne with di(*tert*-butyl)aluminum hydride yielded the pure

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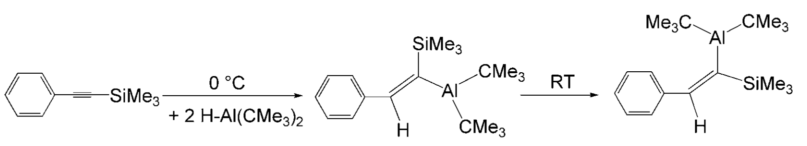

17 (*cis*, *Z*) **18** (*trans*, *E*)

Scheme 2.

cis-addition product (**17**) in the first step (Scheme 2). However, **17** was stable in solution only below 0 °C. Spontaneous *cis*/*trans* rearrangement occurred upon warming to room temperature, and the *trans* product (**18**) was formed quantitatively. Thus, in contrast to the corresponding and stable di(*tert*-butyl)gallium compound **1**, the *cis* product (**17**) of the hydroalumination reaction is thermally unstable and rearranges spontaneously at low temperature. A similar situation holds for the bis(alkenyl) compounds. While a *cis*/*trans* isomerization did not occur upon warming of the gallium compound **6**, the corresponding dialuminum compound showed a rearrangement upon heating of solutions to 60 °C.[2a] These observations underline our hypothesis that the rearrangement is initiated by intermolecular interactions. The higher polarity of the Al–C bonds may favor these interactions and may help to overcome the steric shielding by the relatively bulky *tert*-butyl groups. The melting points of **17** and **18** are below 0 °C. Nevertheless, we were able to determine the crystal structure of **18** (see below). The NMR data (Table 1) correspond to those of the gallium compounds with the $^{3}J_{\text{Si-H}}$ coupling constants as the most reliable criterion for a distinction between both constitutions (21.0 Hz for **17** and 11.9 Hz for **18**).

Molecular structures: We determined the molecular structures of the dialkenyl compound **14** (*Z*, Figure 1) and of the related di(neopentyl)- (**10**, Figure 2) and di(*n*-propyl)gallium derivatives (**8**, Figure 3), which were obtained by hydrogallation. Their synthesis and characterization as well as the molecular structure of the di(isopropyl)gallium compound **9** were reported previously.[6] All compounds reflect the formal *trans* addition of Ga–H bonds (*Z*), and their bond parameters are almost indistinguishable. The C=C bond lengths (134.4 pm on average) correspond to the standard bond length.[12] The molecules deviate considerably from planarity with the gallium atoms 195.9 (**14**), 200.4 (**10**) and 205.6/174.4 pm (**8**) above the plane of the central phenyl ring. By this particular arrange-

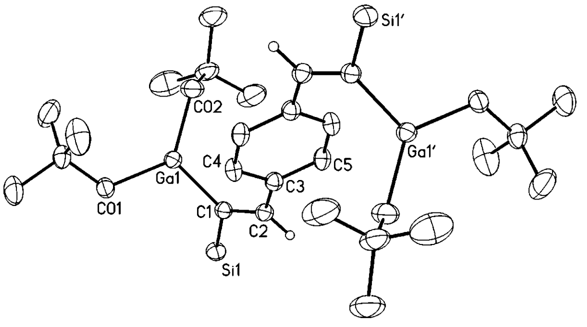

Figure 2. Molecular structure and numbering scheme of compound **10**. The thermal ellipsoids are drawn at the 40 % probability level. Hydrogen atoms with the exception of those attached to the C=C double bond are omitted. Selected bond lengths [pm] and angles [°]: Ga1–C1 197.8(2), Ga1–C01 197.5(3), Ga1–C02 198.9(3), C1–C2 133.3(3), C1–Si11 186.4(3), Ga1-C1-C2 117.4(2), Si11-C1-C2 120.3(2), Ga1-C1-Si11 122.3(4), C1-C2-C3 124.2(2); Ga1′ and Si1′ generated by $-x$, $-y$, $-z+1$.

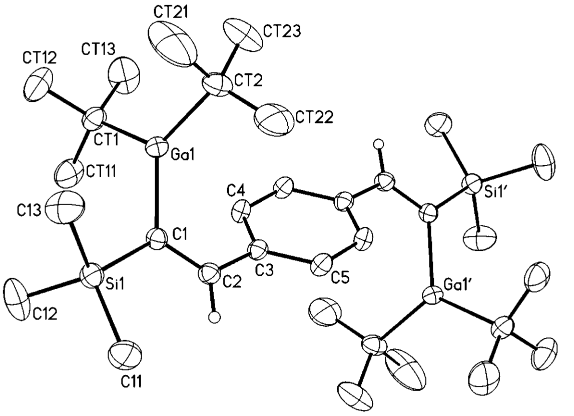

Figure 1. Molecular structure and numbering scheme of compound **14**. The thermal ellipsoids are drawn at the 40 % probability level. Hydrogen atoms with the exception of those attached to the C=C double bond are omitted. Selected bond lengths [pm] and angles [°]: Ga1–C1 198.0(2), Ga1–CT1 200.3(2), Ga1–CT2 200.8(2), C1–C2 134.6(2), C1–Si1 185.9(2), Ga1-C1-C2 116.0(1), Si1-C1-C2 120.1(1), Ga1-C1-Si1 123.31(8), C1-C2-C3 124.1(1); Ga1′ and Si1′ generated by $-x+1$, $-y$, $-z+1$.

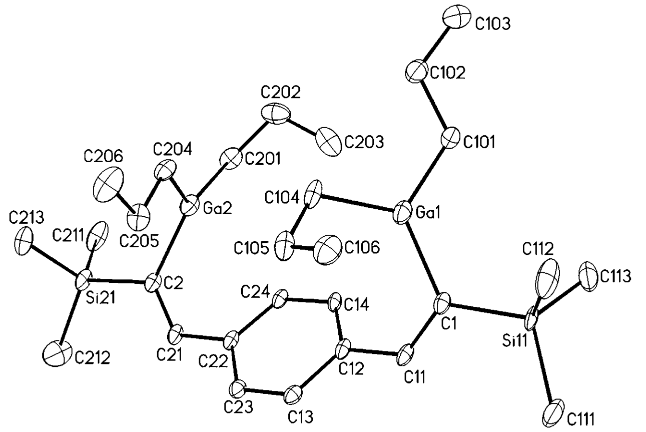

Figure 3. Molecular structure and numbering scheme of compound **8**. The thermal ellipsoids are drawn at the 40 % probability level. Hydrogen atoms are omitted. Selected bond lengths [pm] and angles [°]: Ga1–C1 197.7(3), C1–Si11 186.7(3), C1–C11 135.1(4), Ga2–C2 197.0(3), C2–Si21 186.1(3), C2–C21 134.4(4), Ga1-C1-C11 119.4(2), Si11-C1-C11 119.9(2), Ga1-C1-Si11 120.6(1), C1-C11-C12 125.7(3), Ga2-C2-C21 119.3(2), Si21-C2-C21 122.3(2), Ga2-C2-Si21 117.7(1), C2-C21-C22 124.8(2).

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ment the coordinatively unsaturated gallium atoms approach C–H bonds of the phenyl rings with relatively short Ga–H [243 (H4, **14**), 246 (H4, **10**), and 270/240 pm (H14/H24, **8**)] and Ga–C distances (286.4, 288.7, and 313.3/292.9 pm, respectively). However, the Ga atoms are only slightly above the plane spanned by the directly bonded carbon atoms (2 to 12 pm), indicating a relatively weak interaction. Interestingly, two different structural motifs were observed. The less shielded di(*n*-propyl)gallium compound **8** has both alkenylgallium moieties on the same side of the phenyl ring (point group approximately C_{2v}), while all compounds bearing bulkier alkyl groups possess a center of symmetry with the alkenylgallium groups on different sides. The unusual structure of **8** may be caused by crystal packing. Pairs of molecules result with the alkenylgallium groups on opposite sides. However, π stacking does not occur. Instead, we observe relatively short intermolecular distances between the centroids of the phenyl rings and hydrogen atoms of methylene groups (H20A at C201, 302 pm). These interactions have been interpreted in terms of weak hydrogen bonding.[13] Furthermore, two contacts occur between a hydrogen atom of a methyl group (H21C at C211) and a vinylic carbon atom (C11, 282 pm). The aluminum compound **18** (*Z*, Figure 4) shows quite similar structural parameters, and the Al–C (197.8 pm), Si–C(vinyl) (186.6 pm) and C=C bond lengths (134.7 pm) correspond to the values obtained for **8**, **10**, and **14**. Caused by steric repulsion the angle Si1–C1–Al1 in **18** is enlarged to 129.1°, while a relatively small angle (111.6°) results for the Al1–C1=C2 moiety. The aluminum atom is 189 pm above the average plane of the benzene ring, and a short distance resulted between the metal atom and an *ortho*-C–H bond of the phenyl ring (Al1–H22 222 pm; Al1–C22 261.1 pm). In contrast to these *trans* products, the *cis* isomer of **14** (compound **6**) has a rather flat molecular structure with the gallium atoms almost ideally in plane with the aromatic ring (deviation from the average plane 0.2 pm).[6] Caused by different steric interactions the angles Ga–C–C (113.0°) and Ga–C–Si of **6** (117.4°) are smaller and the angles Si–C–C (129.6°) much larger than those of **14**, **10**, and **8**.

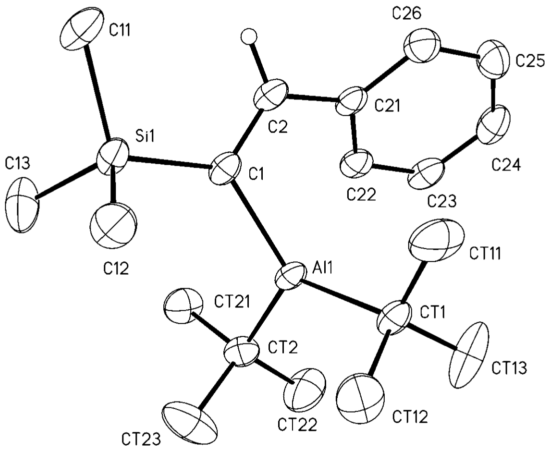

Figure 4. Molecular structure and numbering scheme of compound **18**. The thermal ellipsoids are drawn at the 40 % probability level. Hydrogen atoms are omitted with the exception of the vinylic hydrogen atom. Selected bond lengths [pm] and angles [°]: Al1–C1 197.8(2), C1–Si1 186.6(2), C1–C2 134.7(3), Al1-C1-C2 111.6(2), Si1-C1-C2 118.9(2), Al1-C1-Si1 129.1(1), C1-C2-C21 121.8(2).

The lithium gallanate **15** (Figure 5) was obtained as a minor byproduct of the synthesis of **13**. Its gallium atoms are attached to two hydrogen atoms, one *tert*-butyl group, and a vinylic carbon atom. Gallium and hydrogen are in *trans* positions across the C=C double bonds. A schematic drawing of the relatively complicated tetrameric structure of **15** is shown above. The central Li_2H_2 heterocycle is strongly distorted and has two relatively long Li–H distances (Li2–H110 233 pm, Li3–H320 238 pm compared to 189 pm). Both Li atoms (Li2, Li3) have a coordination number of five with a distorted trigonal-bipyramidal coordination sphere. They are part of two further, more regular Li_2H_2 heterocycles. The hydrogen atoms of these rings are coordinated to two lithium atoms and a gallium atom. The remaining two hydrogen atoms attached to gallium (H220, H420) have a coordination number of two. An interesting feature is the coordination of the lithium atoms Li1 and Li4 to two C=C double bonds. Relatively short distances resulted to the α-carbon atoms (C1 to C4; 232.1 to 240.5 pm).[14] Symmetric bonding only occurred for the double bond C3=C31, with two equal Li–C distances (240.5 and 240.6 pm), in all other cases the distances to the β-carbon atoms C11, C21, and C41 are lengthened by 7 to 22 pm. In addition, these lithium atoms have relatively short contacts to the *ipso*-carbon atoms of two phenyl groups (C22 and C32; 257 and 262 pm). They were not considered in Figure 5. The Li–alkene interactions may cause the small lengthening of the C=C double bonds (135.8 pm on average) compared to the compounds described before.

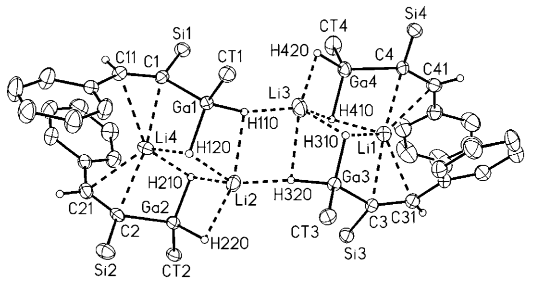

Figure 5. Molecular structure and numbering scheme of compound **15**. The thermal ellipsoids are drawn at the 40 % probability level. Methyl groups and hydrogen atoms of the phenyl groups are omitted. Selected bond lengths [pm] and angles [°]: Li1–C3 241(1), Li1–C31 241(1), Li1–C4 232(1), Li1–C41 256(1), Li4–C1 235.4(9), Li4–C11 257(1), Li4–C2 234.6(9), Li4–C21 241.2(9), C1–C11 136.6(6), C2–C21 134.9(7), C3–C31 135.4(6), C4–C41 136.3(6), Li–H are between 187(5) and 203(6), Li1–H310 216(5), Li2–H110 233(5), Ga–C(vinyl) 202.5(av.), Si–C(vinyl) 187.9 (av), Ga–C=C 128.4 (av.), Si–C=C 116.7 (av.), Ga–C–Si 114.7, C=C–C-(phenyl) 131.2.

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Compound Cl-Ga[CH(SiMe$_3$)$_2$]$_2$ (**16**) was isolated in a very low yield from the reaction of **12** with LiCH(SiMe$_3$)$_2$. In contrast to the facile synthesis of the corresponding aluminum chloride,[15] it is not available on a preparative scale. However, the similar bromide R$_2$Ga−Br was obtained by a less effective disproportionation reaction.[16] Owing to steric shielding by the bulky substituents, compound **16** is monomeric even in the solid state with a tricoordinated, coordinatively unsaturated gallium atom and a large angle C-Ga-C of 132.0° (Figure 6). The low coordination numbers cause a short Ga−Cl bond (219.4 pm), which is similar to the few other monomeric organogallium chlorides known in the literature.[17]

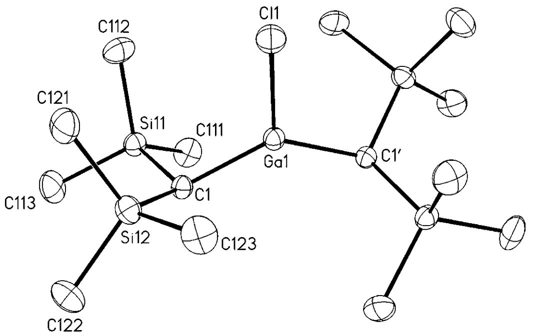

Figure 6. Molecular structure and numbering scheme of compound **16**. The thermal ellipsoids are drawn at the 40 % probability level. Hydrogen atoms are omitted. Selected bond lengths [pm] and angles [°]: Ga1−Cl1 219.35(8), Ga1−C1 194.4(2), C1-Ga1-C1′ 132.0(1), Cl1-Ga1-C1 114.02(6); C1′ generated by $-x+2$, y, $-z+1/2$.

Quantum-chemical calculations: Quantum-chemical calculations at the SCS-MP2/6–311+G(d,p)//B3LYP/6–311+G(d,p) level of theory were performed for 16 products of hydroalumination and hydrogallation reactions with the general compositions H$_5$C$_6$−C(H)=C(SiMe$_3$)−ER$_2$ and H$_5$C$_6$−C(ER$_2$)=C(H)−CMe$_3$ (R = Me, CMe$_3$; E = Al, Ga). Each compound was considered in its *cis* and *trans* (*E*/*Z*) forms. The calculated structural parameters (Table 2) correspond well to the experimental data of mono- and dialkenyl derivatives (e.g., **4**, **6**, **8**–**10**). In all cases the *trans*-addition products proved to be the thermodynamically favored ones. Bulky substituents attached to the metal atoms showed the strongest preference of the *trans* forms, and particularly large differences resulted for the products derived from trimethylsilylphenylethyne. The E−C and C=C bond lengths are not systematically affected by the different configurations.

Silylalkenes: The Si−C=C angles are larger for the *cis*-addition products (about 129° versus 119° for the *trans* forms), while the reverse was observed for the El−C=C angles (112 versus 119°). Thus, in both cases the close approach of the bond angle to the ideal value of 120° may indicate a smaller steric stress for the *trans* products. The torsion angles C−E−C=C indicate a relatively small deviation from a coplanar arrangement of alkenyl and EC$_3$ planes in the *cis*-dimethylelement compounds (27 to 30°), while in all other cases a stronger tilting of >60° was detected. An approach to a coplanar arrangement of the alkenyl and phenyl groups may indicate a better mesomeric interaction. However, there is only a slight advantage for the *trans* forms (34 versus 41°). Only in the *trans*-addition products a close contact of the coordinatively unsaturated aluminum or gallium atoms to C−H bonds of the phenyl groups was detected. Probably caused by these interactions, the metal atoms are slightly above the planes of the surrounding carbon atoms (10 pm). Calculation of the Wiberg bond indices for the compound H$_5$C$_6$−C(H)=C(SiMe$_3$)−GaMe$_2$ (0.04 and 0.02 for the Ga···C and Ga···H interaction, respectively) indicates an at least small contribution of this contact to the particular stability of the *trans* products.

tert-*Butylalkenes*: In these compounds the aluminum and gallium atoms are attached to those carbon atoms of the alkenyl groups that are also bonded to the phenyl groups.

Table 2. Important parameters from quantum-chemical calculations (SCS-MP2/6-31+G(d,p)//B3LYP/6-311+G(d,p); *cis* and *trans* refer to the addition direction; El = Al or Ga).

Compound	E_{rel} [kcal mol^{-1}]	El−C(=C) [pm]	C=C [pm]	El−C=C [°]	C−El−C=C [°]	C=C−C−C [°]
(*Z*)-Me$_2$AlC(SiMe$_3$)=CHPh (*cis*)	4.69	197.4	135.8	111.3	26.3/−149.3	−40.5/142.8
(*E*)-Me$_2$GaC(SiMe$_3$)=CHPh (*cis*)	4.08	199.5	135.5	111.8	26.8/−149.2	−40.7/142.6
(*Z*)-*t*Bu$_2$AlC(SiMe$_3$)=CHPh (*cis*)	7.87	198.5	135.4	112.3	72.6/−103.6	−40.6/142.0
(*E*)-*t*Bu$_2$GaC(SiMe$_3$)=CHPh (*cis*)	7.35	201.3	135.1	113.3	72.8/−102.9	−41.9/140.9
(*E*)-Me$_2$AlC(SiMe$_3$)=CHPh (*trans*)	0.00	198.4	135.2	117.9	71.7/−118.7	35.0/−143.8
(*Z*)-Me$_2$GaC(SiMe$_3$)=CHPh (*trans*)	0.00	200.0	135.0	119.5	68.6/−119.5	34.5/−145.1
(*E*)-*t*Bu$_2$AlC(SiMe$_3$)=CHPh (*trans*)	0.00	199.4	135.3	117.9	75.2/−117.0	33.2/−145.8
(*Z*)-*t*Bu$_2$GaC(SiMe$_3$)=CHPh (*trans*)	0.00	201.4	135.1	119.6	74.3/−114.9	31.8/−148.1
(*E*)-Me$_2$AlC(Ph)=CH−*t*Bu (*cis*)	2.25	197.7	135.0	115.9	1.4/−178.4	−91.0/94.3
(*E*)-Me$_2$GaC(Ph)=CH−*t*Bu (*cis*)	1.88	199.6	134.7	116.6	−1.3/178.9	−93.8/91.3
(*E*)-*t*Bu$_2$AlC(Ph)=CH−*t*Bu (*cis*)	5.92	199.1	134.7	116.1	−62.3/119.7	−76.2/108.6
(*E*)-*t*Bu$_2$GaC(Ph)=CH−*t*Bu (*cis*)	5.50	201.8	134.5	117.0	−58.7/121.3	−74.2/110.4
(*Z*)-Me$_2$AlC(Ph)=CH−*t*Bu (*trans*)	0.00	198.5	134.4	126.9	−94.1/96.1	48.3/−133.4
(*Z*)-Me$_2$GaC(Ph)=CH−*t*Bu (*trans*)	0.00	200.3	134.2	127.0	−93.9/94.5	49.0/−132.5
(*Z*)-*t*Bu$_2$AlC(Ph)=CH−*t*Bu (*trans*)	0.00	199.6	134.4	125.9	−92.9/100.7	−47.5/134.2
(*Z*)-*t*Bu$_2$GaC(Ph)=CH−*t*Bu (*trans*)	0.00	201.8	134.3	127.2	−90.3/100.7	−46.8/134.9

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Once more the E−C=C angles are larger for the *trans* forms (127 versus 116°). However, the remaining angles (C(phenyl)−C=C and $C(CMe_3)$−C=C) are less favorable for the *cis* isomers (126 and 134° versus 119 and 129°). The dimethyl–element groups of the *cis* isomers are almost ideally in plane with the alkenyl groups (torsion angles close to 0°), while in all other cases an almost perpendicular arrangement resulted (60 to 90°). The torsion angles across the C−C bonds between the alkenyl and phenyl groups are about 48° for the *trans* molecules, while an almost perpendicular arrangement was obtained for the *cis* compounds (75 to 90°). These last data indicate a negligible mesomeric interaction, while the other values may verify a stabilization by π interaction.[18] The quantum-chemical calculations substantiate the energetic preference of the *trans*-hydroalumination and -gallation products in all cases. The stabilization depends on several reasons such as the minimization of steric stress, a more or less optimum overlap for mesomeric interactions or weak coordinative intramolecular contacts.

Mechanism of isomerization: Investigations concerning the rotational barrier about the C=C double bond were conducted for the compound H_5C_6−C(H)=$C(SiMe_3)$−$GaMe_2$. The *cis* and *trans* forms were considered as well as the transition state with the C(H)–phenyl plane perpendicular to the CGaSi plane. The C−C bond length of the double bond increases to 140.7 pm in the transition state (vs. 135 pm), and the Ga−C and Si−C bonds are shortened by about 4 pm. Strong charge separations are calculated for the C=C double bonds of the *cis* and *trans* forms with natural charges of −0.9 to −1.0 at the carbon atoms attached to gallium and silicon and −0.2 at the second carbon atom. These differences increase on going to the transition state with charges of −1.3 and +0.1. This high negative charge may influence the shortening of the Ga−C and Si−C bonds by additional electrostatic interactions. The rotational barrier was determined to a relatively low value of 41.9 $kcal\,mol^{-1}$. While the rotation of simple alkenes usually involves a biradical intermediate, our results confirm a zwitterionic mechanism for the gallium compound similar to alkenes possessing a push–pull substitution pattern.[19] Unrestricted (UB3LYP) calculations for the transition state of the gallium compound resulted also in these closed-shell-electron structures.

The strong charge separation in the transient species caused us to consider an interaction of the strongly negatively charged carbon atom with a lithium cation as a Lewis acid and the influence of such an interaction on the isomerization process. The optimized structures have the lithium atom coordinated to the carbon atom of the CGaSi group and to a methyl group. The charges at the carbon atoms of the C=C double bond in the *cis* and *trans* forms (−1.1 and −0.2) are close to the values obtained without lithium; however, a stronger separation was calculated for the transition state with −1.5 and +0.1. The rotational barrier was considerably reduced to +25.6 $kcal\,mol^{-1}$, thus, allowing the isomerization already at room temperature. These results present strong evidence that an intermolecular activation of the *cis*/*trans* isomerization may be required for the occurrence of a spontaneous rearrangement. This might be facilitated by an approach of any Lewis acid, for example, an aluminum or gallium atom of a second molecule in the case of low steric shielding of the hydroalumination or hydrogallation products. Interestingly, such a mechanism is in accordance with predictions given in early publications on hydroalumination.[1] In polyaluminum or gallium compounds *cis*/*trans* isomerization is important for their application as effective chelating Lewis acids, for instance.[10] Hence, these results may strongly influence the further development of this particular area of chemistry and may allow the generation of *trans* isomers in cases where the rearrangement has not been observed yet.

Experimental Section

General: All procedures were carried out under purified argon. Cyclopentane, *n*-pentane, and *n*-hexane were dried over $LiAlH_4$, toluene over Na/benzophenone. The compounds **11**, **12**, and $LiCH(SiMe_3)_2$ were obtained according to literature procedures.[10b,20] Commercially available solutions of *tert*-butyllithium (1.5 M in *n*-pentane, Aldrich) were used as purchased.

Synthesis of the monoalkenyl compound 13: The alkenyldichlorogallium compound **11** (0.85 g, 2.69 mmol based on the monomeric formula unit) was dissolved in *n*-hexane (50 mL) and cooled to 0 °C. *tert*-Butyllithium (1.5 M in *n*-pentane, 3.59 mL, 5.38 mmol) was added. Lithium chloride precipitated, which was filtered off after stirring over night. Concentration and cooling of the filtrate to 4 °C afforded a colorless solid of **13**, which melted upon warming to room temperature. In some cases the colorless compound **15** crystallized as the first fraction with yields between 0 and 5 %. Yield of **13**: 0.434 g (45 %); ^1H NMR (400 MHz, C_6D_6): $\delta = 7.92$ (s, $^3J_{Si\text{-}H} = 11.1$ Hz, 1 H; C=CH), 7.07 (m, 2 H; *meta*-CH of phenyl), 6.96 (m, 2 H; *ortho*-CH of pheny), 6.96 (m, 1 H; *para*-CH of phenyl), 1.11 (s, 18 H; CMe_3), 0.25 ppm (s, 9 H; $SiMe_3$); ^{13}C NMR (100 MHz, C_6D_6,): $\delta =$ 168.5 (C=C(Si)Ga), 150.8 (*C*=*C*(Ga)Si), 147.2 (*ipso*-C of phenyl), 130.4 (*meta*-C of phenyl), 128.1 (*para*-C of phenyl), 124.0 (*ortho*-C of phenyl), 30.4 (CMe_3), 28.5 (CMe_3), 0.40 ppm ($SiMe_3$); ^{29}Si NMR (79.5 MHz, C_6D_6): $\delta = -7.6$ ppm; IR (CsBr plates, paraffin): $\tilde{\nu} = 1577$ (vs), 1558 (vs) νC=C, phenyl; 1462 (vs) paraffin; 1402 (m) δCH_3; 1377 (vs) paraffin; 1112 (s), 1076 (s), 1014 (w) νCC; 927 (vw), 889 (w), 844 (w), 814 (w) ρCH_3(Si); 719 (s) paraffin; 702 (w), 667 (vw) ν_{as}SiC; 621 (vw) ν_sSiC; 579 (w), 563 (vw), 532 (vw), 482 (m), 428 cm^{-1} (w) νGaC.

Characterization of compound 15: ^1H NMR (400 MHz, C_6D_6): $\delta = 7.44$ (s, 1 H; C=CH), 7.32 (m, 2 H; *ortho*-CH of phenyl), 7.09 (m, 2 H; *meta*-CH of phenyl), 6.99 (m, 1 H; *para*-CH of phenyl), 2.92 (br s, 2 H; GaH), 1.39 (s, 9 H; CMe_3), 0.28 ppm (s, 9 H; $SiMe_3$); ^{13}C NMR (100 MHz, C_6D_6): $\delta =$ 163.5 (C=C(Si)Ga), 151.0 (*C*=*C*(Ga)Si), 138.7 (*ipso*-C of phenyl), 129.5 (*para*-C of phenyl), 129.2 (*meta*-C of phenyl), 128.9 (*ortho*-C of phenyl), 33.5 (CMe_3), 20.7 (CMe_3), −0.1 ppm ($SiMe_3$); ^{29}Si NMR (79.5 MHz, C_6D_6): $\delta = -1.6$ ppm; IR (CsBr plates, paraffin): $\tilde{\nu} = 1578$ (vs), 1558 (vs), 1521 (w) νC=C, νGaH, phenyl; 1456 (vs) paraffin; 1404 (w) δCH_3; 1377 (s) paraffin; 1364 (m), 1306 (vw), 1244 (s) δCH_3; 1188 (w), 1155 (w) νCC; 1113 (br w) δGaH; 1078 (w), 1030 (vw), 1011 (vw), 957 (w) νCC; 930 (m), 891 (m), 843 (s), 831 (s), 756 (s) ρCH_3(Si); 719 (m) paraffin; 692 (m) ν_{as}SiC; 625 (vw) ν_sSiC; 573 (vw), 542 (vw), 501 (m), 482 (w), 432 cm^{-1} (w) νGaC; MS (EI, 70 eV): *m*/*z* (%): 301 (100), 302 (23) 303 (78), 304 (15) [H_5C_6−CH=$C(SiMe_3)$−Ga−CMe_3].

Synthesis of the dialkenyl compound 14: The tetrachlorogallium starting compound **12** (0.24 g, 0.43 mmol) was dissolved in *n*-hexane (100 mL) and treated with *tert*-butyllithium (1.5 M in *n*-pentane, 1.16 mL, 1.73 mmol) at room temperature. The mixture was heated under reflux for 2 h. Color change to light red occurred. After further stirring at room temperature for 16 h the precipitate of LiCl was filtered off. The solvent was removed in vacuum, and the residue was dissolved in toluene. The product crystallized as colorless crystals after cooling of the solution to −30 °C. Yield: 0.107 g (39 %); m.p. (argon, sealed capillary): 120 °C (decomp); ^{1}H NMR (400 MHz, C_6D_6): δ = 7.83 (s, $^3J_{Si-H}$ = 11.6 Hz, 2 H; C=C–H), 6.98 (s, 4 H; phenyl), 1.15 (s, 36 H; CMe$_3$), 0.24 ppm (s, 18 H; SiMe$_3$); ^{13}C NMR (100 MHz, C_6D_6): δ = 168.0 8(C=C(Si)Ga), 149.9 (*C*=*C*(Ga)Si), 145.5 (*ipso*-C of phenyl), 126.1 (*ortho*-C of phenyl), 30.5 (C*Me*$_3$), 28.9 (GaCMe$_3$), 0.4 ppm (SiMe$_3$); ^{29}Si NMR (79.5 MHz, C_6D_6): δ = −7.3 ppm; IR (CsBr plates, paraffin): $\tilde{\nu}$ = 1576 (w), 1564 (w), 1549 (w), 1493 (w) νC=C, phenyl; 1464 (vs), 1454 (vs) paraffin; 1402 (vw) δCH$_3$; 1377 (m) paraffin; 1362 (w), 1244 (s) δCH$_3$; 1171 (vw), 1107 (w) νCC; 958 (vw), 908 (m), 881 (m), 833 (s), 808 (s), 745 (m) ρCH$_3$(Si); 727 (w) paraffin; 687 (w) ν_{as}SiC; 621 (vw) ν_sSiC; 556 (w), 521 (vw), 490 (w), 426 cm^{-1} (m) νGaC; MS (EI, 70 eV): *m/z* (%): 623 (0.2), 625 (0.5), 627 (0.3) [M^+−CH$_3$]; 581 (62), 583 (100), 585 (43) [M^+−*t*Bu].

Synthesis of the *cis*-aluminum compound 17: Di(*tert*-butyl)aluminum hydride (0.430 g, 3.03 mmol) was dissolved in *n*-pentane (20 mL) and cooled to 0 °C. The solution was treated with phenyltrimethylsilylethyne (0.60 mL, 0.527 g, 3.03 mmol) dissolved in *n*-pentane (25 mL). The color changed to light brown. The mixture was stirred at 0 °C for 3 h and filtered. The solvent was removed in vacuum at −10 °C. The NMR spectroscopic characterization indicated that the residue contains the pure compound **17**. Yield: 0.890 g (93 %); **17** is solid at −10 °C, but melts upon warming to 0 °C; ^{1}H NMR (400 MHz, [D$_8$]toluene, 220 K): δ = 7.64 (s, $^3J_{Si-H}$ = 21.0 Hz, 1 H; C=C-H), 7.26 (m, 2 H; *ortho*-H of phenyl), 7.12 (m, 2 H; *meta*-H of phenyl), 7.05 (m, 1 H; *para*-H of phenyl), 1.18 (s, 18 H; CMe$_3$), 0.18 ppm (s, 9 H; SiMe$_3$); ^{13}C NMR (100 MHz, [D$_8$]toluene, 220 K): δ = 156.8 (C=C(Si)Al), 154.2 (*C*=*C*(Si)Al), 142.0 (*ipso*-C of phenyl), 128.2 (*meta*-C of phenyl), 127.9 (*ortho*-C of phenyl), 127.6 (*para*-C of phenyl), 29.7 (C*Me*$_3$), 19.2 (AlCMe$_3$), 1.0 ppm (SiMe$_3$); ^{29}Si NMR (79.5 MHz, [D$_8$]toluene, 220 K): δ = −13.6 ppm.

Synthesis of the *trans*-aluminum compound 18: Di(*tert*-butyl)aluminum hydride (0.370 g, 2.60 mmol) was dissolved in *n*-pentane (20 mL) and added to a solution of phenyltrimethylsilylethyne (0.51 mL, 0.453 g, 2.60 mmol) in *n*-pentane (25 mL) at room temperature. The color changed to light brown. The mixture was stirred for 3 h and filtered. The solvent was removed in vacuum at 0 °C. The NMR spectroscopic characterization indicated that the residue contains compound **18** in high purity. Yield: 0.790 g (96 %). Colorless crystals of **18** were obtained by cooling of solutions in cyclopentane to −45 °C. They melted below 0 °C. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ = 7.93 (s, $^3J_{Si-H}$ = 11.9 Hz, 1 H; C=C-H), 7.08 (m, 2 H; *meta*-H of phenyl), 7.06 (m, 2 H; *ortho*-H of phenyl), 6.93 (m, 1 H; *para*-H of phenyl), 1.01 (s, 18 H; CMe$_3$), 0.27 ppm (s, 9 H; SiMe$_3$); ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ = 168.8 (C=C(Si)Al), 154.1 (*C*=*C*(Si)Al), 149.7 (*ipso*-C of phenyl), 132.0 (*meta*-C of phenyl), 128.5 (*para*-C of phenyl), 122.4 (*ortho*-C of phenyl), 30.0 (C*Me*$_3$), 18.5 (AlCMe$_3$), 0.4 ppm (SiMe$_3$); ^{29}Si NMR (79.5 MHz, C_6D_6, 220 K): δ = −7.4 ppm; IR (CsBr plates, paraffin): $\tilde{\nu}$ = 1595 (vw), 1528 (m), 1485 (w) νC=C, phenyl; 1462 (s) paraffin; 1443 (w) δCH$_3$; 1385 (m) paraffin; 1360 (w), 1315 (vw), 1246 (s) δCH$_3$; 1175 (vw), 1074 (vw), 1001 (vw) νCC; 926 (s), 899 (vs), 845 (vs), 831 (vs), 808 (s), 754 (s) ρCH$_3$(Si); 706 (m), 689 (w) ν_{as}SiC; 627 (w) ν_sSiC; 592 (s), 554 (vw), 488 (w), 434 (m), 401 cm^{-1} (m) νAlC; MS (EI, 20 eV, 303 K): *m/z* (%): 316 (4.4) [M^+], 259 (100) [M^+−*t*Bu].

Crystal structure determinations of 8, 10, 14–16, and 18: Single crystals were obtained by recrystallization from different solvents (**8**: *n*-hexane at −80 °C; **10**: *n*-hexane at −30 °C; **14**: toluene at −30 °C; **15**: *n*-hexane at +4 °C; **16**: *n*-hexane at −80 °C; **18**: cyclopentane at −45 °C). Crystal data, data collection parameters, and structure refinement details are given in Table 3. The crystallographic data were collected with a BRUKER apex diffractometer. The structures were solved by direct methods and refined with the program SHELXTL-97[21] by a full-matrix least-squares method based on F^2. The molecules of **10** and **14** were situated on crystallographic centers of symmetry, those of **16** on twofold rotation axes. One *tert*-butyl group of **14** (CT2) showed a disorder, the methyl groups were refined on split positions. The crystals of compound **10** included one *n*-hexane molecule per formula unit, which was strongly disordered over a center of symmetry. CCDC-692591 (**8**), CCDC-692592 (**10**), CCDC-692593 (**14**), CCDC-692594 (**15**), CCDC-692595 (**16**) and CCDC-692596 (**18**) 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.

Quantum-chemical calculations: Quantum-chemical calculations were carried out applying the DFT method (B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p)[22] for geometry optimizations using the GAUSSIAN 03 series of programs. The recently developed SCS-MP2/6-311+D(d,p)//B3LYP/6–11+G(d,p) method was used for the energy determinations.[23] The reported relative energies are corrected for 0 K using the DFT zero-

Table 3. Crystal data for the compounds **8**, **10**, **14–16** and **18**.

	8	**10**	**14**	**15**	**16**	**18**
formula	$C_{28}H_{52}Ga_2Si_2$	$C_{42}H_{68}Ga_2Si_2$	$C_{32}H_{60}Ga_2Si_2$	$C_{60}H_{104}Ga_4Li_4Si_4$	$C_{14}H_{38}ClGaSi_4$	$C_{19}H_{33}AlSi$
crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$C2/c$	$P\bar{1}$
a [pm]	1018.26(4)	998.7(5)	878.9(2)	1299.11(6)	1744.0(1)	856.32(4)
b [pm]	1265.34(5)	2721.0(14)	1599.2(4)	1846.69(9)	661.69(5)	1027.09(4)
c [pm]	1503.02(6)	1017.4(5)	1362.2(3)	2992.4(1)	2206.8(2)	1291.04(6)
α [°]	65.329(2)	90	90	90	90	97.916(3)
β [°]	77.585(2)	118.528(8)	105.391(4)	94.432(3)	108.914(1)	94.884(3)
γ [°]	66.776(2)	90	90	90	90	112.062(3)
V [10^{-30} m^3]	1614.3(1)	2430(10)	1845.9(7)	7157.4(6)	2409.0(3)	1030.67(8)
Z	2	2	2	4	4	2
ρ [g cm^{-3}]	1.202	1.051	1.152	1.155	1.169	1.020
μ [mm^{-1}]	2.834 (Cu$_{K\alpha}$)	1.181 (Mo$_{K\alpha}$)	1.541 (Mo$_{K\alpha}$)	2.578 (Cu$_{K\alpha}$)	1.445 (Mo$_{K\alpha}$)	1.343 (Cu$_{K\alpha}$)
T [°C]	153(2)	153(2)	153(2)	153(2)	153(2)	153(2)
θ_{max} [°]	72.61	30.03	30.05	72.93	31.27	72.05
total reflns	9380	27285	20891	41267	13479	5965
unique reflns	5499	7058	5351	13659	3711	3470
R_{int}	0.0441	0.0395	0.0263	0.0823	0.0395	0.0432
obsvd reflns [$I>2\sigma(I)$]	5285	5189	4480	9456	2937	2671
parameters	299	211	203	705	98	199
R_1 [$I>2\sigma(I)$]	0.0479	0.0510	0.0324	0.0639	0.0430	0.0549
$wR2$ [all data]	0.1314	0.1417	0.0872	0.2109	0.1009	0.1653
GOF	1.100	1.033	1.054	1.009	1.051	1.082
max/min residus [10^{30} e m^{-3}]	0.795/−1.12	1.03/−0.460	1.04/−0.221	1.17/−0.941	1.02/−0.507	0.504/−0.373

point energy (ZPE). The natural charges and bond orders (Wiberg bond indices) given were calculated using the NBO method as implemented into the GAUSSIAN 03 program.

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