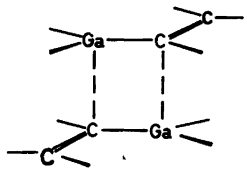
The Molecular Structure of Monomeric Trivinylgallium Determined by Gas Phase Electron Diffraction

TORGNY FJELDBERG,[a] ARNE HAALAND,[b] RAGNHILD SEIP [b] and J. WEIDLEIN [c]

[a] Department of Chemistry, University of Trondheim NLHT, Trondheim, Norway, [b] Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway and [c] Institut für Anorganische Chemie der Universität Stuttgart, D-7 Stuttgart-80, Germany

Trivinylgallium, Vi_3Ga, is dimeric in cyclohexane [1] and benzene.[2] The ^1H and ^{13}C NMR spectra and the vibrational spectra (IR and Raman) of the dimer are easily interpreted in terms of relatively unperturbed monomer units.[2] We believe, therefore, that the dimer consists of two somewhat distorted monomers joined by relatively long and weak bonds between the metal atom of each unit and the unsaturated C_α atom of the other:



Such a mode of association is analogous to that found in dimeric $(CH_3)_2Ga{\equiv}CCH_3$ in the gas phase.[3] However, a more symmetrical structure corresponding to two two-electron three-center Al $-$C(bridge)$-$Al bonds as found in crystalline $[(CH_3)_2CHCH_2]_4Al_2[\mu\text{-}CH{=}CHC(CH_3)_3]_2$,[4] cannot be ruled out.

In the hope of obtaining structural information about the dimer, we have recorded the gas phase electron diffraction data of Vi_3Ga, using Balzers Eldigraph KD-G2 with nozzle temperatures ranging from 60 to 80 °C. Four plates obtained with a nozzle to plate distance of about 50 cm covering the scattering range $s = 1.875$ to 15.250 Å^{-1} were photometered. The data were processed using the standard programs of this laboratory.[5]

Radial distribution curves obtained by Fourier inversion of the experimental modified molecular intensities proved consistent with a monomer concentration of 100% in the gas jet. See Fig. 1.

The molecular structure of the monomer was refined by least squares calculations on the intensity data with a diagonal weight matrix.[6] Initial refinements were based on a planar model of C_{3h} symmetry. All C$-$H bond distances were assumed equal and all valence angles ∠CCH were fixed at 121°. The molecular structure is then determined by the Ga$-$C, C=C and C$-$H bond distances and the valence angle ∠GaCC. The four structure parameters were refined under the constraints of a geometrically consistent r_a structure, along with seven root-mean-square vibrational amplitudes. Since the theoretical RD curve calculated for the best C_{3h} model differed substantially from the experimental RD curve in the region of the C(1)$-$C(2′) and C(1)$-$C(2″) distances, the symmetry fo the model was lowered to C_3 and the torsional angle about the Ga$-$C bonds, τ(Ga$-$C), introduced as a fifth independent structure parameter. The refinement converged to give the parameter values listed in Table 1. The estimated standard deviations have been multiplied by a factor of two to account for data correlation. As shown in Fig. 1 the best model of C_3 symmetry leads to satisfactory agreement between experimental and calculated RD curves.

Though Vi_3Ga has been found to be dimeric in cyclohexane and benzene, the degree of association of dimethyl(vinyl)gallium in benzene has been found to vary between 1.28 and 1.65.[2] Vinyl bridges between Ga atoms are clearly not very stable, and it is perhaps not surprising that gaseous Vi_3Ga is found to consist of monomers only.

Table 1. Interatomic distances, valence angles and root-mean-square vibrational amplitudes (l) of Vi_3Ga obtained by refinement on a model of C_3 symmetry. Estimated standard deviations are given in parentheses in units of the last digit.

	r_a/Å	l/Å
Ga$-$C	1.963(3)	0.041(6)
C=C	1.335(5)	0.04(2)
C$-$H	1.094(8)	0.09(2)
Ga$-$C(2)	2.88	0.081(5)
C(1)$-$C(1′)	3.40	0.12(2)
C(1)$-$C(2′)	4.58	0.10(2)[a]
C1$-$C(2″)	3.71	0.30(5)
C(2)$-$C(2′)	4.93	0.26(2)[a]
Angles (°)		
∠GaCC	120.8(4)	
∠CCH	121 (ass)	
τ(Ga$-$C)[b]	24(5)	

[a] Assumed to differ by 0.16 Å. [b] Torsional angle CGaCC. Defined as zero when the molecule is planar.

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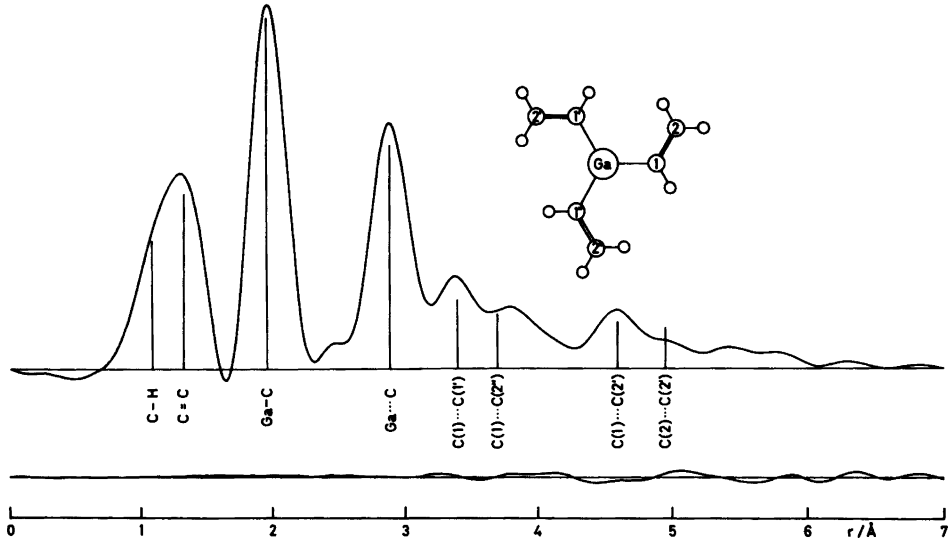

Fig. 1. Molecular model of Vi_3Ga and experimental radial distribution (RD) curve. Artificial damping constant $k=0.003$ Å^2. Major interatomic distances are indicated by bars of height approximately proportional to the area under the corresponding peak. Below: Difference between the experimental RD curve and the theoretical curve calculated for best model.

The Ga–C bond distance in Vi_3Ga is very similar to the Ga–C bond distance in $(CH_3)_3Ga$, 1.967(2) Å.[7]

In other respects the structure of Vi_3Ga is similar to that of Vi_3B which has been studied by Beagley and coworkers.[8] For Vi_3B refinement on a model of C_3 symmetry yielded a torsional angle about the B–C bonds, $\tau(B-C)=31°$. Like Beagley and coworkers we interpret the nonzero value of τ as evidence for large amplitude motion about a planar equilibrium conformation: If rotational motion about Ga–C was non-hindered, the peaks corresponding to C(1)–C(2′) and C(1)–C(2″) should not have been resolved in the RD curve. Since the RD curve does not go to zero between the two peaks, we expect the barrier to rotation to lie in the range 2 to 6 kJ mol^{-1}.

The C=C bond distance in Vi_3B, $r_a=1.370(6)$ Å, is significantly longer than in ethylene, 1.338(2).[9] This elongation is interpreted as evidence for delocalization of the C=C π-electrons into the formally empty p_z orbital on B. Such delocalization is expected to stabilize the planar conformation. The C=C bond distance in Vi_3Ga is not significantly different from a standard value and thus offers no evidence of a similar delocalization. On the other hand the planar configuration of Vi_3B appears to be destabilized by close H---H contacts between H atoms in different Vi groups (H(1)---H(2″)). Due to the larger size of the Ga atom, there are no close H---H contacts in Vi_3Ga.

Since the molecular structure of monomeric Vi_3Ga shows no unexpected features, we did not consider it worth-while to synthesize another sample in order to record more electron diffraction data.

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