

The Molecular Structures of Dimeric Dimethyl(propynyl)-gallium and -indium, $[(\text{CH}_3)_2\text{M}(\mu\text{-C}\equiv\text{CCH}_3)]_2$ M=Ga and In, Determined by Gas Phase Electron Diffraction

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The gas phase electron-diffraction patterns of dimethyl(propynyl)-gallium and -indium have been recorded with nozzle temperatures of about 50 and 90 °C, respectively. The experimental data are consistent with dimeric molecules of C_{2h} symmetry. The molecular structures are similar to that of the analogous Al compound. The three compounds are best described as consisting of somewhat distorted monomer units joined by donation of $\text{C}\equiv\text{C}$ π -electrons into a vacant p_z orbital on the metal atom of the other unit. The corresponding M–C' distances are 2.24(3) Å in the case of Ga and 2.52(4) Å in the case of In.

Trimethylgallium and trimethylindium are monomeric in the gas phase and in hydrocarbon solution.¹ Gas phase electron-diffraction investigations of the two compounds have yielded the bond distances Ga–C=1.967(2) Å² and In–C=2.093(6) Å.³ The latter value is considerably smaller than that obtained in an earlier electron-diffraction study of $(\text{CH}_3)_3\text{In}$,⁴ 2.16 ± 0.04 Å. It is also, as pointed out in Ref. 3, smaller than the In–C bond distances obtained in X-ray studies of several organo-indium compounds, and significantly smaller than the In–C (methyl) bond distance in $[(\text{CH}_3)_2\text{In}(\mu\text{-C}\equiv\text{CCH}_3)]_2$ obtained in this study. We suspect, therefore, that the last study of $(\text{CH}_3)_3\text{In}$ may be marred by a scale error, and that the correct value for the In–C bond distance is around 2.16 Å.

In monomeric $(\text{CH}_3)_3\text{Ga}$ and $(\text{CH}_3)_3\text{In}$ the metal atom is surrounded by six electrons only, and the

valence shell p_z orbital, which is perpendicular to the MC_3 plane of the molecule, must be assumed vacant. In the crystalline phase the monomeric units of trimethylindium can still be recognized, the average In–C distance being 2.22 Å.⁵ But the indium atom in each monomer unit appears to interact weakly with two neighbouring monomer units through the formation of very unsymmetric linear In---H₃C–In bridges, in the positive and negative z -directions. The two In---C distances are about 3.10 and 3.60 Å; much longer than single In–C bonds. The coordination polyhedron of each In atom is thus a distorted trigonal bipyramid.

The coordination polyhedron of In in crystalline triphenylindium may also be described as a trigonal bipyramid.⁶ The monomer units can be clearly recognized, the mean In–C bond distance being 2.140 Å. In the z -direction the In atom appears to interact with a phenyl group C atom in the units above and below, the two In---C distances being 3.07(2) Å. In crystalline triphenylgallium there appear to be similar, but much weaker interactions, the axial Ga---C distances being 3.42(1) Å.⁶

In crystalline dimethyl(propynyl)indium the axial positions on the trigonal bipyramidal coordination polyhedron of each indium atom are occupied by the $\text{C}\equiv\text{C}$ fragments of two neighbouring monomer units.⁷ The distance from the indium atom to the midpoint of the triple bond is 2.90 Å, to the two carbon atoms 2.93(2) and 2.99(2) Å. The average In–C(methyl) group distance is 2.18 Å.

Triphenyl-indium and -gallium are monomeric in cyclohexane and benzene.⁸ By contrast the molec-

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ular weights of dimethyl(propynyl)-indium and -gallium in benzene correspond to the presence of dimers and appear to be independent of concentration. The intermolecular interactions involving propynyl groups are clearly considerably stronger than those involving alkyl or phenyl groups. Since we have recently determined the molecular structure of $[(\text{CH}_3)_2\text{Al}(\mu\text{-C}\equiv\text{CCH}_3)]_2$ by gas phase electron diffraction,⁹ we decided to attempt a similar study of the analogous Ga and In compounds.

EXPERIMENTAL AND STRUCTURE ANALYSIS

$(\text{CH}_3)_2\text{M}(\text{C}\equiv\text{CCH}_3)$, $\text{M}=\text{Ga}$ and In was prepared as described by Weidlein *et al.*⁷ The electron scattering patterns were recorded on Balzers Eldigraph KDG-2 with reservoir and nozzle temperatures of about 50°C (Ga) and 90°C (In). In order to keep the temperature at a minimum, we used a nozzle with a wide opening and the convergent beam geometry previously used in studies of bisneopentylmagnesium¹⁰ and bis(pentamethylcyclopentadienyl)germanium.¹¹

Exposures were made with nozzle-to-plate distances of 50 and 25 cm. The number of plates used were

five 50 cm and three 25 cm plates for Ga, and four 50 cm and four 25 cm plates for In.

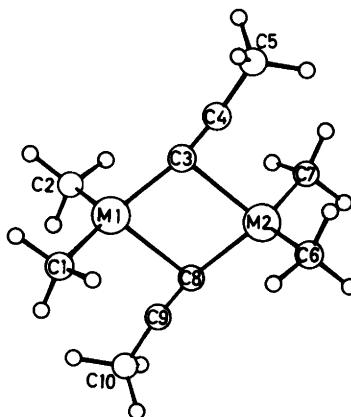


Fig. 1. Molecular model of $[(\text{CH}_3)_2\text{M}(\mu\text{-C}\equiv\text{CCH}_3)]_2$, $\text{M}=\text{Ga}$, In . Symmetry C_{2h} .

The data were processed using the programs described by Andersen *et al.*¹² The complex atomic scattering factors, $f(s)$, were calculated from an analytical representation of the atomic potential¹³ using a program written by Yates.¹⁴ The molecular intensities were modified through multiplication by $s/f_C(s)^2$. The average modified molecular intensities for each plate set were scaled and connected. The connected intensity curves ranged from $s=1.50$ to

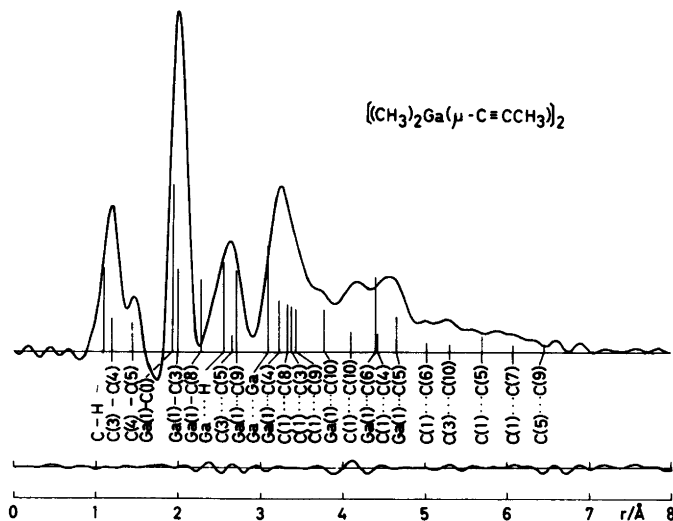


Fig. 2. Above. Experimental radial distribution curve for $[(\text{CH}_3)_2\text{Ga}(\mu\text{-C}\equiv\text{CCH}_3)]_2$. Artificial damping constant $k=0.001 \text{ \AA}^2$. Major interatomic distances are indicated by bars of height proportional to the area under the corresponding peak. Below. Difference between the experimental curve and a theoretical RD curve calculated for the best model.

Table 1. Interatomic distances, valence angles and root mean square vibrational amplitudes of $[(\text{CH}_3)_2\text{M}(\mu-\text{C}\equiv\text{CCH}_3)]_2$, M = Ga and In. Estimated standard deviations in parentheses in units of the last digit.

M	Ga		In	
	$r_a/\text{\AA}$	$l/\text{\AA}$	$r_a/\text{\AA}$	$l/\text{\AA}$
M(1)–C(1)	1.964(6)	0.053(4) ^a	2.18(2)	0.070(11) ^a
M(1)–C(3)	2.02(2)	0.073(4) ^a	2.19(3)	0.090(11) ^a
M(1)–C(8)	2.24(3)	0.20(2)	2.52(4)	0.175(ass)
C(3)–C(4)	1.22(1)	0.035(ass)	1.23(2)	0.035(ass)
C(4)–C(5)	1.45(1)	0.048(10)	1.48(2)	0.048(ass)
C–H	1.107(5)	0.081(7)	1.102(7)	0.099(15)
M---M	3.12(1)	0.129(9)	3.40(2)	0.148(12)
M(1)---C(4)	3.22(2)	0.090(ass)	3.35(3)	0.090(ass)
M(1)---C(5)	4.64(2)	0.101(13)	4.83(3)	0.08(3)
M(1)---C(6)	4.41(2)	0.30(3)	4.74(5)	0.36(11)
M(1)---C(9)	2.68(2)	0.142(10)	3.19(8)	0.5(10)
M(1)---C(10)	3.78(4)	0.250(ass)	4.19(6)	0.250(ass)
M(1)---H(1)	2.542(6)	0.130(ass)	2.73(1)	0.13(3)
\angle C(1)–M(1)–C(2)	120(2)°		123(4)°	
\angle C(1)–M(1)–C(3)	116(1)°		117(2)°	
\angle C(1)–M(1)–C(8)	106(1)°		100(2)°	
\angle C(3)–M(1)–C(8)	86(1)°		88(2)°	
\angle M(1)–C(3)–C(4)	169(2)°		156(6)°	
\angle M(1)–C(3)–M(2)	94(1)°		92(2)°	
\angle C(3)–C(4)–C(5)	174(3)°		170(9)°	
\angle H–C–H	110.5(ass)		110.5(ass)	

^aThese amplitudes were assumed to differ by 0.020 Å.

13.00 Å⁻¹ with $\Delta_S=0.125$ Å⁻¹ and $s=13.25$ to 25.50 Å⁻¹ with $\Delta_S=0.25$ Å⁻¹ for Ga and from $s=2.50$ to 13.00 Å⁻¹ with $\Delta_S=0.125$ Å⁻¹ and $s=13.25$ to 19.25 Å⁻¹ with $\Delta_S=0.25$ Å⁻¹ for In.

A molecular model of $[(\text{CH}_3)_2\text{M}(\mu-\text{C}\equiv\text{CCH}_3)]_2$ is shown in Fig. 1. It was assumed that the molecular symmetry is C_{2h} . It was further assumed that all methyl groups are identical with C_{3v} symmetry, $\angle \text{HCH}=110.5^\circ$ and the threefold axes coinciding with the C–C or C–M bonds. The orientation of the methyl groups were fixed as indicated in the figure with one C(1)–H bond *anti* to the M(1)–C(2) bond. The molecular structure is then determined by eleven parameters, *e.g.* the six bond distances C–H, C≡C, C–C, M(1)–C(1), M(1)–C(3) and M(1)–C(8), and the five valence angles $\angle \text{C(1)M(1)C(2)}$, $\angle \text{C(1)M(1)C(3)}$, $\angle \text{M(1)C(3)C(4)}$, $\angle \text{C(3)C(4)C(5)}$ and $\angle \text{C(8)M(1)C(3)}$. These eleven parameters were refined by least-squares calculations on the intensity data with a diagonal weight matrix using a program written by H.M. Seip and modified by G. Gundersen.¹⁵ For M=Ga eleven root-mean square vibrational amplitudes (l) were included in the refinement, for M=In six amplitudes

were refined.

The molecular parameters obtained and their estimated standard deviations are listed in Table 1. The standard deviations have been doubled to take into account the added uncertainty due to correlation in the experimental data and to assumptions made about local symmetry of methyl groups and the magnitude of vibrational amplitudes that could not be refined.

Radial distribution functions calculated by Fourier inversion of the experimental intensity data are shown in Figs. 2 and 3 along with the differences between these curves and theoretical curves calculated for the best models. We consider the agreement satisfactory.

DISCUSSION

The electron-diffraction data of dimethyl(propynyl)-gallium and -indium are consistent with dimeric molecules of C_{2h} symmetry, the symmetry plane containing the two metal atoms and the three carbon atoms in each bridging propynyl group. See

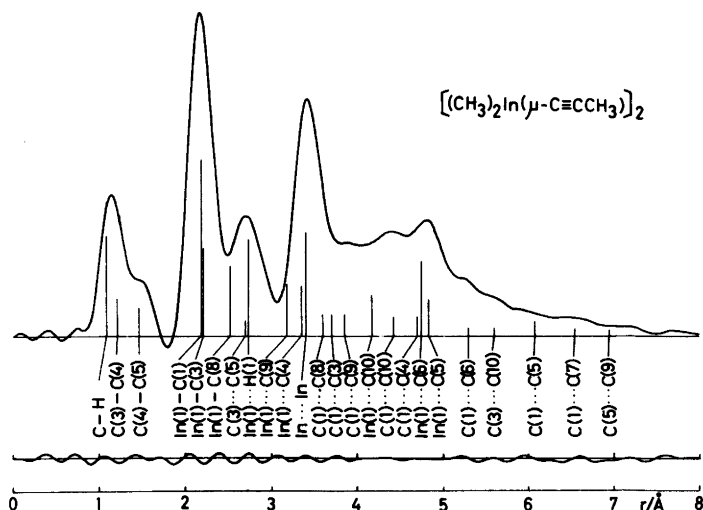


Fig. 3. Above. Experimental radial distribution curve for $[(\text{CH}_3)_2\text{In}(\mu\text{-C}\equiv\text{CCH}_3)_2]$. Artificial damping constant $k=0.001 \text{ \AA}^2$. Major interatomic distances are indicated by bars of height proportional to the area under the corresponding peak. Below. Difference between the experimental curve and a theoretical RD curve calculated for the best model.

Fig. 1. The molecules deviate considerably from D_{2h} symmetry: In particular the M—C (bridge) bond distances are $\text{M}(1)\text{—C}(3)=2.02(2) \text{ \AA}$ and $\text{M}(1)\text{—C}(8)=2.24(3) \text{ \AA}$ in the case of Ga, and $2.19(3)$ and $2.52(4) \text{ \AA}$ in the case of In. The sum of the three valence angles $\angle \text{C}(1)\text{M}(1)\text{C}(2)$ and $\angle \text{C}(1)\text{M}(1)\text{C}(3) = \angle \text{C}(2)\text{M}(1)\text{C}(3)$ is equal to 352° in the case of Ga and 357° in the case of In. As a first rough approximation the three bonds may be described as coplanar, while the $\text{M}(1)\text{—C}(8)$ bond is approximately perpendicular to this plane. The angle $\angle \text{M}(1)\text{C}(3)\text{C}(4)$ is $169(2)^\circ$ in the case of Ga and $156(5)^\circ$ in the case of In. The other exocyclic valence angle at the bridging carbon atoms, $\angle \text{M}(2)\text{C}(3)\text{C}(4)$ is 50 to 60° smaller, $97(2)^\circ$ in the case of Ga and $112(5)^\circ$ in the case of In. The structures are therefore very similar to the molecular structure of the analogous Al compound, $[(\text{CH}_3)_2\text{Al}(\mu\text{-C}\equiv\text{CCH}_3)_2]$.⁹ We believe that the three dimers are best described as consisting of two somewhat distorted monomers joined by donation of $\text{C}\equiv\text{C} \pi$ -electrons into a vacant p_z orbital on the metal atom in the other unit.

From their studies of the vibrational spectra of the three compounds, Weidlein and coworkers concluded that the interaction between monomers is weaker for Ga than for Al.⁷ The molecular structures are in agreement with this conclusion; even though the covalent radii of Al and Ga are very similar (compare for instance $\text{Al}(1)\text{—C}(1)=1.965(5) \text{ \AA}$ with $\text{Ga}(1)\text{—C}(1)=1.964(6) \text{ \AA}$, $\text{Al}(1)\text{—C}(8)=2.15(3) \text{ \AA}$ and $\text{Ga}(1)\text{—C}(8)=2.24(3) \text{ \AA}$. The deviation

from linearity at C(3) is also greater in the Al compound, $\angle \text{Al}(1)\text{C}(3)\text{C}(4)=158(2)^\circ$ while $\angle \text{Ga}(1)\text{—C}(3)\text{C}(4)=169(2)^\circ$.

In the Al compound the atoms $\text{M}(1)\text{C}(3)\text{C}(4)\text{C}(5)$ are in a *trans* configuration with $\angle \text{C}(3)\text{C}(4)\text{C}(5)=167.8(1.6)^\circ$. In the Ga and In compounds the best agreement is obtained with $\text{M}(1)\text{C}(3)\text{C}(4)\text{C}(5)$ in a *cis* configuration, but the angles $\angle \text{C}(3)\text{C}(4)\text{C}(5)$ are not significantly different from 180° .

In dimeric $(\text{CH}_3)_2\text{In}(\text{C}\equiv\text{CCH}_3)_2$ where the metal atoms are four coordinated, the $\text{In}(1)\text{—C}(8)$ distance, $2.52(4) \text{ \AA}$, is about 0.40 \AA shorter than in the crystalline polymer where the In atom is fivecoordinate, $\text{In}\text{—C}=2.93(2) \text{ \AA}$.⁷

The structures of $[(\text{CH}_3)_2\text{M}(\mu\text{-C}\equiv\text{CCH}_3)_2]$ in the gas phase show some relationship to the crystal structures of $(\text{CH}_3)_2\text{Ga}(\text{C}_5\text{H}_5)$ ¹⁶ and $\text{In}(\text{C}_5\text{H}_5)_3$.¹⁷ In both cyclopentadienyl compounds the metal atoms are four coordinated. The Ga atom is surrounded by two terminal methyl groups (mean $\text{Ga}\text{—C}=1.967 \text{ \AA}$) and two bridging cyclopentadienyl groups. The distances from a Ga atom to the nearest C atom in each ring are, however, significantly different: $\text{Ga}\text{—C}=2.215(2) \text{ \AA}$ and $\text{Ga}\text{—C}'=2.314(2) \text{ \AA}$. In crystalline $\text{In}(\text{C}_5\text{H}_5)_3$ the In atom is surrounded by two terminal σ -bonded cyclopentadienyl groups, (mean $\text{In}\text{—C}=2.24 \text{ \AA}$) and two bridging Cp groups. The distances from In to the nearest C atom in each ring are $2.37(1)$ and $2.47(1) \text{ \AA}$. Though the distinction is less clear cut than for the propynyl derivatives, these compounds too can be described in terms of interacting monomer units.

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Note added in proof. A gas phase electron diffraction investigation of $(\text{CH}_3)_3\text{In}$ carried out in this laboratory has yielded an In–C bond distance of $r_a = 2.160(3)$ Å. (T. Fjeldberg, A. Haaland, Q. Shen, R. Seip and J. Weidlein, unpublished result).

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