Acta Chemica Scandinavica, 1994: 48: 172–174
Printed in Belgium – all rights reserved

ACTA
CHEMICA SCANDINAVICA
ISSN 0904–213X

Short Communication

The Molecular Structure of Pentamethylcyclopentadienylgallium, Ga(η-C_5Me_5), by Gas-Phase Electron Diffraction. The First Monomeric Organogallium(I) Compound

Arne Haaland,[a,*] Kjell-Gunnar Martinsen,[a] Hans Vidar Volden,[a] Dagmar Loos[b] and Hansgeorg Schnöckel[b,*]

[a]Department of Chemistry, University of Oslo, Box 1033 Blindern, N-0315 Oslo, Norway and [b]Institute of Inorganic Chemistry, University of Karlsruhe, Box 6980, D-7500 Karlsruhe, Germany

Haaland, A., Martinsen, K.-G., Volden, H.V., Loos, D. and Schnöckel, H., 1994. The Molecular Structure of Pentamethylcyclopentadienylgallium, Ga(η-C_5Me_5), by Gas-Phase Electron Diffraction. The First Monomeric Organogallium(I) Compound. – Acta Chem. Scand. 48: 172–174 © Acta Chemica Scandinavica 1994.

The synthesis of the first organogallium(I) compounds were reported only in late 1992: Uhl *et al.* reported the synthesis of the Ga(I) alkyl $GaC(SiMe)_3$, $Me = CH_3$; X-ray diffraction showed that the compound was tetrameric with a tetrahedral Ga_4 core in the crystalline phase.[1] A similar structure has been reported for the analogous boron compound $[BCMe_3]_4$.[2] Schnöckel and coworkers reported the synthesis of cyclopentadienylgallium(I), $Ga(C_5H_5)$, which was characterized by the parent peak in the mass spectrum and by ^{71}Ga, ^{13}C and ^1H NMR spectra in solution, but could not be isolated from the solvent.[3] More recently the same group has succeeded in synthesizing monomeric pentamethylcyclopentadienylgallium or GaCp*.[4]

GaCp* was synthesized as described in Ref. 4. ^{13}C and ^1H NMR spectra indicated that the liquid sample contained about 7% 1,2,3,4,5-pentamethylcyclopentadiene, Cp*H, and traces (<1%) of toluene.

The gas-phase electron diffraction data were recorded on a Baltzers Eldigraph KDG-2 instrument with a conventional inlet system made of brass. The nozzle temperature was 60 ± 5 °C. Structure refinements were based on data from six plates recorded with a nozzle-to-plate distance of 50 cm and three plates recorded with a distance of 25 cm. Atomic scattering factors were taken from standard sources.[5] Backgrounds were drawn as polynominals to the least-squares adjusted difference between total experimental and calculated molecular intensity curves. The resulting modified molecular intensity curves extended from $s = 17.50$ to 130.00 nm^{-1} with increment $\delta s = 1.25$ nm^{-1} (50 cm plates) and from $s = 35.00$ to 270.00 nm^{-1} with increment $\delta s = 2.50$ nm^{-1} (25 cm plates) (Fig. 1).

Structure refinements were based on a molecular model of C_{5v} symmetry as shown in Fig. 2. Methyl groups were assumed to have local C_{3v} symmetry with the symmetry axes coinciding with the exocyclic C–C(Me) bonds. The orientation of the methyl groups is such that one C–H bond points away from the metal atom as indicated in the

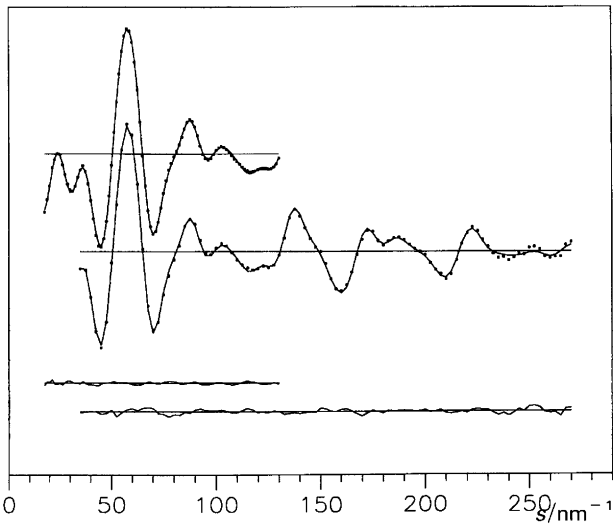

Fig. 1. Experimental (dots) and calculated (lines) modified molecular intensity curves for GaCp*. The vertical scale is arbitrary. Below: Difference curves.

* To whom correspondence should be addressed.

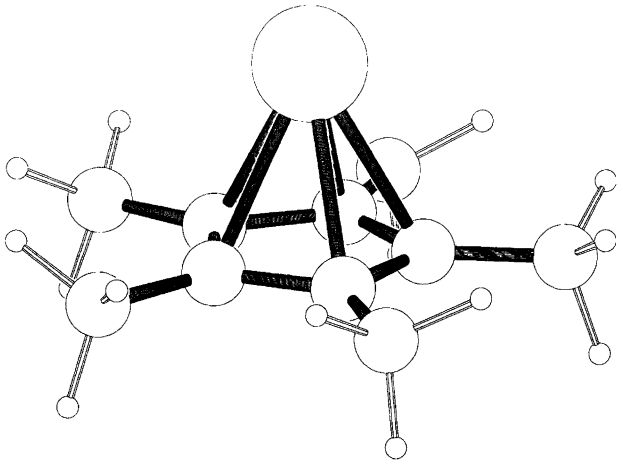

Fig. 2. Molecular model of GaCp*, point group C_{5v}.

figure. The molecular geometry is then determined by six independent parameters, e.g. the endocyclic C(Cp)–C(Cp) bond distance, the exocyclic C(Cp)–C(Me) bond distance, the Ga–C and C–H bond distances, the valence angle ∠CCH and the angle between the C(Cp)–C(Me) bonds and the C_5 ring plane, which we denote by ∠C_5,C–C and define as positive when the exocyclic bonds are bent towards the metal atom.

Since the NMR spectra indicated that the liquid sample contained several percent of Cp*H, the mole fraction of such an impurity was refined as an additional variable. The structure of Cp*H has never been studied by gas electron diffraction. A molecular model was therefore constructed from the known structure of the dimer Cp^*_2 by breaking the bond between the rings and adding a hydrogen atom.[6]

The six independent structure parameters and the most important root mean square vibrational amplitudes of GaCp* were refined by least-squares calculations on the molecular intensity data under the constraints of a geometrically consistent r_a-structure, along with the mole fraction of the possible impurity of Cp*H. Non-refined vibrational amplitudes were fixed at the values in InCp*.[7] The mole fraction of Cp*H was found not to be significantly different from zero; $\chi = 2.6(22)\%$. The values obtained for the major structure parameters are listed in Table 1. The estimated standard deviations calculated by the program have been multiplied by a factor of 2.0 to include the added uncertainty due to data correlation[8] and further expanded to include an estimated scale uncertainty of 0.1%. Experimental and calculated radial distribution (RD) curves, obtained by Fourier inversion of the connected experimental and calculated modified molecular intensity curves, are compared in Fig. 3.

The Ga atom ($Z = 31$) is the heaviest atom in the molecule. The terms representing the five Ga–C bond distances and the five non-bonded Ga–C(Me) distances are the largest terms in the molecular intensity curve, and the corresponding peaks are the largest single peaks in the RD curve. The good agreement between experimental and calculated curves obtained for the C_{5v} model shows that the five Ga–C bond distances must be equal or nearly equal. If the metal atom in GaCp* were monohapto-bonded to the ring, the peak representing the five Ga–C(Cp) bond distances would split into one peak at

Table 1. Interatomic distances (r_a), root mean square vibrational amplitudes (l) and valence angles in Ga(η-C_5Me_5) and mole fraction of the 1,2,3,4,5-pentamethylcyclopentadiene impurity.[a]

	r_a	l
Ga–C	240.5(4)	8.4(5)
C–C(Cp)	142.0(3)	[4.0]
C–C(Me)	152.2(3)	[4.5]
C–H	111.7(4)	8.6(4)
Nonbonded distances:		
Ga–C(Me)	343.9(8)	14.5(5)
C(Cp)–C(Cp)	229.7(4)	[5.8]
C(Cp)–C(Me)	262.1(3)	7.1(5)
C(Cp)–C(Me)	377.4(3)	7.7(5)
C(Me)–C(Me)	320.8(3)	[13.1]
C(Me)–C(Me)	519.1(3)	10.3(12)
Ga–H	361(2)	76(12)
Ga–H	442(1)	32(9)
h^b	208.1(5)	
∠CCH	110.5(7)	
∠C_5,C–C	0.2(3)	
χ(Cp*H)	2.6(22)%	
R-factors (%) 2.7(50 cm)	6.6(25 cm)	3.7% (total)

[a] Distances in pm, angles in degrees. Estimated standard deviations in parentheses in units of the last digit. Non-refined amplitudes in square brackets, see text. [b] Perpendicular distance from the Ga atom to the C_5 ring. [c] $R = [\sum w(I_{exp} - I_{calc})^2 / \sum w I_{exp}^2]^{1/2}$.

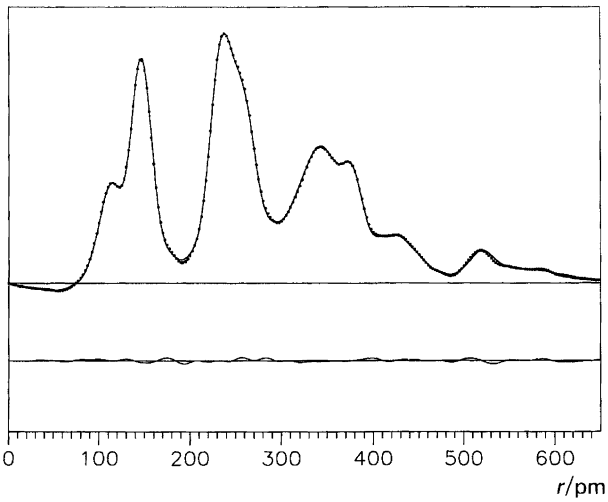

Fig. 3. Experimental (dots) and calculated (lines) radial distribution functions of GaCp*. The vertical scale is arbitrary. Below: Difference curve. Artificial damping constant $k = 25$ pm^2.

197 pm representing the Ga–C σ-bond distance, another peak at about 280 pm representing two nonbonded Ga–C(Cp) distances, and a third peak at about 360 pm representing two more nonbonded Ga–C(Cp) distances. The peak at 340 pm representing the five nonbonded Ga–C(Me) distances would be split in a similar manner. Such a model is clearly incompatible with the GED data.

The refinements therefore confirm the conclusion based on *ab initio* molecular orbital calculations on the unsubstituted $Ga(C_5H_5)$;[3] the metal atom is pentahapto-bonded to the ring. The Ga–C bond distance obtained by the MO calculations, Ga–C = 242.0 pm, is also in good agreement with the experimental value.

In Fig. 4 we compare the M–C bond distances in gaseous MCp*, In–C = 259.2(4) pm[7] and Tl–C = 266.3(5) pm,[9] and M–Cl bond distances in the gaseous monomeric monochlorides, MCl, Ga–Cl = 220.2 pm, In–Cl = 240.1 pm and Tl–Cl = 248.5 pm.[10] The similarity of the M–C and M–Cl bond distance curves suggests that both M–C and M–Cl bond distances are determined by the size of the metal atom.

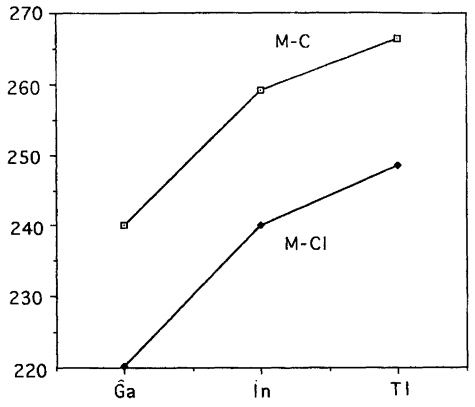

Fig. 4. M–C bond distances (in pm) in gaseous MCp* and M–Cl bond distances in gaseous monomeric monochlorides MCl, M=Ga, In or Tl.

The Ga–C vibrational amplitude in GaCp*, 8.4(5) pm, is not significantly different from the metal–carbon amplitude found in gaseous InCp*, 9.0(7) pm.[7] Both M–C bond distances and vibrational amplitudes thus indicate that metal to ring bonding is about equally strong in the two compounds. The reason for the ellusiveness of GaCp* is therefore probably not an inherent instability of the compound, but rather the unavailability of a suitable Ga(I) starting material.

Acknowledgements. We are grateful to the VISTA program of the Norwegian Academy for Science and Letters and STATOIL, and to the Deutschen Forschungsgemeinschaft and Fonds der Chemischen Industrie for financial support.

References

1. Uhl, W., Hiller, W., Lay, M. and Schwarz, W. *Angew. Chem., Int. Ed. Engl. 31* (1992) 1364.
2. Mennekes, T., Paetzold, P., Boese, R. and Bläser, D. *Angew. Chem., Int. Ed. Engl. 30* (1991) 173.
3. Loos, D., Schnöckel, H., Gauss, J. and Schneider, U. *Angew. Chem., Int. Ed. Engl. 31* (1992) 1362.
4. Loos, D. and Schnöckel, H. *J. Organomet. Chem. In press.*
5. Schäfer, L., Yates, A. C. and Bonham, R. A. *J. Chem. Phys. 55* (1971) 3055; *International Tables for X-Ray Crystallography*, Vol. 4, Kynoch Press, Birmingham 1974.
6. Blom, R. *Acta Chem. Scand., Ser. A 42* (1988) 445.
7. Beachley, O. T., Jr., Blom, R., Churchhill, M. R., Faegri, K., Fettinger, J. C., Pazik, J. C. and Victoriano, L. *Organometallics 8* (1989) 346.
8. Seip, H. M., Strand, T. G. and Stølevik, R. *Chem. Phys. Lett. 3* (1969) 617.
9. Blom, R., Werner, H. and Wolf, J. *J. Organomet. Chem. 354* (1988) 293.
10. Huber, K. P. and Herzberg, G. *Molecular Spectra and Molecular Structure*, Vol. 4, Van Nostrand, New York 1979.

Received August 19, 1993.