Journal of Organometallic Chemistry, 354 (1988) 293–299
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

The molecular gas phase structure of $Tl(C_5Me_5)$

R. Blom *

Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, 0315 Oslo 3 (Norway)

H. Werner and J. Wolf

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-8700 Würzburg (B.R.D.)

(Received April 29th, 1988)

Abstract

The thermal average molecular structure of $Tl(C_5Me_5)$ has been determined by gas phase electron diffraction (GED). The molecule has a half sandwich structure of C_{5v} symmetry. The Tl–C bond distance is 266.3(5) pm, with a root-mean-square amplitude of vibration (l-value) of 5.2(24) ppm. The results indicate that the methyl groups of the ring tend to decrease the thallium–carbon bond distance compared with that in the non-methylated compound.

Introduction

In the gas phase both $In(C_5H_5)$ and $Tl(C_5H_5)$ form monomeric units with open-faced half sandwich structures of C_{5v} symmetry [1,2]. The gas phase structure of $In(C_5Me_5)$ is similar to that of the non-methylated compound; the only difference when methyl groups are introduced on the ring is a shortening of the In–C bond distance by approximately 3 pm; r(In–C) 259.2(4) and 261.9(5) pm in $In(C_5Me_5)$ [3] and $In(C_5H_5)$ [1], respectively. We decided to carry out a structural investigation of $Tl(C_5Me_5)$ in the gas phase in order to find out if methylation of the cyclopentadienyl ring has the same effect upon the Tl–C bond distance.

Experimental and structure refinements

$Tl(C_5Me_5)$ were prepared from Tl_2SO_4 and $Na(C_5Me_5)$ in toluene as described by Werner et al. [4]. Gas phase electron diffraction (GED) patterns of the compound was recorded on a Balzers Eldiograph KD-G2 [5] with an accelerating potential of 42 kV. The electron wavelength was calibrated against diffraction patterns of benzene (r(C–C) 139.75 pm), with an estimated uncertainty of 0.1%. In order to keep the temperature at a minimum, and thus minimize the thermal

0022-328X/88/$03.50

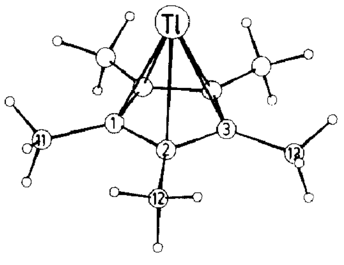

Fig. 1. Molecular model of Tl(C_5Me_5). The model has C_{5v} symmetry with the Tl atom situated at the symmetry axis. Numbering of the C-atoms are drawn.

decomposition, we used a torus-shaped nozzle [6], which permits the diffraction pattern to be recorded with a vapor pressure of approximately 1 mmHg. Nozzle and reservoir temperature was 133(5) °C. Exposure was made with nozzle-to-plate distance of about 50 cm. The plates were subjected to photometry and the optical densities processed by standard procedures [7]. Six plates were used, with s ranging from 15.0 to 145.0 nm^{-1} with Δs 1.25 mm^{-1}. The backgrounds were computer drawn by a least-squares fit of the sum of a polynomial and a theoretical molecular intensity curve to the experimental levelled intensity curve. The degree of the polynomial was 6. Least-squares refinements were performed on an average curve. Complex atomic scattering factors, $f'(s)$, were calculated from an analytical representation of the atomic potentials for C [8], and from a bonded potential for H [9]. Tabulated scattering factors were used for Tl [10]. The molecular intensities were modified by multiplication by $s/|f'_C||f'_{Tl}|$.

The molecular model of Tl(C_5Me_5) is shown in Fig. 1. The model has C_{5v} symmetry, and the CCH_3 fragments have C_{3v} symmetry fixed in a position with one hydrogen atom pointed away from the metal atom. With these assumptions the molecular geometry is described by six independent parameters; the bond distances C–C, C–C(Me), and C–H, the height from the center of the cyclopentadienyl ring to the metal atom, h, the CCH valence angle, and the angle between the ring plane and the C–C(Me) bond, (C_5, C–C(Me) defined as positiv when the methyl groups are bent towards the metal atom. In addition eight root-mean-square amplitudes of vibrations (l-values) were refined as noted with their estimated standard deviation in Table 1. Non-refined l-values were taken from a recent GED investigation of In(C_5Me_5) [3].

Residues of metallic thallium in the broken ampoule after the GED experiment had been performed, indicated that small amounts of the compound decomposed during the experiment. A reasonable decomposition product is bis(pentamethylcyclopentadienyl), $(C_5Me_5)_2$; $2Tl(C_5Me_5) \rightarrow 2Tl^0 + (C_5Me_5)_2$. Bis(pentamethylcyclopentadienyl) has previously been obtained in similar ways from other permethylated metal cyclopentadienyls [11,12], and the decomposition of In(C_5Me_5) to In^0 and $(C_5Me_5)_2$ has recently been monitored by ^1H NMR [3]. The GED experiment

Table 1

The geometrical parameters and root-mean-square amplitudes of vibration (*l*-values) for $Tl(C_5H_5)$ and $Tl(C_5Me_5)$ in the gas phase

	$Tl(C_5H_5)$ [a]	$Tl(C_5Me_5)$	
	r (pm)	r_2 (pm)	*l* (pm)
bond distances:			
Tl–C	270.5(5)	266.3(5)	5.2(24)
h [b]	241(1)	237.2(5)	–
C(1)–C(2)	143(2)	142.2(6)	4.3(10) [d]
C(1)–C(11)	–	152.0(7)	4.8(10) [d]
C–H	108 [c]	109.1(8)	9.1(8)
other distances:			
Ti · · · C(11)	–	372	14.2(14)
Tl · · · H(long)	–	470	26(11)
Tl · · · H(short)	–	394	48(9)
C(1) · · · C(3)	232	230	5.8 [c]
C(2) · · · C(11)	–	262	8.8(11)
C(3) · · · C(11)	–	377	8.8(14)
C(11) · · · C(12)	–	320	13.5 [c]
C(11) · · · C(13)	–	517	9.9 [c]
angles:			
C_5,C–C(Me)	0 [c,e]	−6.4(6)°	–
CCH	–	114(2)°	–

[a] Values taken from a microwave study, ref. 2. [b] The perpendicular height from the metal atom to the ring centroid. [c] Fixed values. [d] *l*-values with identical index were refined with constant difference. [e] The C_5, C–H angle.

of analytically pure $(C_5Me_5)_2$ has recently been performed with nozzle and reservoir temperature of about 115° C [12], which means that $(C_5Me_5)_2$ is somewhat more volatile than $Tl(C_5Me_5)$. A number of the refinements of $Tl(C_5Me_5)$ were

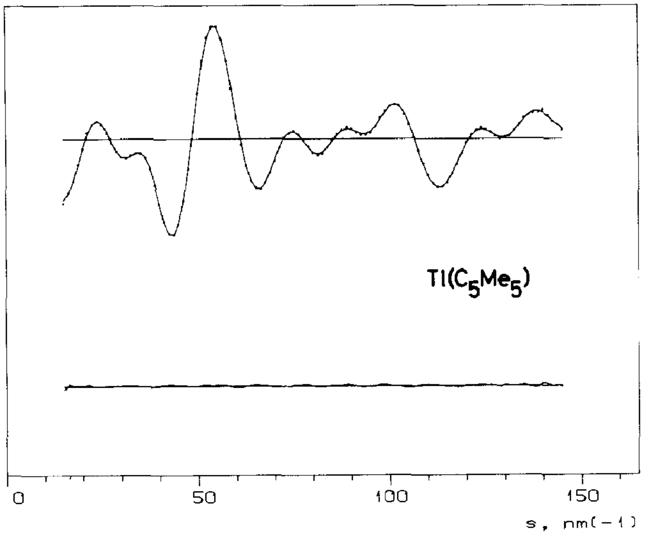

Fig. 2. Theoretical molecular intensity curve with experimental points for $Tl(C_5Me_5)$. The difference between experimental and theoretical intensity curves are drawn in the lower part of the figure.

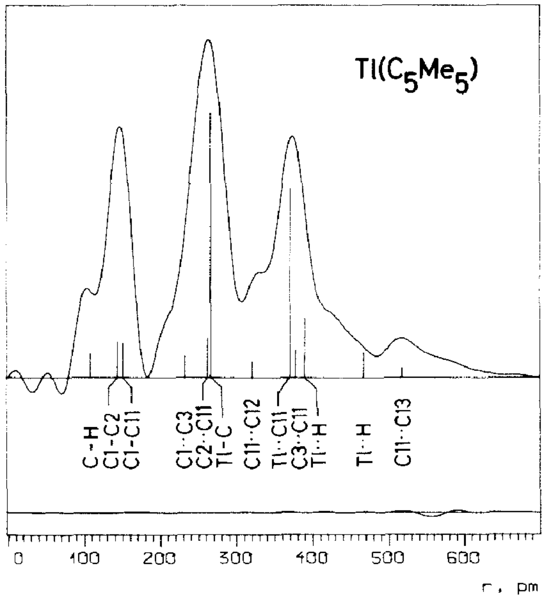

Fig. 3. Experimental radial distribution (RD) curve for $Tl(C_5Me_5)$. The most important distances are indicated by bars of height approximately proportional to the area under the corresponding peak. The difference between the experimental and theoretical RD-curves are drawn in the lower part of the figure. Artificial damping constant, *k*, is 20 pm^2.

therefore carried out by including the experimental intensity curve of $(C_5Me_5)_2$, and in this way stepwise increase the amount of $(C_5Me_5)_2$ present in the molecular beam. The background were redrawn for each step. The best fit between experimental and theoretical curves was obtained by using a theoretical curve which included 2.0% dimer. In the latter case the R_2 factor [13*] were lowered to 2.4% as compared to 4.4% in the case when no $(C_5Me_5)_2$ were assumed.

The theoretical molecular intensity curve with experimental points are drawn in Fig. 2, and the corresponding radial distribution curve is drawn in Fig. 3.

Results and discussion

The geometrical parameters and root-mean-square amplitudes of vibration (*l*-values) of $Tl(C_5Me_5)$ are listed in Table 1, together with results from a previous microwave spectroscopic study of $Tl(C_5H_5)$. The estimated errors in the parameters for $Tl(C_5Me_5)$ are the least-squares standard deviations multiplied by a factor of three in order to compensate for uncertainties in the assumptions and systematic errors.

In the gas phase both $Tl(C_5H_5)$ and $Tl(C_5Me_5)$ consist of monomeric units of C_{5v} symmetry, where the thallium atom is situated at the symmetry axis. The thallium-carbon bond distances are 270.5(5) and 266.3(5) pm in $Tl(C_5H_5)$ and $Tl(C_5Me_5)$, respectively, which show that there is a significant shortening of the thallium-carbon bond when methyl groups are introduced on the ring. The same

---

* Reference number with asterisk indicates a note in the list of references.

effect on methyl substitution has been observed for the indium analogues, for which the In–C bond distance is shortened by approximately 3 pm when going from $In(C_5H_5)$ to $In(C_5Me_5)$ [1,3]. Recent ab initio calculations on the latter compounds indicate that for the permethylated compound the negative charge of the ring of approximately -0.5 is polarized towards the methyl groups [3]. The stabilisation of charge by polarisation of the whole molecule (ion) has its parallel in the increased *gas phase* acidity of alcohols when the number of carbon atoms increases [14]. The opposite trend has been observed for alcohols *in solution*, which is probably a consequence of steric inhibition of solvation of the anion by the methyl groups [15].

For $Tl(C_5Me_5)$ the polarisation of the negative charge on the ring allows for a closer approach of the ring to the center of the positively charged metal atom before the equilibrium of attractive and repulsive forces are established as compared to $Tl(C_5H_5)$. The question now arises whether this effect of the methyl substitution is a general trend among cyclopentadienyl compounds.

To find this out, it would be best to compare the metal–cyclopentadienyl bond distances for compounds for which the only difference was the presence of methyl substituents on the cyclopentadienyl ring. Not many structure investigations have been done to allow such a comparison, but there are some. The perpendicular metal–ring centroid distance in $Ge(C_5Me_5)_2$ is 1 pm shorter as compared to $Ge(C_5H_4Me)_2$ [16], in $Sn(C_5Me_5)_2$ about 3 pm shorter than in $Sn(C_5H_5)_2$ [17], and in $Pb(C_5Me_5)_2$ 2 pm shorter than in $Pb(C_5H_5)_2$ [17b,18]. The Fe–C bond distances in ferrocene and decamethylferrocene are identical [19], and the same is true for the magnesium analogues [20]. In the two latter cases the inter-ring distances are about twice the Van der Waals radius for methyl groups [21] or shorter, so the shortening upon methylation can be prohibited by steric repulsions between the rings. We feel nevertheless that these few examples indicate that there is a general trend towards shorter metal–cyclopentadienyl bond distance when methyl groups are introduced on the ring provided that no steric factors prevent it.

A direct comparison of the thallium–carbon and indium–carbon bond distances found in the gas phase with those found in the solid phase is not possible owing to oligomerization and polymerization in the solid state for all cyclopentadienyl-thallium and -indium compound reported so far: Both $In(C_5H_5)$ and $Tl(C_5H_5)$ exhibit polymeric zig-zag chain structures, $[In(C_5H_5)]_n$ and $[Tl(C_5H_5)]_n$, respectively, where the metal atoms are pentahapto bonded to two bridging cyclopentadienyl rings with linear metal-ring centroid-metal fragments and ring centroid-metal-ring centroid angles of approximately 137° [22,23]. The introduction of bulky groups on the cyclopentadienyl rings increase the steric repulsions between the chains, which in the case of $In(C_5Me_5)$ leads to a solid state structure where six indium atoms form an octahedral cluster with terminal pentamethylcyclopentadienyl rings, each pentahapto bonded to only one indium atom [3,24]. The structural consequences when methyl groups are introduced on the ring are not so drastic for the permethylated cyclopentadienyl-thallium compound; $Tl(C_5Me_5)$ can still maintain the zig-zag chain structure with bridging cyclopentadienyl rings [4].

The structural differences between the indium and thallium analogues in the solid state seem to be a consequence of decreased metal–metal bonding ability upon going down group 13. Measures for this are the enthalpy of atomization, ΔH_f^0, and the homonuclear single bond energies, E, for the two metals; indium has ΔH_f^0 243.3 kJ/mol and E 125.8 kJ/mol while thallium has ΔH_f^0 186.0 kJ/mol and E

61.4 kJ/mol [25]. In the three cyclopentadienylindium structures that have been reported, direct indium–indium distances are all in the range 394–399 pm [3,22,23,24] indicating that these interactions are the determining factors for how the overall structures turn out. In the cyclopentadienylthallium compounds the direct thallium $\cdots$ thallium interactions are weaker, and so when the substituents on the cyclopentadienyl ring are bulkier the zig-zag structures can still be maintained by loosening these interactions. This is reflected in the increased interchain thallium $\cdots$ thallium distances of 399, 460 and 641 in $[\mathrm{Tl(C_5H_5)}]_n$ [22], $[\mathrm{Tl(C_5H_4C(CN){=}C(CN)_2}]_n$ [26] and $[\mathrm{Tl(C_5Me_5)}]_n$ [4], respectively. One consequence of the decreased interchain thallium $\cdots$ thallium interaction is shortening of the mean thallium-ring centroid distances; 319, 304, 295, 278 and 276 pm in $[\mathrm{Tl(C_5H_5)}]_n$ [22], $[\mathrm{Tl(C_5H_4C(CN){=}C(CN)_2)}]_n$ [26], $[\mathrm{Tl(C_5Me_5)}]_n$ [4], $[\mathrm{Tl(C_5H_4SiMe_3)}]_n$ [27] and the hexamer $[\mathrm{Tl(C_5H_3(SiMe_3)_2)}]_6$ [27], respectively. The only solid state cyclopentadienylthallium structure which do not exhibit zig-zag chain structure with bridging cyclopentadienyl rings, is the pentabenzylcyclopentadienylthallium dimer, $[\mathrm{Tl(C_5(CH_2C_6H_5)_5)}]_2$, where the pentabenzylcyclopentadienyl rings are terminally bonded to each thallium atom with mean thallium-ring centroid distance of 249.0 pm [28]. This is as expected to be somewhat longer (12 pm) than in gaseous $\mathrm{Tl(C_5Me_5)}$, owing to thallium–thallium interaction and also metal interaction with the benzyl groups.

References

1 S. Shibata, L.S. Bartell and R.M. Gavin, Jr., J. Chem. Phys., 41 (1964) 717.

2 J.K. Tyler, A.P. Cox and J. Sheridan, Nature, 183 (1959) 1182.

3 O.T. Beachley, Jr., R. Blom, M.R. Churchill, K. Faegri, Jr., J.C. Fettinger, J.C. Pazik and L. Victoriano, Organometallics, in press.

4 H. Werner, H. Otto and H.J. Kraus, J. Organomet. Chem., 315 (1986) C57.

5 W. Zeil, J. Haase and L. Wegmann, Instrumentenkd., 74 (1966) 84; O. Bastiansen, R. Graber and L. Wegmann, Balzers' High Vacuum Report, 25 (1969) 1.

6 E.C. Ashby, L. Fernholt, A. Haaland, R. Seip and R.S. Smith, Acta Chem. Scand. Ser. A, 34 (1980) 213; Annual Report of the Norwegian Electron Diffraction Group, 1980.

7 B. Andersen, H.M. Seip, T.G. Strand and R. Stølevik, Acta.Chem. Scand., 23 (1969) 3224.

8 T.G. Strand and R.A. Bonham, J. Chem. Phys., 40 (1964) 1686; A.C. Yates, Comput. Phys. Commun., 2 (1971) 175.

9 R.F. Stewart, E.R. Davidson and W.T. Simpson, J. Chem. Phys., 42 (1965) 3175.

10 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham 1974, Vol 4, section 2.5.

11 P. Jutzi and F. Kohl, J. Organomet. Chem., 164 (1979) 141; D.W. Macomber and M.D. Rausch, J. Am. Chem. Soc., 105 (1983) 5325.

12 R. Blom, Acta. Chem. Scand., in press.

13 $R_2 = \sqrt{[w(I_{\mathrm{obs}} - I_{\mathrm{calc}})^2/wI_{\mathrm{obs}}^2]}$; H.M. Seip, T.G. Strand and R. Stølevik, Chem. Phys., Lett., 3 (1969) 617.

14 J.I. Braumann and L.K. Blair, J. Am. Chem. Soc., 92 (1970) 5986.

15 F.G. Bordwell and M.J. Bausch, J. Am. Chem. Soc., 105 (1983) 6188.

16 L. Fernholt, A. Haaland, P. Jutzi, F.X. Kohl and R. Seip, Acta Chem. Scand., A, 38 (1984) 211; J. Almlöf, L. Fernholt, K. Fægri, Jr., A. Haaland, B.E.R. Schilling, R. Seip and K. Taugbøl, Acta Chem. Scand., A37 (1983) 131.

17 P. Jutzi, F. Kohl, P. Hofmann, C. Krüger and Y.H. Tsay, Chem. Ber., 113 (1980) 757; J.L. Atwood, W.E. Hunter, A.H. Cowley, R.A. Jones and C.A. Stewart, J. Chem. Soc., Chem. Commun., (1981) 925.

18 A. Almenningen, A. Haaland and T. Motzfeldt, J. Organomet. Chem., 7 (1967) 97.

19 A. Haaland and J.E. Nilsson, Acta. Chem. Scand., 22 (1968) 2653; A. Almenningen, A. Haaland, S. Samdal, J. Brunvoll, J.L. Robbins and J.C. Smart, J. Organomet. Chem., 173 (1979) 293.

20 A. Haaland, J. Lusztyk, J. Brunvoll and K.B. Starowieyski, J. Organomet. Chem., 85 (1975) 729; R.A. Andersen, R. Blom, J.M. Boncella, C.J. Burns and H.V. Volden, Acta Chem. Scand., A 41 (1987) 24.

21 L. Pauling, The Nature of the Chemical Bond, 3 edit., Cornell University Press, New York 1960, p. 261.

22 E. Frasson, F. Menegus and C. Panattoni, Nature, 199 (1963) 1087.

23 O.T. Beachley, Jr., J.C. Pazik, T.E. Glassman, M.R. Churchill, J.C. Fettinger and R. Blom, Organometallics, 7 (1988) 1051.

24 O.T. Beachley, Jr., M.R. Churchill, J.C. Fettinger, J.C. Pazik and L. Victoriano, J. Am. Chem. Soc., 108 (1986) 4666.

25 R.E. Howald, J. Chem. Educ., 45 (1968) 163; R.T. Sanderson, J. Inorg. Nucl. Chem., 28 (1966) 1553.

26 M.B. Freeman, L.G. Sneddon and J.C. Huffman, J. Am. Chem. Soc., 99 (1977) 5194.

27 S. Harvey, C.L. Raston, B.W. Skelton, A.H. White, M.F. Lappert and G. Srivastava, J. Organomet. Chem., 328 (1987) C1.

28 H. Schumann, C. Janiak, J. Pickardt and U. Börner, Angew. Chem., 99 (1987) 788; Angew. Chem. Int. Ed. Engl., 26 (1987) 789.