The Methyl Group Geometry in Trichloromethyltitanium: a Reinvestigation by Gas Electron Diffraction

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The Methyl Group Geometry in Trichloromethyltitanium: A Reinvestigation by Gas Electron Diffraction

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A recent preliminary communication on the molecular structure of Cl_3TiCH_3 as determined by gas electron diffraction[1] suggested an unusual methyl group geometry: C–H bond distance 115.8 (1.6) pm and valence angle $\angle TiCH = 101.0$ (2.2)°, presumably due to partial donation of C–H bonding electrons into vacant d orbitals on Ti. Such an interaction is also consistent with the observation of an unusually large positive H,H coupling constant of +11.3 Hz and an unusually low CH_3 rocking mode of 580 cm^{-1} as compared to 825 cm^{-1} in Cl_3GeCH_3.[1]

Very recently Williamson and Hall have reported the results of extensive SCFMO and GVB calculations on Cl_3TiCH_3.[2] On the basis of structure optimizations at different levels they predict a normal C–H bond distance of 110 ± 1 pm and a slightly less-than-tetrahedral angle of $107 \pm 1°$.[2] The calculations reproduce the lowering of the rocking mode relative to Cl_3GeCH_3 but provide no indication for Ti··(C–H) interactions.
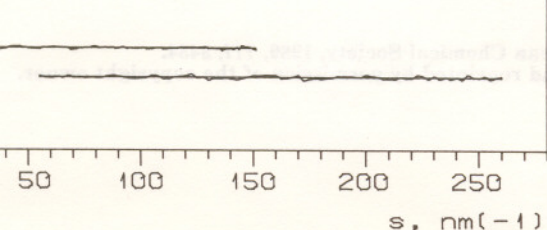
We prepared Cl_3TiMe (Me = CH_3 or CD_3) with the intention of determining the molecular structure by MW spectroscopy. We have, however, been unable to record a MW spectrum, probably because Cl_3TiMe decomposes rapidly on the metal walls of the waveguide. It was then decided to record the GED data for both compounds with use of an all-glass inlet system. These experiments proceeded without difficulty. We hope to record MW spectra

(1) Berry, A.; Dawoodi, Z.; Derome, A. E.; Dickinson, J. M.; Downs, A. J.; Green, J. C.; Green, M. L. H.; Hare, P. M.; Payne, M. P.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Chem. Commun.* **1986**, 520.

(2) Williamson, R. L.; Hall, M. B. *J. Am. Chem. Soc.* **1988**, *110*, 4428.

(3) For a discussion of the rocking mode of H_3TiCH_3 see also: Eisenstein, O.; Jean, Y. *J. Am. Chem. Soc.* **1985**, *107*, 1177. Shiga, A.; Kojima, J.; Sasaki, T.; Kikuzono, Y. *J. Organomet. Chem.* **1988**, *345*, 275.

$l(Ti–Cl)$, pm	4.4 (2)	4.6 (2)	5.0 (2)
$l(Ti–C)$, pm	4.5 (13)	7.0 (11)	11.2 (18)
$l(C–H)$, pm		3.9 (21)	2.0 (21)
$l(Cl··Cl)$, pm	10.8 (11)	12.1 (6)	13.9 (15)
$l(Cl··C)$, pm	11.7 (5)	12.4 (3)	12.9 (6)
R^b	7.7%	2.4%	3.9%

[a] Dihedral angle ClTiCH. $\phi = 0°$ for eclipsed conformation. [b] $R = [\sum P(I_{exp} - I_{calc})^2/\sum PI_{exp}^2]^{1/2}$. [c] Estimated standard deviations in parentheses in units of the last digit.

(left column, partially cut text)

Experimental (●) and calculated (—) modified molecular
...curves for Cl_3TiCH_3. Below: difference curves.

...all-glass MW cell at Universität Tübingen and to carry
...ure refinements based on both GED and MW data. In
...he great interest in metal··(C–H) interactions,[2,4,5] we wish
... the results of structure refinements on the GED data
...hese provide no indication for an unusual methyl group
...y.

...e-black crystals of Cl_3TiMe (Me = CH_3 or CD_3) were
... from $TiCl_4$ and $ZnMe_2$ in 2-methylbutane[1] and re-
...ed twice from the same solvent. The identity of the
...was established by gas-phase IR spectra. The spectra
...d a band at about 502 cm^{-1}, indicating the presence of
... the gas if not in the solid phase. (We return to this point
... The sample was stored at −80 °C until immediately before
... experiment. The data for Cl_3TiCH_3 were recorded with
...le at 0 °C and the inlet system at room temperature.[1]
...s were made with nozzle-to-plate distances of 50 and 25
... modified molecular intensity curves shown in Figure 1
...d on six plates for each distance. The data for Cl_3TiCD_3
...orded with the sample at room temperature. Due to lack
...ial we obtained only two 50-cm plates and four 25-cm

...ure refinements by least-squares calculations were based
...s of C_3 symmetry. Shrinkage effects were neglected, but
... average dihedral angle $\phi(ClTiCH)$ was refined along
...three bond distances, the two valence angles, and five
...n-square vibrational amplitudes (l). The best values are
...Table I. The estimated standard deviations have been
...d to compensate for data correlation and a scale uncer-
...0.1%. Calculated modified molecular intensity curves
... and radial distribution curves (Figure 2) are in good
...t with their experimental counterparts.

...tructures of Cl_3TiCH_3 and Cl_3TiD_3 are of course expected
...y similar, though the vibrational amplitude of the C–H
...pected to be somewhat larger than that of the C–D bond:
...ated amplitudes in methane at 25 °C are $l(C–H) = 7.8$
...C–D) = 6.0 pm, respectively.[6] The structure parameters
...Table I are indeed equal to well within their combined
...ties. Bond distances and valence angles are in reasonable
...t with those obtained by Williamson and Hall by SCF
...ons with their largest basis: Ti–Cl = 221.9 pm, Ti–C
...m, C–H = 109.1 pm, ∠ClTiC = 103.7°, and ∠TiCH
... In neither compound do we find evidence for deviations
...al methyl group geometry; deviations of the magnitude

(right column)

suggested by Berry and co-workers appear inconsistent with our data.

In view of the reactivity and thermal instability of Cl_3TiCH_3, it appears likely that the reason for the disagreement between the GED studies is the presence of significant amounts of impurities in the molecular beam in one or both studies. We have therefore carried out additional least-squares refinements in which the mole fractions of possible $TiCl_4$[7] or methane[8] impurities were introduced as an additional parameter. Neither mole fraction refined to values significantly different from zero;[9] structure parameters and their error limits changed inconsiderably from the values listed in Table I. The presence of significant amounts of solvent molecules can be ruled out since neither the experimental RD curves nor the difference curves have a peak near 1.54 Å corresponding to C–C bond distances.

We feel that our use of an all-glass inlet system may have eliminated an important source of error. Furthermore, the flow-through nature of the experiment may have led to elimination of water and other impurities in the inlet system. Finally, we wish to point out that our studies of Cl_3TiCH_3 and Cl_3TiCD_3 represent two independent structure determinations, including the prepa-

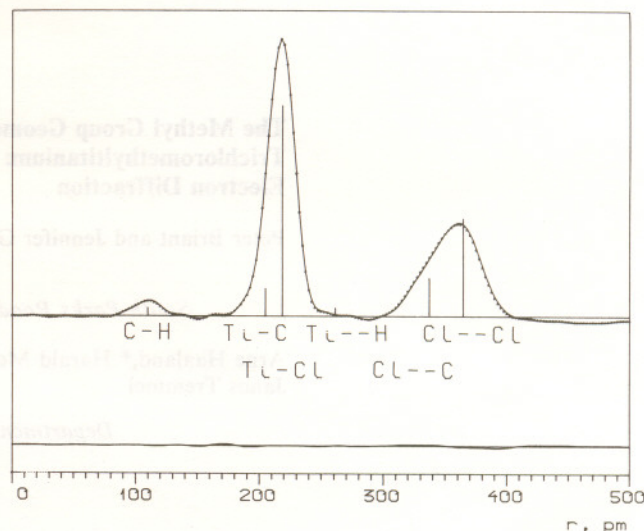**Figure 2.** Experimental (●) and calculated (—) radial distribution curves for Cl_3TiCH_3. Artificial damping constant $k = 4 \times 10^{-7}$ nm². Below: difference curve.

...okhart, M.; Green, M. L. H. J. Organomet. Chem. 1983, 250, 395.
...otree, R. H. Chem. Rev. 1985, 85, 245.
...n, S. J. Molecular Vibrations and Mean Square Amplitudes; ...sforlaget: Oslo, 1968; p 217f.

(7) Morino, Y.; Uehara, H. J. Chem. Phys. 1966, 45, 4543.
(8) Bartell, L. S.; Kuchitsu, K.; deNeui, R. J. J. Chem. Phys. 1961, 35, 1211.
(9) For Cl_3TiCH_3, $\chi(TiCl_4) = -0.01$ (3) and $\chi(CH_4) = 0.02$ (4). For Cl_3TiCD_3, $\chi(TiCl_4) = -0.02$ (5) Å and $\chi(CD_4) = 0.02$ (5). The numbers in parentheses are formal estimated standard deviations.