

Additions and Corrections

The Structure of Trichloromethyltitanium: A Redetermination of the Relative Sign of ${}^2J(\text{H-D})$ in $(\text{CH}_2\text{D})\text{TiCl}_3$

Malcolm L. H. Green and Andrew K. Hughes

Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, UK

The relative sign of the ${}^2J(\text{H-D})$ coupling constant in $(\text{CH}_2\text{D})\text{TiCl}_3$ has been redetermined and found to be negative.

The structure and geometry of the formally 8 valence electron complex MeTiCl_3 has been an area of intensive scientific study. The molecular structure determined by gas electron diffraction was shown to display a flattened CH_3 fragment with $\angle\text{TiCH} = 101.0(2.2)^\circ$;¹ this was interpreted in terms of partial donation of the C-H bonding electrons into vacant orbitals on Ti. The magnitude of the H-H coupling constant, as determined from the CH_2D isotopomer, was found to be 11.3 Hz and the relative sign determined to be positive. This represented the only formally sp^3 H-C-H group with a positive coupling constant; calculations suggested that the flattening of the methyl group might account for this coupling constant.^{1,2}

Subsequent work by Williamson and Hall using SCFMO and GVB calculations has predicted an undistorted CH_3 group with $\angle\text{TiCH} = 107 \pm 1^\circ$.³ These calculations also accounted for the observed low CH_3 rocking mode in the gas-phase IR spectrum. In contrast, other calculations using LCGTO- $X\alpha$ methods have predicted a flattened geometry.⁴ The factors determining the distortion of the methyl group have also been discussed by other workers.⁵

A redetermination of the gas-phase structure of $(\text{CH}_3)\text{TiCl}_3$ and $(\text{CD}_3)\text{TiCl}_3$ resulted in two independent structural determinations.⁶ These show $\angle\text{TiCH} = 109.0(1.7)^\circ$ and $\angle\text{TiCD} = 108.4(2.5)^\circ$ and show no deviation from normal methyl group geometry. These structural determinations used an all-glass inlet system to avoid decomposition of the complex, and this resulted in an improvement of the quality of the data, as shown by the better agreement factors (R).⁶

The observation of a positive ${}^2J(\text{H-D})$ for $(\text{CH}_2\text{D})\text{TiCl}_3$, and the interpretation of this in terms of a flattening of the CH_3 group, thus appears to contradict this second gas-phase structural determination and the numerous calculations per-

formed on this molecule. Thus we decided to redetermine the relative sign of ${}^2J(\text{H-D})$, using both the spin-tickling technique and an alternative method. The complex $(\text{CH}_2\text{D})\text{TiCl}_3$ was prepared by the reaction between $\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_2\text{D})_2$ and TiCl_4 in CD_2Cl_2 followed by distillation of the product into a 5 mm NMR tube.⁷

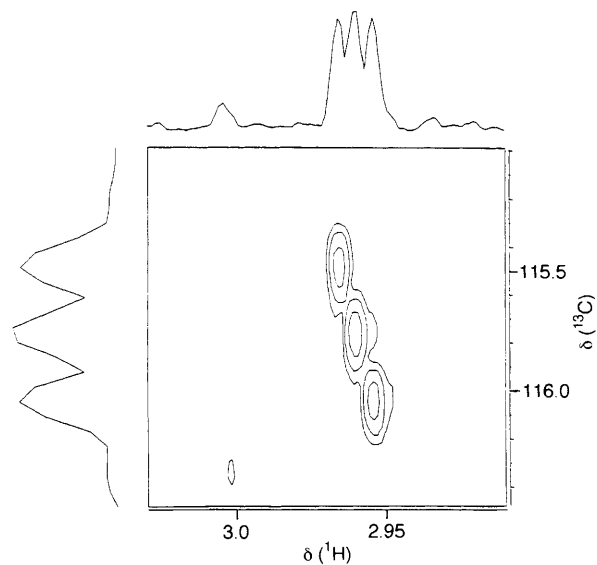


Fig. 1 The high-resolution inverse-mode proton-detected ${}^1\text{H}$ - ${}^{13}\text{C}$ heteronuclear shift correlation spectrum of $(\text{CH}_2\text{D})\text{TiCl}_3$ recorded at 253 K in CD_2Cl_2 , showing the ${}^1\text{H}$ and ${}^{13}\text{C}$ projections

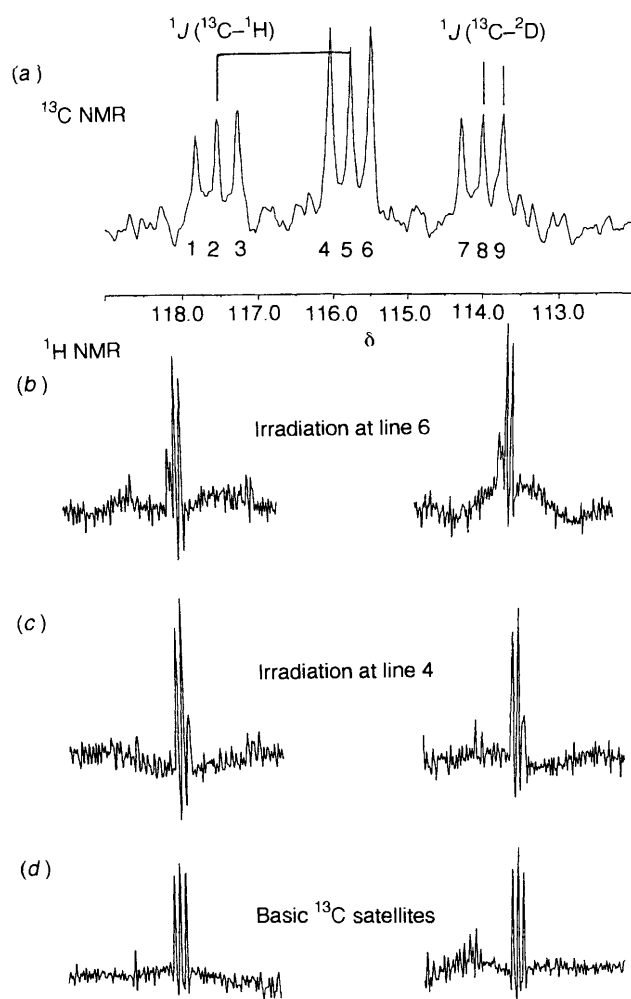


Fig. 2 Determination of the sign of $^2J(^1\text{H}-^2\text{D})$ for $(\text{CH}_2\text{D})\text{TiCl}_3$ in CD_2Cl_2 solution at 253 K. (a) The 75.43 MHz ^{13}C NMR spectrum. (b)–(d) The effect on the ^{13}C satellites in the ^1H NMR during irradiation of the ^{13}C spectrum at the lines indicated.

The high-resolution inverse-mode proton-detected ^1H - ^{13}C heteronuclear shift correlation spectrum⁸ of $(\text{CH}_2\text{D})\text{TiCl}_3$ at 253 K is shown in Fig. 1 together with the ^1H and ^{13}C projections. The spectrum was recorded in this fashion in

order to reduce experiment time for the thermally sensitive complex by utilising the enhanced sensitivity of the proton-detected experiment. In the ^1H projection, the small peak to low field of the triplet is due to the $(\text{CH}_3)\text{TiCl}_3$ isotopomer. The cross peaks provide a means of determining the relative signs of the $^2J(\text{H}-\text{D})$ and $^1J(\text{C}-\text{D})$ coupling constants. Thus, the high field ^1H line correlates with the low field ^{13}C line and it follows that $^2J(\text{H}-\text{D})$ and $^1J(\text{C}-\text{D})$ are opposite in sign;⁹ since $^1J(\text{C}-\text{H})$ is taken to be positive, this gives a negative sign for $^2J(\text{H}-\text{D})$ in $(\text{CH}_2\text{D})\text{TiCl}_3$. This result is the opposite to that reported in ref. 1.

Fig. 2a shows the 75.43 MHz ^{13}C NMR spectrum of $(\text{CH}_2\text{D})\text{TiCl}_3$ at 253 K in CD_2Cl_2 together with the labelling used for the lines. The spectra in Fig. 2c and 2b show the effect on the ^{13}C satellites of the CH_2D ^1H resonance (Fig. 2d) as a result of low-power irradiation of the lines labelled 4 and 6 (spin-tickling). These spectra show the reduction in intensity of some lines as a consequence of the spin-tickling; however, in these results the sets of lines that are affected indicate that the relative sign is opposite to that previously reported.¹ We feel that the most likely cause of this error was the incorrect transcription of the irradiation frequencies used in obtaining the spectra in the original experiments. The determination of the relative signs from the 2-dimensional experiment does not require written records to be made of the decoupling frequencies used, and is thus not subject to transcription errors.

Received, 9th April 1991; Com. 1/01646F

References

- 1 A. Berry, Z. Dawoodi, A. E. Derome, J. M. Dickinson, A. J. Downs, J. C. Green, M. L. H. Green, P. M. Hare, M. P. Payne, D. W. Rankin and H. E. Robertson, *J. Chem. Soc., Chem. Commun.*, 1986, 520.
- 2 J. C. Green and M. P. Payne, *Magn. Reson. Chem.*, 1987, **25**, 544.
- 3 R. L. Williamson and M. B. Hall, *J. Am. Chem. Soc.*, 1988, **110**, 4428.
- 4 P. Knappe and N. Rösch, *J. Organomet. Chem.*, 1989, **359**, C5.
- 5 O. Eisenstein and Y. Jean, *J. Am. Chem. Soc.*, 1985, **107**, 1177.
- 6 P. Briant, J. Green, A. Haaland, H. Møllendal, K. Rypdal and J. Tremmel, *J. Am. Chem. Soc.*, 1988, **111**, 3434.
- 7 C. Beermann and H. Bestian, *Angew. Chem.*, 1959, **71**, 618.
- 8 A. Bax and S. Subramanian, *J. Magn. Reson.*, 1986, **67**, 565.
- 9 For other examples of the use of the 2-dimensional method to determine the relative signs of coupling constants see: R. Benn, H. Brenneke, J. Heck and A. Ruffinska, *Inorg. Chem.*, 1987, **26**, 2826; R. Benn, H. Brenneke, E. Jousen, H. Lehmkuhl and F. López Ortiz, *Organometallics*, 1990, **9**, 756.