Carbon–Hydrogen Bond Properties and Alkyl Group Geometries in Dichloro(η^5-cyclopentadienyl)-methyltitanium(IV) and Dichloro(η^5-cyclopentadienyl)-ethyltitanium(IV) [TiR(η^5-C$_5$H$_5$)Cl$_2$] (R = Me or Et)†

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Infrared spectra have been recorded for various isotopomers of [TiMe(cp)Cl$_2$] (cp = cyclopentadienyl, η^5-C$_5$H$_5$; Me = CH$_3$, CD$_3$ or CHD$_2$) and [TiEt(cp)Cl$_2$] (Et = CH$_3$CH$_2$, CD$_3$CH$_2$, CH$_3$CD$_2$ or CHD$_2$CD$_2$) and assignments proposed for the alkyl group vibrations. A method was elaborated for the calculation of Fermi-resonance shifts on CH and CD stretching modes in methyl groups with C_{3v} and C_s symmetry. Estimates of CH bond lengths, bond strengths and HCH angles were derived from the resonance-corrected frequency data. The results show the methyl group in [TiMe(cp)Cl$_2$] to be markedly asymmetric, with the CH bond *trans* to the cyclopentadienyl ligand being *ca.* 0.005 Å longer and 15 kJ mol^{-1} weaker than those *trans* to chlorine. In the ethyl compound, the terminal methyl group is similarly asymmetric, again with one weak bond and two stronger bonds. The νCH$_2$ and νCD$_2$ frequencies for the methylene group are anomalous and can only be satisfactorily interpreted in terms of a model in which the two methylene CH bonds are inequivalent. The estimated bond lengths are 1.100$_5$ and 1.105$_9$ Å, and the corresponding bond dissociation energies are 403 and 383 kJ mol^{-1}, respectively. These results appear to point to a direct α-interaction between at least one of the methylene CH bonds and the titanium atom. A similar effect may also occur in [TiMe(cp)Cl$_2$].

Information on the properties of CH bonds in alkyl–metal compounds is most often obtained by means of nuclear magnetic resonance spectroscopy. The NMR data yield much useful information, but do not lead directly to the accurate estimates of CH bond lengths, bond dissociation energies or HCH angles which are particularly desirable in studies relating to CH bond activation, hydride transfer or the identification of 'agostic' C–H···M interactions.[1,2] Diffraction techniques, apart from neutron diffraction in a few isolated cases, do not locate hydrogen atoms with sufficient precision to provide useful bond length or bond angle data.

In principle, the required information is contained in the vibrational spectrum but the interpretative problems are severe and in the past have restricted quantitative studies to very simple molecules. In practical terms, vibrational spectroscopy offers two important potential advantages: it can be used in all phases, and the very short time-scale of the vibrational transition makes it possible to characterise near-instantaneous conformations in molecules undergoing almost unhindered internal rotation.[3] The problems of time-averaging which affect the NMR specta of non-rigid molecules only arise in the vibrational experiment at very much lower barriers ($\leqslant$4 kJ mol^{-1} for internal rotation).

The difficulties associated with vibrational spectroscopy arise from several sources. Vibrational assignments are not always obvious, even in very simple molecules (for example, a definitive assignment for chloroethane has only just become available).[4] The relationships between the observed vibrational modes and individual bond properties are often complex and can be difficult to establish in precise quantitative terms. Proper allowances must be made for the effects of anharmonicity, and also, most importantly for CH and CD vibrations, for Fermi-resonance perturbations. In extreme cases, these resonances can create serious problems in assignment, and even where assignments are secure it is often difficult to make the accurate estimates of the resonance shifts which are needed to establish the unperturbed frequencies of the fundamental modes.

In earlier papers[5–9] we have shown that in methyl–metal compounds many of these problems may be overcome by making use of frequency data obtained from the CH$_3$, CD$_3$ and CHD$_2$ isotopomers. The 'isolated' CH stretching frequency, ν^{is}CH, observed in the CHD$_2$ species, is essentially a local mode involving the stretching of a single CH bond, virtually uncoupled from other molecular motions and unaffected by Fermi resonance as the bending overtones which lie close to the CH stretching region in CH$_3$X compounds are moved to much lower frequencies in the CHD$_2$ isotopomers. There is now a wealth of data, from both experimental and *ab initio* sources,[3,10,11] to show that ν^{is}CH is linearly and very precisely related to the CH bond length, and in certain circumstances to the bond dissociation energy.[12] Estimates of HCH angles can be derived from the ν_{asym}CH$_3$/ν_{asym}CD$_3$ ratio, and checked by force constant calculations for the CH and CD stretching modes in the CH$_3$, CD$_3$ and CHD$_2$ compounds.

In this paper, we report our first attempt to extend the partial deuteriation technique from methyl- to ethyl–metal systems. Information on ethylmetal compounds is particularly desirable in view of their importance in hydride transfer processes, and of the involvement of β-CH bonds in agostic interactions.[1,2] We describe here the vibrational spectra of various isotopomers of [TiMe(cp)Cl$_2$] and [TiEt(cp)Cl$_2$] (cp = η^5-C$_5$H$_5$): these two compounds illustrate the utility of partial deuteriation studies, and also some of their limitations, and are important in their own right given the current interest in alkyltitanium systems.[13–16]

Experimental

[TiR(cp)Cl$_2$] (R = Me *or* Et).—These compounds were prepared using an adaptation of the method of Erskine *et*

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† *Non-SI unit employed:* dyn = 10^{-5} N.

$$\begin{array}{ccccccc}
\nu^{is}\mathrm{CH}^{s} - 2 & & & & & & \\
\lambda_{a,s} & \nu^{is}\mathrm{CH}^{a} - 2 & & & & & \\
\lambda_{a,s} & \lambda_{a,a} & \nu^{is}\mathrm{CH}^{a} - 2 & & & & \\
3^{-\frac{1}{2}}W_{122} & 3^{-\frac{1}{2}}W_{122} & 3^{-\frac{1}{2}}W_{122} & 2(\delta_{sym} + x_{sym}) & & & \\
3^{-\frac{1}{2}}W_{155} & 3^{-\frac{1}{2}}W_{155} & 3^{-\frac{1}{2}}W_{155} & 0 & 2(\delta_{asym} + x_{asym} - g_{asym}) & & \\
3^{-\frac{1}{2}}W_{455} & -12^{-\frac{1}{2}}W_{455} & -12^{-\frac{1}{2}}W_{455} & 0 & 0 & 2(\delta_{asym} + x_{asym} + g_{asym}) & \\
0 & 2^{-1}W_{455} & -2^{-1}W_{455} & 0 & 0 & 0 & 2(\delta_{asym} + x_{asym} + g_{asym})
\end{array}$$

Scheme 1

al.[17,18] The compound [Ti(cp)Cl$_3$] was obtained from the reaction of [Ti(cp)$_2$Cl$_2$] with TiCl$_4$ in refluxing toluene.[19] Dialkylzinc compounds were prepared from the direct reactions of CH$_3$I, CD$_3$I, CHD$_2$I, CH$_3$CD$_2$Br, CD$_3$CH$_2$Br and CHD$_2$CD$_2$I with copper-activated zinc. (Ethyl halides with partially deuteriated methylene groups, *e.g.* CD$_3$CHDX, were not available.) All reactions were carried out using rigorously dried solvents in an atmosphere of dry nitrogen, or in a vacuum system.

A solution of the dialkylzinc (0.5 g) in benzene (10 cm^3) was added slowly, with stirring, to a solution of [Ti(cp)Cl$_3$] (1 g) in benzene (25 cm^3) at room temperature. Stirring was continued for a further 10–15 min, during which the solution became deeper in colour and ZnCl$_2$ precipitated. The solvent was removed under vacuum and the product sublimed by gentle warming (R = Me, 55 °C; R = Et, 35 °C) onto an ice-cooled probe. The methyl compound was obtained as orange crystals and the ethyl compound as dark red crystals.

IR Spectra.—Spectra were measured for freshly prepared CCl$_4$ solutions at various pathlengths using a Nicolet 7199 FTIR spectrophotometer at 1 cm^{-1} resolution. Solvent absorptions tend to obscure weak sample peaks in the region 810–700 cm^{-1}: this region is not directly relevant to the present study. Additional very weak peaks arising from traces of decomposition products {*e.g.* [Ti(OMe)(cp)Cl$_2$], [{Ti(cp)Cl$_2$}$_2$O][17]} were observed in some samples.

Theoretical Treatment

In methyl groups with C_{3v} symmetry, only one ν^{is}CH band is observed in the spectrum of the CHD$_2$ isotopomer. If the symmetry is reduced to C_s, two bands appear, arising from stretching of the in-plane (CH^s) and out-of-plane (CH^a) bonds. In the CH$_3$ and CD$_3$ isotopomers, the reduction in symmetry splits the initially degenerate ν_{asym}CH$_3$ (e) or ν_{asym}CD$_3$ (e) levels into a′ and a″ components. The a″ component lies above the a′ if there are two strong bonds and one weaker one, and *vice versa*.

For the νCH vibrations in the CH$_3$ and CHD$_2$ species, the approximate frequency-sum rule, equations (1) or (2), provides a

$$C_{3v}\ \nu_{sym}\mathrm{CH}_3 + 2\nu_{asym}\mathrm{CH}_3 = 3\nu^{is}\mathrm{CH} \qquad (1)$$

$$C_s\ \nu_{sym}\mathrm{CH}_3 + \nu_{asym}\mathrm{CH}_3\,(a') + \nu_{asym}\mathrm{CH}_3\,(a'') = \nu^{is}\mathrm{CH}^{s} + 2\nu^{is}\mathrm{CH}^{a} \qquad (2)$$

check on assignments and makes it possible in the case of a group with C_s symmetry to determine whether the group has $\nu^{is}\mathrm{CH}^a > \nu^{is}\mathrm{CH}^s$ (*i.e.* two strong bonds and one weak one), or $\nu^{is}\mathrm{CH}^a < \nu^{is}\mathrm{CH}^s$.

Fermi Resonance.—In methyl groups with C_{3v} symmetry, the most obvious and well documented interaction involves ν_{sym}CH$_3$ (a$_1$) and the bending overtone 2δ_{asym}CH$_3$ (A$_1$). If the bending fundamental, δ_{asym}CH$_3$ (e) is reliably identified, the unperturbed overtone frequency can be calculated, with an appropriate correction for anharmonicity (typically −10 cm^{-1}), giving an estimate of the Fermi-resonance shift on the observed band, and hence of the corresponding shift on ν_{sym}CH$_3$. However, the reliability of shifts calculated in this way is variable, and can leave significant uncertainties in the unperturbed frequencies ν°_{sym}CH$_3$.*

In earlier work, resonances affecting ν_{asym}CH$_3$, or involving 2δ_{sym}CH$_3$, were assumed to be negligible and were ignored, or at the most covered by small arbitrary adjustments to the observed frequencies. Recent studies on methyl halides[20] and CH$_3$CD$_3$[21] have shown that these resonances can be significant and should be taken into account in serious quantitative work. Further possibilities arise in groups with C_s symmetry, where the ν_{asym}CH$_3$ mode splits into a′ and a″ components.

To calculate these resonances, we have extended the local/normal mode model used by Duncan and Law[20] and Tullini *et al.*[21] for Fermi resonances in the A$_1$ species of a symmetrical methyl group to cover the case of an asymmetric (C_s) methyl group, as described below.

For a symmetrical group, the above model diagonalises a 5 × 5 matrix whose diagonal elements are the three identical local mode frequencies ($\omega_M + 2x_M$) (*i.e.* ν^{is}CH in the CHD$_2$ isotopomer) plus the unperturbed overtone levels 2δ_{asym}CH$_3$ (A$_1$) and 2δ_{sym}CH$_3$ (A$_1$); ω_M is the harmonic local mode frequency and x_M the associated anharmonicity constant.[20]

The off-diagonal term between the local mode levels is the quantity λ, defined by equation (3), where f', f, g', g are the off-

$$\lambda = -\tfrac{1}{2}\omega_M[(f'/f) + (g'/g)] \qquad (3)$$

diagonal and diagonal elements of the f and g matrices; $g' = m_C^{-1}\cos \mathrm{HCH}$, $g = m_C^{-1} + m_H^{-1}$, as for a diatomic molecule.

The off-diagonal terms for the overtone levels incorporate the Fermi-resonance parameters[20,22] W_{155} and W_{122} [*e.g.* for CH$_3$X, W_{155} refers to the resonance between ν_1 (ν_{asym}CH$_3$, a$_1$) and 2ν_5 (2δ_{asym}CH$_3$, A$_1$)] multiplied by the appropriate element of the symmetry internal coordinate involved.

Our extension for a C_s methyl group involves adding further resonances with the 2δ_{asym}CH$_3$ (A′) and (A″) levels derived from 2δ_{asym}CH$_3$ (E). To do this, we use the parameter W_{455} which connects ν_4 (ν_{asym}CH$_3$, e) with 2ν_5 (2δ_{asym}CH$_3$, E) transferred from a symmetrical methyl group† and reduced by $2^{-\frac{1}{2}}$ because the resonance is now with the non-degenerate A′ and A″ levels, and we introduce different local mode levels for the in-plane (CH^s) and out of plane (CH^a) stretching motions. The (ω_M + 2x_M) values for these modes are given by (ν^{is}CH^s − 2) and (ν^{is}CH^a − 2) measured in the spectrum of the CHD$_2$ isotopomer; the reduction of 2 cm^{-1} is made to allow for the very small coupling between the CH and CD stretching motions in the CHD$_2$ group.

The 7 × 7 matrix to be diagonalised is as in Scheme 1.

Two parameters $\lambda_{a,s}$, $\lambda_{a,a}$ are needed because the interaction constants $f'_{a,a}$, $f'_{a,s}$ and the H^{a}CH^a and H^{a}CH^s angles may differ. Geometric means of the quantities ω_M, f' and f should be used in equation (3) for $\lambda_{a,s}$. Standard values of the interaction parameters W_{ijk} are taken from work on methyl halides:[18,20] W_{155} = 32 cm^{-1}; W_{455} = 20 cm^{-1}; W_{122} = 40 cm^{-1}. The latter

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* Frequencies corrected for Fermi resonance are denoted ν°, experimentally measured ones unaffected or uncorrected by resonance as ν.

† The model assumes that δ_{asym}CH$_3$ is not significantly split into a′ and a″ components. This is the case, or almost so, in the titanium compounds. Our approximation could not be used for molecules like chloroethane, in which δ_{asym}CH$_3$ is more obviously split.

is well-determined in CH_3F (ref. 22) but not in the chloride, bromide or iodide.[20] In CD_3 groups, W values appear to be reduced by a factor of 1.2–1.3.[21] The unperturbed frequency of the first overtone of the non-degenerate symmetric bending mode, $\delta_{sym}CH_3$ is given by $2(\delta_{sym} + x_{sym})$ where x_{sym} is the corresponding anharmonicity constant. For degenerate modes, two anharmonicity constants, x and g, are required.[20] In a C_{3v} methyl group, the first overtone levels of $\delta_{asym}CH_3$ (e) are $2(\delta_{asym} + x_{asym} - g_{asym})$ (A_1) and $2(\delta_{asym} + x_{asym} + g_{asym})$ (E).* In a C_s group, the E level will split into A′ and A″ components. If the parent fundamental, $\delta_{asym}CH_3$, is not significantly split, these components will have identical, or very similar, unperturbed frequencies and any observed separation will arise from Fermi-resonance effects.

For the methyl group in $[TiEt(cp)Cl_2]$, our procedure involved refining five parameters: $\lambda_{a,s}$, $\lambda_{a,a}$ and the three overtone levels, $2(\delta_{sym} + x_{sym})$, $2(\delta_{asym} + x_{asym} - g_{asym})$ and $2(\delta_{asym} + x_{asym} + g_{asym})$,† to fit six observed transitions (see discussion of assignments and Table 7, below). The calculation was repeated with the refined values of $\lambda_{a,s}$ and $\lambda_{a,a}$ but with all the W values set to zero (*i.e.* with no allowance for Fermi resonances). The changes in the computed values then gave the Fermi-resonance shifts on the normal CH_3 stretching modes. These shifts were applied to the *observed* frequencies.

Harmonic Local Mode (HLM) Force Constant Calculation.—This is a so-called energy-factored force field which treats the CH and CD stretching motions in isolation from all others. Comparisons with molecules for which complete force fields are available[4,9,23] confirm the validity of this approach. For a given HCH angle, the calculation refines the CH stretching and stretch–stretch interaction force constants to values which most accurately reproduce the observed frequencies, corrected where appropriate for Fermi resonance. Differences in the effects of anharmonicity on the CH and CD stretching levels are taken into account by decreasing all CD frequencies by a factor of 1.011.[3,24] The experimental frequencies employed are taken from the CH_3, CD_3 and CHD_2 isotopomers; in the refinement, the calculation is required to reproduce exactly those frequencies which are accurately known, but is less severely constrained, or unconstrained, for vibrations which may be affected by resonances which are not reliably determined.

A successful refinement reproduces the observed frequencies with realistic values for the force constants. Failure to refine to the required frequencies, or the appearance of unacceptable force constants (*e.g.* large or very different values for the interaction constants) indicates an incorrect HCH angle, faulty assignments or the presence of undetected resonances.

A C_{3v} methyl group generates a two-parameter force field (f,f') based on a single HCH angle. For a C_s group, the force field may involve up to four parameters, f_s, f_a, $f'_{a,s}$ $f'_{a,a}$ with either an average HCH angle, as before, or two angles, H^aCH^s and H^aCH^a.

HCH Angles.—The G-matrix elements for $\nu_{asym}CH_3$ and $\nu_{asym}CD_3$ in a symmetric methyl group are given by equations (4) and (5).

$$G^{asym}CH_3 = m_H^{-1} + m_c^{-1}(1 - \cos\alpha) \qquad (4)$$

$$G^{asym}CD_3 = m_D^{-1} + m_c^{-1}(1 - \cos\alpha) \qquad (5)$$

The ratio of the observed frequencies, $\nu_{asym}CH_3/\nu_{asym}CD_3$ is then given by $(G^{asym}CH_3/G^{asym}CD_3)^{\frac{1}{2}} \div 1.011$, the factor 1.011 being again introduced to allow for the differing effects of anharmonicity.[24] The value of the HCH angle α can thus be directly deduced from the ratio of the experimentally measured frequencies, although the sensitivity to angle is not great. For a C_s methyl group, the ratio $\nu_{asym}CH_3$ (a″)/$\nu_{asym}CD_3$ (a″) similarly yields the H^aCH^a angle. Angles obtained in this way can be tested in the HLM force-field refinement—failure to fit the data suggests that the experimental frequencies must be perturbed by unsuspected resonances. In cases where reliable frequency data are not available, the force field calculation may be carried out with a series of trial HCH values to determine which one leads to the most satisfactory fit.

Results and Assignments

Infrared spectra for the isotopomers of the two compounds are illustrated in Figs. 1 and 2, and wavenumbers are given in Tables 1, 2, 4 and 5. Table 1 contains all the bands obviously due to the cyclopentadienyl moiety, which are clearly identical, or nearly so, in the methyl and ethyl derivatives. The strong $\delta_{op}CH(e_1, a_1)$ bands near 800 cm^{-1} are poorly defined because of the intense solvent absorption in this region. Our assignments follow the definitive work of Aleksanyan and Lokshin.[25]

$[TiMe(cp)Cl_2]$.—The bands in Table 2 all move significantly upon deuteriation and hence must be associated with the MeTi moiety. There is some uncertainty below 550 cm^{-1} because of high noise levels: analysis in this region must await a more detailed study. Assignments for $[TiMeCl_3]$[9] are included in the Table for comparison.

The spectrum of $[Ti(CHD_2)(cp)Cl_2]$ contains two $\nu^{is}CH$ bands, separated by 40 cm^{-1}, and the $\nu_{asym}CH_3$ and $\nu_{asym}CD_3$ bands in the CH_3 and CD_3 isotopomers are split into well-resolved a′ and a″ components. The methyl group thus has clearly defined C_s symmetry, like those in $[TiMe_2(cp)_2]$[6] (where however the $\nu^{is}CH$ bands are separated by only 17 cm^{-1}) and unlike $[TiMeCl_3]$, in which the methyl group retains its three-fold symmetry.

The CH deformations are readily assigned by comparison with $[TiMeCl_3]$, being found in both compounds at lower frequencies than is usually the case for these vibrations. The antisymmetric mode $\delta_{asym}CH_3$ is about 15 cm^{-1} higher in $[Ti(CH_3)(cp)Cl_2]$ than in $[Ti(CH_3)Cl_3]$ and $\delta_{asym}CD_3$ is inferred (see below) to be about the same amount higher in

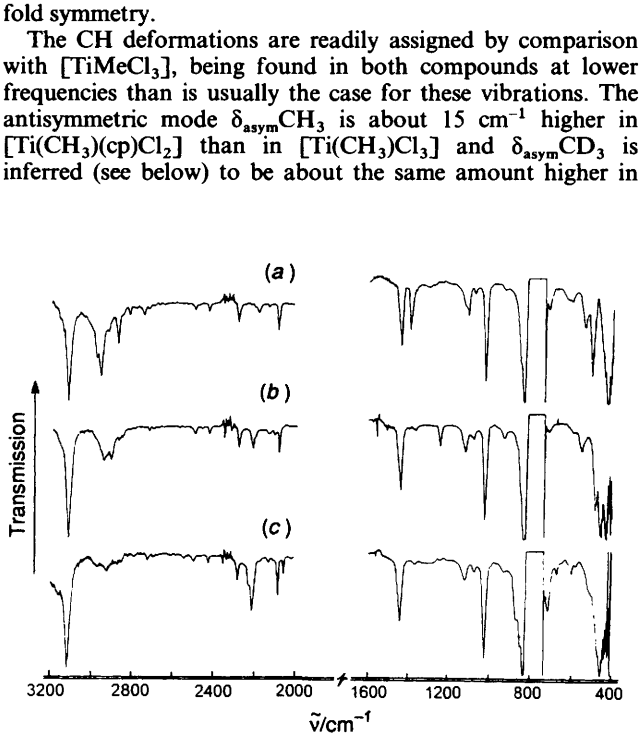

Fig. 1 Infrared spectra of isotopomers of $[TiMe(cp)Cl_2]$ (CCl_4 solutions, highest feasible concentrations, various pathlengths 0.01–0.1 mm); Me = (*a*) CH_3, (*b*) CHD_2, (*c*) CD_3. The region around 800 cm^{-1} is obscured by solvent absorptions

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* In this discussion, we have used the general descriptive terms δ_{sym}, δ_{asym}, $2\delta_{sym}$ *etc.* In specific cases, these modes and the corresponding anharmonicity constants will follow the relevant numbering system for the molecule concerned. Thus for C_{3v} CH_3X, $\delta_{sym}CH_3$ is ν_2, $\delta_{asym}CH_3$ is ν_5, x_{sym} becomes $x_{2,2}$ and x_{asym} and g_{asym} become $x_{5,5}$ and $g_{5,5}$, respectively.[20]

† The combination level $\delta_{asym}CH_3 + \delta_{sym}CH_3$ is ignored.

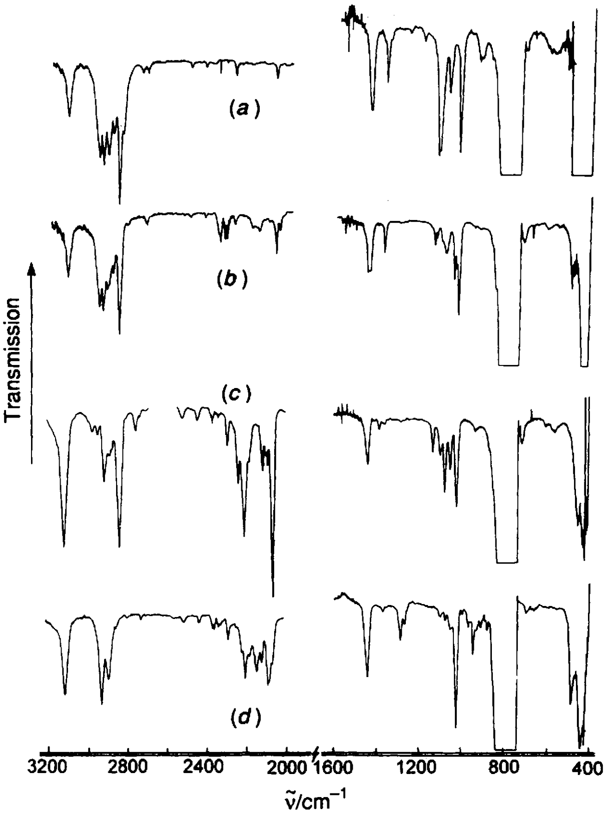

Fig. 2 Infrared spectra of isotopomers of [TiEt(cp)Cl$_2$] (CCl$_4$ solutions, highest feasible concentrations, various pathlengths 0.01–0.1 mm); Et = (*a*) C$_2$H$_5$, (*b*) CH$_3$CD$_2$, (*c*) CD$_3$CH$_2$, (*d*) CHD$_2$CD$_2$. The region around 800 cm^{-1} is obscured by solvent absorptions

Table 1 Infrared bands (cm^{-1}) attributed to the cyclopentadienyl moiety[a]

[TiMe(cp)Cl$_2$]	[TiEt(cp)Cl$_2$]	Assignment[b]
3948w	3955w	νCH + 846, 835
3115m	3115m	νCH a$_1$, e$_1$
2507vw	2506vw	1440 + 1074 E$_2$
2435vw	2435vw	1366 + 1074 A$_1$, E$_1$
2288w	2288w	1366 + 928 A$_1$, E$_1$ 1440 + 846 A$_1$, E$_1$ 1260 + 1021 E$_2$
2208 (sh)		1366 + 846 E$_2$
2189vw		1118 + 1074 E$_2$
2139vw		1118 + 1021 E$_1$
2089w	2089w	1074 + 1021 E$_1$
1992vw		1074 + 928 A$_1$, E$_2$
1913vvw	1913vvw	1074 + 846 E$_2$
1844w	1840w	2 × 928 A$_1$, E$_1$
1761w	1757mw	928 + 846 E$_2$ 928 + 835 E$_2$
1666w	1665w	846 + 835 E$_1$ 2 × 835 A$_1$
1440ms	1439ms	νCC e$_1$
1366vw	1363w	νCC e$_2$
1130 (sh)		
1118m	1115mw	νCC a$_1$
1074w	1070w	δ_{ip}CH e$_2$ (β_{CH})
1021s	1021s	δ_{ip}CH e$_1$ (β_{CH})
928w	923mw	δ_{ip}CC e$_2$
846 (sh)	844 (sh)	δ_{op}CH e$_1$ (δ_{CH})
≈835s	≈830ms	δ_{op}CH a$_1$
710w	708mw	
	≈680vw	
≈600w	≈603w	δ CCC e$_2$ (X_{CCC})

[a] Observed in all species. [b] For convenience, combination sums quote frequencies for the methyl compound only.

[Ti(CD$_3$)(cp)Cl$_2$] than in [Ti(CD$_3$)Cl$_3$]. The symmetric modes, δ_{sym}CH$_3$ and δ_{sym}CD$_3$, in contrast, are lower in [TiMe(cp)Cl$_2$] than in [TiMeCl$_3$], the difference being greater for the CD$_3$ mode. We attribute this to the TiC stretching motion present in a δ_{sym}Me mode and to a lower Ti–C stretching force constant in the cyclopentadienyl compound.

The δ_{asym}CH$_3$ band has a weak shoulder at 1388 cm^{-1}, about 4 cm^{-1} below the absorption maximum; apart from this it shows no sign of splitting into a′ and a″ components. Only one band appears in the 2δ_{asym}CH$_3$ (or 2δ_{asym}CD$_3$) overtone region. Bands due to 2δ_{sym}CH$_3$ and 2δ_{sym}CD$_3$ are not observed.

At lower frequencies, a moderately intense band at 538 cm^{-1} in [Ti(CH$_3$)(cp)Cl$_2$] appears to rise to 550 cm^{-1} in the CHD$_2$ species. This can only occur if a methyl rocking mode initially higher than 538 cm^{-1} has crossed over a less deuterium-sensitive mode as a result of the substitution, and indicates that at least one methyl rocking frequency must be higher in [TiMe(cp)Cl$_2$] than in [TiMeCl$_3$], in which the highest methyl rock is found at 464 cm^{-1}.[9]

Fermi resonances. As both the δ_{asym}CH$_3$ and δ_{sym}CH$_3$ modes have low frequencies, yielding overtones near 2770 and 2200 cm^{-1} respectively, the only significant resonance is likely to be with the ν_{sym}CH$_3$ $v = 1$ level.

Table 3 shows results of some trial calculations made with the local/normal mode model described above. As the transitions to 2δ_{sym} and the split 2δ_{asym} (E) levels are not observed, the only parameters permitted to refine were $\lambda_{a,s}$, $\lambda_{a,s}$ and the 2δ_{asym} (A$_1$) level, the latter given by $2(\delta_{asym} + x_{asym} - g_{asym})$. The results shown under column 1, where conventional W values were employed, reveal an anomaly similar to that previously found in [TiMeCl$_3$],[9] in that the value of −11.2 cm^{-1} for $(x_{asym} - g_{asym})$ is numerically much larger than the value of −5.8 cm^{-1} found in CH$_3$Cl.[18]

As the results in column 3 show, W_{155} would need to be over 47 cm^{-1} for $(x_{asym} - g_{asym})$ to approach −5.8 cm^{-1}. As we have no means of knowing whether W_{155}, or $(x_{asym} - g_{asym})$, or both, are anomalous, we adopt as a compromise the results under column 2, for $W_{155} = 43$ cm^{-1}. The resonance shift on ν_{sym}CH$_3$ is then 18.2 cm^{-1} placing ν°_{sym}CH$_3$ at ≈2858 cm^{-1}

A similar treatment for the CD$_3$ group is inhibited by an absence of W values from model compounds, and because δ_{asym}CD$_3$ is obscured by a strong cyclopentadienyl band. Using δ_{asym}CH$_3$ = 1391.8 cm^{-1} and the ratio δ_{asym}CD$_3$/δ_{asym}CH$_3$ = 0.7343 found in [TiMeCl$_3$], we predict that δ_{asym}CD$_3$ should lie near 1022 cm^{-1}. Its overtone is observed at 2022 cm^{-1} from which a resonance shift, with ν_{sym}CD$_3$, of about 12 cm^{-1} seems likely, assuming $(x_{asym} - g_{asym})$ to be −5 cm^{-1}. With a little extra shift derived from 2δ_{sym}CD$_3$, ν_{sym}CD$_3$ is estimated at 2076 cm^{-1}.

Using ν°_{sym}CH$_3$ = 2858 cm^{-1} in the frequency sum rule [equation (2)], we obtain ΣνCH$_3$ = 8792 cm^{-1}. The values of Σν^{is}CH are 8803 and 8763 cm^{-1}, respectively, for ν^{is}-CH^a > ν^{is}CH^s and ν^{is}CH^s > ν^{is}CH^a. Accordingly, we conclude that the methyl group contains two strong bonds, (CH^a) roughly comparable with the CH bonds in [TiMeCl$_3$] (ν^{is}CH = 2952 cm^{-1}) and one weaker bond, CH^s.

HLM force field. We now combine the CH$_3$, CD$_3$ and CHD$_2$ frequencies corrected for Fermi resonance, in a full harmonic local mode refinement of the force field. The ratio ν_{asym}CH$_3$ (a″)/ν_{asym}CD$_3$ (a″) indicates an HCH angle of 107.5°. In Table 4, we show under columns 1 and 2 the force constants and frequency fit for three- and four-parameter force fields using an average HCH angle of 107.5°, under columns 3 and 4 similar force fields for HCH = 110°, and under column 5 a modification of column 2 in which the H^{a}CH^s angle is adjusted so that the off-diagonal constants $f'_{a,a}$ and $f'_{a,s}$ become equal. Throughout, no weight has been placed on the frequencies most affected by Fermi resonance, ν°_{sym}CH$_3$ and ν°_{sym}CD$_3$. It is pleasing to find their calculated values close to the corrected observed ones.

Table 2 Infrared bands (cm^{-1}) in isotopomers of [TiMe(cp)Cl$_2$] assigned to the TiMeCl$_2$ moiety

Group	ν_{obs}\{[TiMe(cp)Cl$_2$\}	Assignment	ν_{obs}\{[TiMeCl$_3$]\}[a]
CH$_3$[b]	2976.8w	$\nu_{asym}CH_3$ a″	2981
	2957.1mw	$\nu_{asym}CH_3$ a′	
	2876.4w	$\nu_{sym}CH_3$ a′	2894
	2752.6vw	$2\delta_{asym}CH_3$ A′	2727
	1391.8ms	$\delta_{asym}CH_3$ a′, a″	1375
	1388 (sh)		
	1105.1m	$\delta_{sym}CH_3$	1112
	622 (sh)	ρCH_3 ?	484
	537.8m	$\nu_{asym}TiCl_2$	
	501.2s	νTiC, $\nu_{sym}TiCl_2$	464
	≈427 (100%)	ρCH_3	
CHD$_2$[c]	2947.8w	$\nu^{is}CH^a$	2952
	2907.6w	$\nu^{is}CH^s$	
	2219.0w	$\nu_{asym}CD_2$	2231
	2113vw	$\nu_{sym}CD_2$	2125
	1241.2m	δCH a″	1230
	1084 (sh)	δCH a′	1080
	927w	δCD_2 a′	935
	587w		
	549.9m		
	481s		
	455vs		
	≈428vs		
CD$_3$[d]	2231 (sh)	$\nu_{asym}CD_3$ a″	2238
	2215.3w	$\nu_{asym}CD_3$ a′	
	~2090w[e]	$\nu_{sym}CD_3$ a′	2100
	2022vw	$2\delta_{asym}CD_3$ a′	
	(1021)[f]	$\delta_{asym}CD_3$ a′, a″	1009
	867 (sh)	$\delta_{sym}CD_3$ a′	880
	669w		
	516 (sh)		
	452vs		

[a] Relevant methyl group modes only. [b] Impurity bands at 2919 (sh) and 2024vw cm^{-1} (these also remain in a decomposed sample). [c] Impurity bands at 2871 (sh), 2856 (sh) and 2930 (sh) cm^{-1}. [d] Impurity bands at 2060vw and 578 (sh) cm^{-1}. [e] Coincident with cp band. [f] Value estimated from overtone with an allowance for Fermi resonance.

Table 3 Fermi-resonance calculations for the CH$_3$ group in [Ti(CH$_3$)(cp)Cl$_2$][a]

	1	2	3	4
W_{155}[b]	32	43	47	50
W_{122}[b]	40	40	40	40
W_{455}[b]	20	20	20	20
$\Delta\nu_{asym}$ (a″)[c]	1.0	1.0	1.0	1.0
$\Delta\nu_{asym}$ (a′)[c]	1.4	1.6	1.7	1.7
$\Delta\nu_{sym}$ (a′)[c]	10.7	18.2	21.6	24.4
$\lambda_{a,s}$	−31.62	−34.16	−35.27	−36.15
$\lambda_{a,a}$	−30.03	−32.44	−33.47	−34.29
$2(\delta_{asym} + x_{asym} - g_{asym})$[d]	2761.2	2768.5	2771.6	2774.1
$x_{asym} - g_{asym}$	−11.2	−7.6	−6.0	−4.9
$2(\delta_{asym} + x_{asym} + g_{asym})$[e]	2773.6	2773.6	2773.6	2773.6
$2(\delta_{sym} + x_{sym})$[f]	2200.8	2200.8	2200.8	2200.8

[a] Units: cm^{-1}. [b] W values used in initial refinement of $\lambda_{a,s}$, $\lambda_{a,a}$ and $2(\delta_{asym} + x_{asym} - g_{asym})$. [c] Calculated Fermi-resonance shifts. [d] $2\delta_{asym}$A′ (A$_1$) frequencies calculated with refined values of $\lambda_{a,s}$, $\lambda_{a,a}$ and all $W_{ijk} = 0$. [e] $2\delta_{asym}$A″, frequency constrained. [f] $2\delta_{sym}$, A′, frequency constrained.

Overall there is a clear preference for an angle close to 107.5°, and either for $f'_{a,s} < f'_{a,a}$, or for H^{s}CH^a > H^{a}CH^a. In either case, at angles close to 108°, the f' values are markedly less than those in compounds previously studied, including [TiMeCl$_3$] (0.025 mdyn Å^{-1}).[9] The effects of f' and the HCH angle are combined in the parameter λ so that all the experiment directly shows is that $\lambda_{a,s}$ is more negative than $\lambda_{a,a}$, as seen in Table 3. However, given the clear difference between the CH^a and CH^s bonds, a modest difference between the H^{a}CH^a and H^{a}CH^s angles is reasonable and likely. In effect, the calculation sets an upper limit of about 2° on this difference.

[TiEt(cp)Cl$_3$].—Wavenumbers and assignments for the ethyl group vibrations in [Ti(CH$_2$CH$_3$)(cp)Cl$_2$]([^{2}H$_0$]), [Ti(CD$_2$CH$_3$)(cp)Cl$_2$]([^{2}H$_2$]), [Ti(CH$_2$CD$_3$)(cp)Cl$_2$](^{2}H$_3$) and [Ti(CD$_2$CHD$_2$)(cp)Cl$_2$]([^{2}H$_4$]) in Table 5. The methyl group is clearly asymmetric: two ν^{is}CH modes, separated by 35 cm^{-1}, are observed in the [^{2}H$_4$] species, and $\nu_{asym}CH_3$ in the [^{2}H$_2$] species is split into a′ and a″ components.

In assigning the bands below 1500 cm^{-1}, we have to be guided by the recent assignments for various isotopic species of chloroethane.[4] Experience with [TiMeCl$_3$][9] and with [TiMe(cp)Cl$_2$] suggests that the force constants associated with the bending motions of the methylene group, in particular, will be significantly lower in the EtTi moiety than in EtCl, so that these modes are likely to be shifted to substantially lower wavenumbers in the titanium compound.

The potential-energy distributions for the relevant modes of EtCl isotopomers are summarised in Table 6. As an aid to the comparison, we number the ethyl modes in Table 5 in the same way as the EtCl modes in Table 6, ignoring the TiCl$_2$ and Ti(cp) contributions to the overall vibrations of the molecule.*

Methyl group: [Ti(CD$_2$CH$_3$)(cp)Cl$_2$]([^{2}H$_2$]).—In the νCH region we observe a pattern of five major bands between 2960

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* Certain bands 'cross over' from EtCl to [TiEt(cp)Cl$_2$]. Thus in the [^{2}H$_3$] species ν_5 in [TiEt(cp)Cl$_2$] corresponds to ν_6 in EtCl, and *vice versa*; and in the [^{2}H$_2$] species ν_7 [TiEt(cp)Cl$_2$] corresponds to ν_6 in EtCl, and *vice versa*.

Table 4 Harmonic local-mode treatments for [TiMe(cp)Cl$_2$]

			1	2	3	4	5
	ν_{obs} [a]	σ_v [a,b]	ε_v [a,c]	ε_v [a,c]	ε_v [a,c]	ε_v [a,c]	ε_v [a,c]
CH$_3$	2976.8	1	−1.4	0.0	−1.4	0.0	0.0
	2957.1	1	1.6	0.0	1.7	0.0	0.0
	2858.0 [d]	100	0.0	−0.4	0.7	0.2	−0.2
CD$_3$	2231.1	10	−1.1	0.0	−3.9	−2.8	0.0
	2215.3	10	1.5	0.6	−1.2	−2.1	−1.6
	2076.0 [d]	100	2.0	−2.5	5.0	4.3	0.2
CH^{a}D$_2$	2947.8	1	0.6	0.0	0.6	0.0	0.0
	2219.0	10	−0.4	−0.8	−3.0	−3.4	−2.3
	2113.2	100	−3.5	−3.1	0.3	0.6	−1.2
CH^{s}D$_2$	2907.6	1	−0.8	0.0	−0.8	0.0	0.0
	—		(2232.2)	(2231.1)	(2235.0)	(2233.9)	(2131.1)
	—		(2132.7)	(2134.8)	(2128.7)	(2130.8)	(2134.4)
Angles [e]	H^{a}CH^a		107.5	107.5	110.0	110.0	107.5
	H^{a}CH^s						108.88
Force constants [f]	f_s		4.6226(30)	4.6198(2)	4.6227(32)	4.6198(7)	4.6198(5)
	f_a		4.7477(34)	4.7502(2)	4.7476(36)	4.7503(8)	4.7502(5)
	$f'_{a,s}$		−0.0005(40)	−0.0015(2)	0.0142(43)	0.0132(9)	0.0067(6)
	$f'_{a,a}$			0.0066(2)		0.0216(11)	0.0067(7)
	Σw.s.e. [g]		5.73	0.012	6.35	0.248	0.080

[a] Units: cm^{-1}. [b] Uncertainty in ν_{obs}. [c] $\nu_{obs} - \nu_{calc}$; ν_{calc} in parentheses. [d] Fermi-resonance correction applied. [e] HCH angles in °. [f] Valence force constants in mdyn Å^{-1}. [g] Sum of weighted squares of errors.

and 2850 cm^{-1}, plus two minor bands just below (Fig. 2). The two highest peaks, at 2959.8 and 2940.1 cm^{-1}, are the a″ and a′ components of ν_{asym}CH$_3$, and the lowest, at 2859.4 cm^{-1}, ν_{sym}CH$_3$. Using these assignments, we obtain $\Sigma\nu$CH$_3$ = 8759.3 cm^{-1}, in very good agreement with $\Sigma\nu^{is}$CH = 8760.6 cm^{-1} (from the [^{2}H$_4$] spectrum) for the case of a methyl group with two strong bonds and one weak one, but not with the alternative value of $\Sigma\nu^{is}$CH = 8725.8 cm^{-1} for two weak bonds and one strong one. The two remaining bands in the νCH region must derive from the bending overtones, 2δ_{asym}CH$_3$. In principle, three such overtones are to be expected: the A′ and A″ levels derived from 2δ_{asym}CH$_3$ (E) and a further A′ level corresponding to 2δ_{asym}CH$_3$ (A$_1$) in a symmetrical group. Of the two experimentally observed peaks the lesser one, at 2888.4 cm^{-1}, is close to the expected unperturbed value of 2δ_{asym}CH$_3$ and hence is assigned to the A″ 2δ_{asym}CH$_3$ (E) level. The second band (2919.6 cm^{-1}) is then the A′ (A$_1$) component of 2δ_{asym}CH$_3$, displaced upwards by resonance with ν_{sym}CH$_3$ (a′) (2859.4 cm^{-1}). The A′ 2δ_{asym}CH$_3$ (E) level is not observed as a separate band.

The δ_{sym}CH$_3$ band is readily assigned at 1372.4 cm^{-1}, close to its value of 1370.6 cm^{-1} in the [^{2}H$_0$] species, and in the corresponding chloroethanes (1384 cm^{-1}). The weak band at 2724 cm^{-1} is then clearly 2δ_{sym}CH$_3$ (A′) and the second weak band, at 2818 cm^{-1}, is δ_{sym}CH$_3$ + δ_{asym}CH$_3$ (A′).

Table 7 shows the results of a local/normal mode Fermi-resonance calculation, with *W* values taken as before from the methyl halides. Five parameters were refined: the two *gf* coupling terms $\lambda_{a,s}$ and $\lambda_{a,a}$ and the unperturbed values of $(2\delta_{asym} + x_{asym} - g_{asym})$, $2(\delta_{asym} + x_{asym} + g_{asym})$ and $2(\delta_{sym} + x_{sym})$. As one of the two 2$\delta_{asym}CH_3$ levels derived from the 2δ_{asym}CH$_3$ (E) pair was not observed, the calculation was carried out with the 2888.4 cm^{-1} band assigned first as the A′ 2δ_{asym}CH$_3$ (E) level, then as the A″ level. Switching the assignment of the 2888.4 cm^{-1} band in this way affected the calculated Fermi-resonance shifts by only 0.1 cm^{-1}. The results shown in Table 7 are with the 2888.4 cm^{-1} band assigned as the A′ mode; the A″ level is then computed to lie 1.7 cm^{-1} above this.

The shifts on ν_{asym}CH$_3$ (a″), ν_{asym}CH$_3$ (a′) and ν_{sym}CH$_3$ (a′) are calculated to be 3.1, 7.6 and −9.8 cm^{-1} respectively. Using the resonance-corrected frequencies, $\Sigma\nu$CH$_3$ is altered by only 0.9 cm^{-1} and confirms the initial assumption that the methyl group has two strong bonds and one weak one. The assignment of ν_{asym}CH$_3$ (a″) *above* ν_{asym}CH$_3$ (a′) is an immediate consequence of this structural arrangement.

The value of x_{sym} for δ_{sym}CH$_3$ is found to be −4.7 cm^{-1}, which is reasonable for a mode of this kind.[20] The value of g_{asym} for δ_{asym}CH$_3$, −2.3 cm^{-1}, is not out of line with those found in the methyl halides, which range from −0.1 to −3.0 cm^{-1} but x_{asym}, at −1.1 cm^{-1}, is distinctly smaller than the typical values of −5.9 cm^{-1} (CH$_3$Cl) and −5.74 cm^{-1} (CH$_3$I).[18] The difference may arise from uncertainties about the exact position of the bending fundamental, coupled with a likely small splitting in this mode.

Methyl group: [Ti(CH$_2$CD$_3$)(cp)Cl$_2$]([^{2}H$_3$]). In the νCD$_3$ region (Fig. 2) instead of the expected split ν_{asym}CD$_3$ (a′, a″) band, we observe a prominent band at 2236 cm^{-1} and a complex one at 2208 cm^{-1}, with shoulders at 2202 and 2183 cm^{-1}. The band due to ν_{sym}CD$_3$ is readily identified at 2066 cm^{-1}. Analysis of the ν_{asym}CD$_3$ levels entails a prior study of the region below 1200 cm^{-1} in order to identify fundamentals whose overtones or combinations could appear near 2200 cm^{-1}.

On the basis of the data for CD$_3$CH$_2$Cl (Table 6) we expect four A′ modes (ν_5, ν_6, ν_7, ν_8) and three A″ modes (ν_{14}, ν_{15}, ν_{16}) between 1200 and 850 cm^{-1}. Two of these, ν_7 and ν_{15}, are the split components of δ_{asym} CD$_3$ and are clearly the 1054.5/1049.3 cm^{-1} pair, with overtones at 2114.2 and 2097 cm^{-1}, just above ν_{sym}CD$_3$. The wCH$_2$ mode ν_5 in CD$_3$CH$_2$Cl (1290 cm^{-1}) is expected to fall appreciably in the titanium compound and is assigned to the strong band at 1075.6 cm^{-1}, where it becomes ν_6. The weak band at 930.5 cm^{-1} is assigned to ν_8, which being essentially a νCC/δ_{sym}CD$_3$ motion should lie close to its value of 937 cm^{-1} in CD$_3$CH$_2$Cl.

The moderately strong band at 1131.9 cm^{-1} is at the upper limit of the possible range for ν_5 (δ_{sym}CD$_3$/νCC) given its value of 1135 cm^{-1} in CD$_3$CH$_2$Cl (where it is ν_6), but its intensity is variable relative to other bands in different samples and must be due at least in part to impurity. If this band does arise from ν_5,

Table 5 Infrared bands attributed to the $TiEtCl_2$ moiety

$[Ti(CH_2CH_3)(cp)Cl_2]$[a]			$[Ti(CD_2CH_3)(cp)Cl_2]$[a]			$[Ti(CH_2CD_3)(cp)Cl_2]$[b]			$[Ti(CD_2CHD_2)(cp)Cl_2]$[c]	
ν_{obs}/cm^{-1}	Assignment	Mode[d]	ν_{obs}/cm^{-1}	Assignment	Mode[b]	ν_{obs}/cm^{-1}	Assignment	Mode[d]	ν_{obs}/cm^{-1}	Assignment
2961.7m	$\nu_{asym}CH_3\ a''$	12	2959.8m	$\nu_{asym}CH_3\ a''$	12	2911.5m	$\nu_{asym}CH_2\ a''$	12	2931.8m	$\nu_{is}CH^a$
2940.4m	$\nu_{asym}CH_3\ a'$	1	2940.1m	$\nu_{asym}CH_3\ a'$	1	2837.6ms	$\nu_{sym}CH_2\ a'$	1	2897.0mw	$\nu_{is}CH^s$
2915.3m	$\nu_{asym}CH_2\ a''$	13	2919.6mw	$2\delta_{asym}CH_3\ A'$		2749.3w	$2\delta_{sym}CH_2\ A'$		2219 (sh)	
2888.6mw	$2\delta_{asym}CH_3\ A'$		2888.4mw	$2\delta_{asym}CH_3\ A''$		2235.9m	$\nu_{asym}CD_3\ a''$/	13	2201.7mw	
2861.6ms	$\nu_{sym}CH_3\ a'$	2	2859.4m	$\nu_{sym}CH_3\ a'$	2		1132 + 1088 A″ or			
2841 (sh)	$\nu_{sym}CH_2\ a'$	3	2818vw	1448 + 1372 A′		2202 (sh)	1120 + 1098 A′		2181.0 (sh)	
2750vw	$2\delta_{sym}CH_2\ A'$		2724.0w	$2\delta_{sym}CH_3\ A'$		2208ms	$\nu_{asym}CD_3\ a'$/	2	2161 (sh)	
2730vw	$2\delta_{sym}CH_3\ A'$		2204.0vw (br)	1098 + 1081 A″/	13		1132 + 1052 A′ or			
1452 (sh)	$\delta_{asym}CH_3$	4, 14	2169vw	$\nu_{asym}CD_2\ a''$		2183ms	1120 + 1076 A′		2145.7mw	
1385 (sh)	$\delta_{sym}CH_2\ a'$	5	2120vvw	1081 + 1042 A′		2114.2m	$2\delta_{asym}CD_3\ A'$		2120.4w	
1370.6m	$\delta_{sym}CH_3\ a'$	6	2090.3w	$\nu_{sym}CD_2\ a'$	3	2097 (sh)	$2\delta_{asym}CD_3\ A'', A'$		2083mw	
1199.5w	$tCH_2\ a''$	15	2069vw	2 × 1042	4,14	2066.6s	$\nu_{sym}CD_3\ a'$	3	2071 (sh)	
1115vs	$wCH_2\ a'$	7	≈1448 (sh)	$\delta_{asym}CH_3\ a', a''$	5	1385.3m	$\delta_{sym}CH_2\ a'$	4	1289 (sh)	δCH
1074.5ms	$\rho CH_3/\nu_{CC}$	8	1372.4m	$\delta_{sym}CH_3\ a'$		1131.9ms	Impurity +		1283.9m	
933.8mw	$\rho CH_3/\nu_{CC}$	9	1134.1m	Impurity ?	15		? $\delta_{sym}CD_3$	5	1265.8mw	
876 (sh)	Mixed	16	1098 (sh)	ρCH_3	6	1098 (sh)	$tCH_2\ a''$,	4	1254 (sh)	
575w (br)	$\rho CH_3/\rho CH_2$	17	1081m	ρCH_3	7	1088 (sh)	2 × 557 A′		1049.0w	
< 500	(Not observed)		1041.9ms	$\delta_{sym}CD_2/\nu_{CC}$		1075.6vs	$wCH_2\ a'$	6	1043 (sh)	
			1032 (sh)	Impurity ?	8	1054.5 (sh)	$\delta_{asym}CD_3\ a', a''$	7, 15	989.4w	
			950vw	$\delta_{sym}CD_2/\nu_{CC}$		1049.3s			963.7mw	
			≈865 (sh)	?		930.5m	$\nu_{CC}/\delta_{sym}CD_3\ a'$	8	939.3m	
			652vw	tCD_2 ?	16	865 (sh)	$\rho CH_2/\rho CD_3\ a''$	16	899.8w	
			600w	cp + ?			or $\rho CD_3\ a'$	9	875 (sh)	
			550vw	ρCD_2 ?	17	557m	$\rho CD_3/\rho CH_2\ a''$	17	871.6w	
			487vs	νTiC,					863.3w	
			≈435 100%	$\nu_{asym}TiCl_2$					855 (sh)	
									686w	
									654w	
									638 (sh)	
									482.3s	
									435 100%	

[a] Impurity band also seen: 1811 cm^{-1}. [b] Impurity bands also seen: 2969, 2882 and 1811 cm^{-1}. [c] Impurity band also seen: 2855 cm^{-1}. [d] Mode numbering as for EtCl, see Table 6, and comments in text.

Table 6 Some fundamental bands and PE distributions in chloroethane species (ref. 4)*

A′		ν_{obs}	$\delta_{asym}CH_3(CD_3)$	$\delta_{sym}CH_3(CD_3)$	$\rho CH_3(CD_3)$	$\delta_{sym}CH_2(CD_2)$	$wCH_2(CD_2)$	ν_{CC}	ν_{CCl}
CH_3CH_2Cl	ν_4	1467	62			34			
	ν_5	1459	30			65			
	ν_6	1384		96				10	
	ν_7	1289					95		
	ν_8	1073			40				
	ν_9	973			33			40	11
CH_3CD_2Cl	ν_4	1459	94					47	
	ν_5	1384		100					
	ν_6	1126						11	
	ν_7	1099			53	43	25	45	
	ν_8	1008			11	12	22		
	ν_9	851			16	48		25	
CD_3CH_2Cl	ν_4	1461					55	21	
	ν_5	1290				102	101		
	ν_6	1135		39					
	ν_7	1062	98					50	
	ν_8	937		36	13			28	
	ν_9	856			43				35

A″			$\delta_{asym}CH_3(CD_3)$	$\rho CH_3(CD_3)$	$tCH_2(CD_2)$	$\rho CH_2(CD_2)$
CH_3CH_2Cl	ν_{14}	1447	92			
	ν_{15}	1251		22	55	
	ν_{16}	1082		24	37	33
	ν_{17}	785		50	15	63
CH_3CD_2Cl	ν_{14}	1449	93			
	ν_{15}	1122		61		10
	ν_{16}	815			80	13
	ν_{17}	651		32	15	78
CD_3CH_2Cl	ν_{14}	1203			87	
	ν_{15}	1053	86			
	ν_{16}	1028	11	13		59
	ν_{17}	663		61	10	37

* Units: cm^{-1}.

Table 7 Local/normal mode Fermi-resonance calculations for the CH_3 group in $[Ti(CD_2CH_3)(cp)Cl_2]$[a]

ν_{obs}	$\nu_{calc}(1)$	Assignment	$\nu_{calc}(2)$[b]	$\Delta\nu[(1) - (2)]$[c]
2959.8	2958.6	ν_{asym} a″	2955.6	3.07
2940.1	2939.0	ν_{asym} a′	2931.4	7.60
2919.6	2920.7	$2\delta_{asym}$ A′		
—	2890.2	$2\delta_{asym}$ A″		
2888.4	2888.5	$2\delta_{asym}$ A′		
2859.4	2858.0	ν_{sym} a′	2867.7	−9.76
2724.0	2724.1	$2\delta_{sym}$		

Parameters refined in (1)		Parameters constrained in (1)	
$\lambda_{a,s}$	−22.27[d]	$\nu^{is}CH^a$	2929.8[d,e]
$\lambda_{a,a}$	−25.75[d]	$\nu^{is}CH^s$	2895.0[d,e]
$2(\delta_{asym} + x_{asym} - g_{asym})$	2902.23	W_{155}	32
$2(\delta_{asym} + x_{asym} + g_{asym})$	2893.26	W_{122}	40
$2(\delta_{sym} + x_{sym})$	2735.47	W_{455}	20

[a] ν In cm^{-1}. [b] Calculated unperturbed frequencies. [c] Fermi-resonance shifts. [d] Parameters constrained in (2) (no Fermi resonance present). [e] Experimental frequencies − 2.

we would expect to find an overtone near 2260 cm^{-1}, where nothing is visible. Instead, if the prominent band at 2235.9 cm^{-1} arises from a $\nu_{asym}CD_3$ mode affected by resonance with an overtone or combination mode, we might look for an unperturbed fundamental ν_5 between 1110 and 1120 cm^{-1}. The nearest absorptions are the 1132 cm^{-1} band and two shoulders, at 1098 and 1088 cm^{-1}, on ν_6. These two bands are reasonably assigned to 2 × 557 (probably ν_{17}, ρCD_3) and ν_{14}, tCH_2. A resonance between ν_5 and $2\nu_{17}$ would then move the former from an unperturbed frequency of ≈1120 cm^{-1} to the observed frequency of 1132 cm^{-1}.

Given these assignments, we feel that the bands at 2236/2202 cm^{-1} are likely to arise from a close resonance between $\nu_{asym}CD_3$ a″ and an A″ combination 1120 + 1098 cm^{-1} (assuming ν_5° to be 1120 cm^{-1}) or 1132 + 1088 cm^{-1} (if ν_5 is not significantly perturbed by Fermi resonance). The value of $\nu^\circ_{asym}CD_3$ (a″) would then be about 2215 cm^{-1}. The bands at 2208 and 2183 cm^{-1} are attributed to the A′ resonance between $\nu_{asym}CD_3$ (a′) and 1120 + 1076 cm^{-1}, or possibly 1132 + 1056 cm^{-1}, suggesting a value of ≈2200 cm^{-1} for $\nu^\circ_{asym}CD_3$ (a′).

Table 8 shows the results of a trial local/normal mode calculation analogous to that for the CH_3 group. The diagonal elements for the CD^a and CD^s bonds were those for CH^a and CH^s divided by 1.347 15,† the coupling parameters $\lambda_{a,s}$ and $\lambda_{a,a}$ were calculated using a common HCH angle of 108° and the f' values associated with it (see below), the W values were $2^{-\frac{1}{2}}$ times those for the CH_3 problem, and sensible values of $2\delta^\circ_{sym}$ (2213 cm^{-1}), $2\delta^\circ_{asym}$ (2097 cm^{-1}) were adopted. The computed values of the higher $2\delta_{asym}CD_3$ (A′) level, 2112 cm^{-1}, and the lower A′, A″ pair, 2096 cm^{-1}, are very close to the observed bands at 2114.2 and 2097 cm^{-1}, suggesting that the W values assumed here are appropriate. The calculation predicts the $\nu_{asym}CD_3$ levels at 2215 cm^{-1} (a″) and 2199 cm^{-1} (a′) very close to our estimated frequencies for the unperturbed modes and lending support to the assumption that these modes in the experimental spectrum are shifted by resonances with combination modes and not with the bending overtones. (The local/normal mode calculation only takes account of the latter interactions: effects involving combination bands are not included.)

The main point of interest arising from the calculation is the resonance shift of 21.2 cm^{-1} predicted in $\nu_{sym}CD_3$, which when applied to the observed $\nu_{sym}CD_3$ frequency yields $\nu^\circ_{sym}CD_3$ at 2088 cm^{-1}.

HLM force field for the methyl group. As we do not have an

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† The ratio $(gCH/gCD)^{\frac{1}{2}}$ ÷ 1.011.

unequivocal value for $\nu^{\circ}_{\mathrm{asym}}\mathrm{CD_3}$, we have no means of making an initial estimate of the HCH angle, and therefore have carried out trial force-field calculations for HCH = 106, 108 and 110° (Table 9, columns 1, 3 and 5) and for two further situations, columns 2 and 4, in which $\mathrm{H^aCH^a}$ is 2° less than $\mathrm{H^aCH^s}$. In carrying out the refinement, we attach the most weight to $\nu^{\circ}_{\mathrm{asym}}\mathrm{CH_3}$ (a″), $\nu^{\circ}_{\mathrm{asym}}\mathrm{CH_3}$ (a′), $\nu^{\circ}_{\mathrm{sym}}\mathrm{CH_3}$, $\nu^{\circ}_{\mathrm{sym}}\mathrm{CD_3}$, $\nu^{\mathrm{is}}\mathrm{CH^a}$ and $\nu^{\mathrm{is}}\mathrm{CH^s}$, implying confidence, in particular, in the Fermi-resonance correction calculated for $\nu_{\mathrm{sym}}\mathrm{CD_3}$. The $\nu_{\mathrm{asym}}\mathrm{CD_3}$ modes were allowed to refine without constraint.

For the 110° calculation (column 5), the error in $\nu^{\circ}_{\mathrm{sym}}\mathrm{CD_3}$ is becoming uncomfortably large. At the other end, the 106° calculation (column 1) produces f' values of 0.016 and 0.027 mdyn Å^{-1}, which are rather small when compared with the expected values for a substituted ethane. In chloroethane, for example, $f'_{\mathrm{a,a}}$ and $f'_{\mathrm{a,s}}$ are 0.0411 and 0.0416 mdyn Å^{-1} respectively, from the scaled *ab initio* force field.[4] We therefore prefer 108° as the most likely mean angle. Setting $\mathrm{H^aCH^s}$ to 110°, with $\mathrm{H^aCH^a}$ kept at 108°, has the effect of making $f'_{\mathrm{a,s}}$ and $f'_{\mathrm{a,a}}$ converge at values close to those found in chloroethane. The calculation here depends critically on the reliability of the Fermi-resonance corrections applied to $\nu_{\mathrm{asym}}\mathrm{CH_3}$ (a″) and $\nu_{\mathrm{asym}}\mathrm{CH_3}$ (a′). We conclude that our results are consistent with a wider $\mathrm{H^aCH^s}$ angle, but do not conclusively prove this to be the case.

Methylene group: $[\mathrm{Ti(CH_2CD_3)(cp)Cl_2}]$. As seen in Fig. 2, the $2\delta_{\mathrm{sym}}\mathrm{CH_2}$ band at 2749.3 cm^{-1} is clearly in resonance with $\nu_{\mathrm{sym}}\mathrm{CH_2}$ at 2837.6 cm^{-1}. Assuming a normal anharmonicity ($x_{\mathrm{sym}} \approx -5$ cm^{-1}) for the $\delta_{\mathrm{sym}}\mathrm{CH_2}$ mode, the resonance shift would be 11.3 cm^{-1}, putting $\nu^{\circ}_{\mathrm{sym}}\mathrm{CH_2}$ at 2826.3 cm^{-1}. With $\nu_{\mathrm{asym}}\mathrm{CH_2}$ at 2911.5 cm^{-1}, the average νCH value is 2869(3) cm^{-1} and the $\nu_{\mathrm{asym}}\mathrm{CH_2} - \nu^{\circ}_{\mathrm{sym}}\mathrm{CH_2}$ separation is 85(5) cm^{-1}, the uncertainties arising from our ignorance of the exact value of x_{sym} for $\delta_{\mathrm{sym}}\mathrm{CH_2}$. Both of these results are anomalous and will be further discussed further below.

Table 8 Local/normal mode Fermi-resonance estimates for the $\mathrm{CD_3}$ group in $[\mathrm{Ti(CH_2CD_3)(cp)Cl_2}]$. Assumed parameters (cm^{-1}): $\nu^{\mathrm{a}}_{\mathrm{CD}}$ 2174.8, $\nu^{\mathrm{s}}_{\mathrm{CD}}$ 2149.0, $\lambda_{\mathrm{a,a}}$ −39.65, $\lambda_{\mathrm{a,s}}$ −39.31, $2\delta^{\circ}_{\mathrm{asym}}$ (A,E) 2097, $2\delta^{\circ}_{\mathrm{sym}}$ 2213, W_{155} $32.2^{-\frac{1}{2}}$, W_{122} $40.2^{-\frac{1}{2}}$, W_{455} 20.2^{-1}, HCH = 108°. Output frequencies and assignment: 1, W as above; 2, all $W = 0$

	1	2	Δν*
$2\delta_{\mathrm{sym}}$ A′	2219.6	2213.0	6.6
ν_{asym} a″	2215.3	2214.5	0.8
ν_{asym} a′	2198.7	2198.1	0.6
$2\delta_{\mathrm{asym}}$ A′	2112.0	2097.0	15.0
$2\delta_{\mathrm{asym}}$ A″	2096.2	2097.0	−0.8
$2\delta_{\mathrm{asym}}$ A′	2096.0	2097.0	−1.0
ν_{sym} a′	2064.9	2086.1	−21.2

* Fermi-resonance shifts.

Methylene group: $[\mathrm{Ti(CD_2CH_3)(cp)Cl_2}]$. In the $\nu\mathrm{CD_2}$ region we encounter similar difficulties to those in the $\nu\mathrm{CD_3}$ region in the $[^2\mathrm{H_3}]$ species. The $\nu_{\mathrm{sym}}\mathrm{CD_2}$ band is obvious at 2090.3 cm^{-1}, although a small part of its intensity derives from an underlying cp band, but where $\nu_{\mathrm{asym}}\mathrm{CD_2}$ is expected there is a broad region of absorption between 2169 cm^{-1} and *ca.* 2204 cm^{-1}. Between 1300 and 900 cm^{-1}, we expect three A′ modes (ν_6, ν_7 and ν_8) and ν_{15} (A″). Of these, ν_7 and ν_{15} in $\mathrm{CH_3CD_2Cl}$ are substantially $\rho\mathrm{CH_3}$ modes (Table 6) and should fall just a little on passing to the titanium compound. Mode ν_6 in $\mathrm{CH_3CD_2Cl}$ (1126 cm^{-1}) is mostly $\mathrm{CD_2}$ motion and should fall substantially in $[\mathrm{Ti(CD_2CH_3)(cp)Cl_2}]$. The highest band observed in this region (1134 cm^{-1}) thus appears to be too high to be due to ν_6, ν_7 and ν_{15} and we attribute it to an impurity. The moderate band at 1081 cm^{-1}, with a shoulder at 1098 cm^{-1}, is appropriately placed for the two $\rho\mathrm{CH_3}$ modes, renumbered in the titanium compound as ν_6 and ν_{15}. The strong band at 1041.9 cm^{-1} is then assigned as ν_7, displaced from 1126 cm^{-1} in $\mathrm{CH_3CD_2Cl}$ where it is ν_6. Mode ν_8 in $\mathrm{CH_3CD_2Cl}$ (1008 cm^{-1}) should fall by a similar amount to ν_6 and the only candidate is a very weak band at 950 cm^{-1}. There remains a prominent shoulder at 1032 cm^{-1}, which may represent a combination or overtone or resonance with ν_7, or else arise from impurity.

Placing ν_7, a predominantly $\delta_{\mathrm{sym}}\mathrm{CD_2}$ mode, at 1042 cm^{-1} provides a satisfactory explanation for the weak band at 2069 cm^{-1} as $2\delta_{\mathrm{sym}}\mathrm{CD_2}$ in resonance with $\nu_{\mathrm{sym}}\mathrm{CD_2}$ at 2082 ± 3 cm^{-1}.

The antisymmetric stretch, $\nu_{\mathrm{asym}}\mathrm{CD_2}$, is expected in the region 2150–2200 cm^{-1}: the broad band of absorption in this region could also contain overtone contributions (2 × 1098 = 2196, A′, and 2 × 1081 = 2162 cm^{-1}, A′) as well as a combination 1098 + 1081 = 2179 cm^{-1} (A″). Of these, only the A″ combination could be in resonance with $\nu_{\mathrm{asym}}\mathrm{CD_2}$.

From the average νCH value of 2869 cm^{-1} deduced for the $\mathrm{CH_2}$ group in $[\mathrm{Ti(CH_2CD_3)(cp)Cl_2}]$, we predict a corresponding $\nu_{\mathrm{av}}\mathrm{CD}$ value of 2130 cm^{-1} for the $\mathrm{CD_2}$ group in $[\mathrm{Ti(CD_2CH_3)(cp)Cl_2}]$, using the factor $(g_{\mathrm{CH}}/g_{\mathrm{CD}})^{\frac{1}{2}} \div 1.011 = 1.347\,15$, as before.† With $\nu^{\circ}_{\mathrm{sym}}\mathrm{CD_2}$ placed at 2082 cm^{-1} and

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† This treatment works very well in the chloroethanes, where an independent check is possible.[4]

Table 9 Harmonic local-mode calculations for the methyl group in $[\mathrm{TiEt(cp)Cl_2}]$

Group	ν_{obs}/cm^{-1}	σ_ν [a]	1 ε_ν [b]	2 ε_ν [b]	3 ε_ν [b]	4 ε_ν [b]	5 ε_ν [b]
$\mathrm{CH_3}$	2956.7 [c]	1	0.2	0.2	0.3	0.3	0.4
	2932.5 [c]	2	0.7	0.8	1.1	1.1	1.4
	2869.2 [c]	4	2.4	2.2	1.6	1.3	0.7
$\mathrm{CD_3}$	—	—	(2214.2)	(2216.4)	(2216.4)	(2218.6)	(2218.5)
	—	—	(2194.2)	(2193.1)	(2196.1)	(2195.0)	(2197.9)
	2088.0 [c]	5	−0.5	0.9	4.2	5.4	8.6
$\mathrm{CH^sD_2}$	2897.0	1	−0.2	−0.2	−0.2	−0.2	−0.3
	—	—	(2214.2)	(2216.4)	(2216.4)	(2218.6)	(2218.5)
	—	—	(2132.5)	(2130.0)	(2130.0)	(2127.6)	(2127.6)
$\mathrm{CH^aD_2}$	2931.8	1	−0.3	−0.4	−0.6	−0.6	−0.8
	—	—	(2200.5)	(2200.3)	(2202.3)	(2202.2)	(2204.2)
	—	—	(2120.1)	(2120.2)	(2117.9)	(2177.9)	(2115.6)
$\mathrm{H^aCH^a}$/°			106	108	108	110	110
$\mathrm{H^aCH^s}$/°			106	106	108	108	110
f_{a}			4.5933	4.5934	4.5941	4.5942	4.5950
f_{s}			4.7043	4.7047	4.7056	4.7061	4.7070
$f'_{\mathrm{a,a}}$			0.0162	0.0286	0.0297	0.0419	0.0482
$f'_{\mathrm{a,s}}$			0.0273	0.0279	0.0412	0.0418	0.0550
Σw.s.e.			0.63	0.70	1.51	2.16	4.32

[a] Uncertainties in wavenumbers. [b] $\varepsilon_\nu = \nu_{\mathrm{obs}} - \nu_{\mathrm{calc}}$; ν_{calc} in parentheses. [c] Corrected for Fermi resonance.

ν°_{av}CD calculated to be 2130 cm^{-1}, $\nu^{\circ}_{asym}CD_2$ is estimated at 2178 ± 5 cm^{-1}. We therefore provisionally assign the weak peak observed at 2169 cm^{-1} to $\nu_{asym}CD_2$, in resonance with the combination (1098 + 1081 = 2179 cm^{-1}) (A″).

The estimated separation $\nu^{\circ}_{asym}CD_2 - \nu^{\circ}_{sym}CD_2$ is therefore 2178 − 2082 = 96 ± 10 cm^{-1}, which leads to the unexpected conclusion that the methylene group is asymmetric, as discussed below.

HLM Calculations for the methylene group. The $\nu_{asym}CH_2 - \nu^{\circ}_{sym}CH_2$ separation in the titanium compound is about twice that in chloroethane (Table 10). The $\nu_{asym}CD_2 - \nu^{\circ}_{sym}CD_2$ separation in chloroethane is twice as much as the $\nu_{asym}CH_2 - \nu_{sym}CH_2$ separation, but in the titanium compound it is only 13% more than $\nu_{asym}CH_2 - \nu^{\circ}_{sym}CH_2$, albeit with an uncertainty of about 20%. Together, these two results cast doubt on the symmetry of the methylene group.

The difficulty is highlighted in a quantitative fashion by calculating the force constants *f* and *f′* required to reproduce the $\nu^{\circ}_{asym}CH_2$ and $\nu^{\circ}_{sym}CD_2$ frequencies, for various HCH angles, and comparing the values of $\nu^{\circ}_{asym}CD_2$ and $\nu^{\circ}_{sym}CD_2$, which then result, with the experimental frequencies. Table 11 shows the results for HCH angles from 104 to 114°. Values of *f′* compatible with those found in [TiMe(cp)Cl$_2$] appear only at the top end of the range, around 113°, and for these the $\nu^{\circ}_{asym}CD_2 - \nu^{\circ}_{asym}CD_2$ separation of 116 cm^{-1} is much greater than that deduced from the spectrum, and well outside the uncertainty imposed by the Fermi-resonance corrections. It is not possible to find a solution, for a CH$_2$ group with two equivalent CH bonds, which will reproduce the $\nu^{\circ}_{asym}CD_2 - \nu^{\circ}_{sym}CD_2$ separation with a realistic value for the interaction constant. The simplest explanation is that the methylene CH bonds are inequivalent and have different ν^{is}CH values.

Table 10 νCH and νCD data (in cm^{-1}) for the methylene groups[a] in EtCl and [TiEt(cp)Cl$_2$]

	EtCl[b]	[TiEt(cp)Cl$_2$]
$\nu_{asym}CH_2$	3004.7	2911.5
$\nu^{\circ}_{sym}CH_2$	≈2962	2826(3)
$\nu_{asym} - \nu^{\circ}_{sym}$	43	85(5)
ν_{av}CH	2983.4	2869(3)
$\nu^{\circ}_{asym}CD_2$	2258	[2178(5)][c]
$\nu^{\circ}_{sym}CD_2$	2171	2083(3)
$\nu^{\circ}_{asym} - \nu^{\circ}_{sym}$	87	96(10)
ν_{av}CD	2214.5	[2130(4)][d]
$\nu_{av}CH/\nu_{av}CD$	1.3472	1.347 15[e]

[a] Based on the partially deuteriated species CD$_3$CH$_2$ and CH$_3$CD$_2$. [b] Data from ref. 4. [c] Derived from ν_{av}CD and $\nu_{sym}CD_2$. [d] Derived from ν_{av}CH/1.347 15. [e] Assumed.

In part (*b*) of Table 11 we explore the range of isolated CH stretching frequencies and HCH angles which together reproduce the $\nu_{asym} - \nu_{sym}$ splittings of 85.2 and 96.0 cm^{-1} for the CH$_2$ and CD$_2$ groups respectively, as a function of the interaction force constant *f′*. Once the latter is fixed, then both the ν^{is}CH values and the HCH angle are determined. We choose values of *f′* of −0.01 and +0.01 as spanning the likely range of *f′* for the methyl group in [TiMe(cp)Cl$_2$] (see above), while that of 0.025 mdyn Å^{-1}, is similar to those found in [TiMeCl$_3$].[9] The HCH angles found using these interaction constants are in the range 106–108°, which is compatible with the angle of 107.5° observed in [TiMeCl$_3$], and a difference of 50–60 cm^{-1} is required in the two ν^{is}CH values.

A further calculation with $\nu_{asym}CH_2 - \nu^{\circ}_{sym}CH_2$ kept at 85.2 cm^{-1} but $\nu^{\circ}_{asym}CD_2 - \nu^{\circ}_{sym}CD_2$ increased to 101 cm^{-1} shows that the splitting ν^{is}CH (1) − ν^{is}CH (2) falls by about 6 cm^{-1} and the angle increases by 1.6°. The main factor determining the splitting is in fact the choice of the *f′* value. Our final choice of the two ν^{is}CH values is 2900(5) and 2847(5) cm^{-1}, implying a marked degree of asymmetry in the methylene group.

[Ti(CH$_2$CH$_3$)(cp)Cl$_2$]. The collection of bands in the νCH region is very close to being the sum of those in the [$^2H_2$] and [$^2H_3$] species. Small differences in frequencies are as likely to arise from variations in Fermi resonance as from coupling between the CH$_3$ and CH$_2$ stretching motions, the interaction force constants for which are very small.[26] The relative constancy of the $\delta_{asym}CH_3$, $\delta_{sym}CH_3$ and $\delta_{sym}CH_2$ frequencies has already been mentioned. There remain the modes ν_7, ν_8, ν_9, ν_{15}, ν_{16} and ν_{17} to be assigned. In CH$_3$CH$_2$Cl, ν_7 (1289 cm^{-1}) is primarily a wCH$_2$ motion which in the titanium compound will have a lower force constant, and must mix with CC motion. The very strong band at 1115 cm^{-1} is suitably placed. Bands ν_8 and ν_9 at 1073 and 973 cm^{-1} in CH$_3$CH$_2$Cl are a pair of coupled ρCH$_3$/νCC modes which should remain little changed in [Ti(CH$_2$CH$_3$)(cp)Cl$_2$]: the bands at 1075 and 934 cm^{-1} in the titanium compound are plausibly assigned to these modes. The weakband at 1199.5 cm^{-1}, if a fundamental, can only be due to ν_{15}, tCH$_2$, perhaps raised in frequency by coupling to ρCH$_3$ motion. A shoulder at 876 cm^{-1} could arise from ν_{16} and the weak band at 575 cm^{-1} is probably ν_{17}, a coupled ρCH$_3$/ρCH$_2$ mode.

Discussion

In Table 12, we list the predicted CH bond lengths, bond dissociation energies and HCH angles for the two compounds.

Table 11 Harmonic local-mode calculations for the methylene group in [TiEt(cp)Cl$_2$]

(*a*) Symmetrical CH$_2$ groups. Force constants (mdyn Å^{-1}) and HCH angles fitting $\nu^{\circ}_{asym}CH_2$ = 2911.5, $\nu^{\circ}_{sym}CH_2$ = 2826.3 cm^{-1}

HCH/°	104	106	108	110	112	114
f	4.5087	4.5088	4.5090	4.5092	4.5095	4.5099
f′	−0.0494	−0.0376	−0.0259	−0.0144	−0.0030	0.0082
$\nu_{asym}CD_2$*	2131.0	2133.3	2135.5	2137.7	2139.8	2141.9
$\nu_{sym}CD_2$*	2035.7	2033.3	2030.9	2028.6	2026.2	2023.8
Δν(CD$_2$)	95.3	100.0	104.6	109.1	113.6	118.1

(*b*) Asymmetric CH$_2$ group. ν^{is} values and HCH angles fitting Δν(CH$_2$) = 85.2 cm^{-1} for several values of *f′* and Δν(CD$_2$) = 96.0 or 101.0 cm^{-1}

	f′	−0.01	0.01	0.025
ΔνCD$_2$ = 96.0 cm^{-1}	ν^{is}CH(1)	2897	2902	2904
	ν^{is}CH(2)	2845	2840	2837
	HCH/°	105.75	106.9	107.8
ΔνCD$_2$ = 101.0 cm^{-1}	ν^{is}CH(1)	2894	2899	2902
	ν^{is}CH(2)	2849	2843	2840
	HCH/°	107.2	108.5	109.4

* Computed values × 1.011.

Table 12 Predicted CH bond lengths, bond angles and bond dissociation energies in $[TiR(cp)Cl_2]$ (R = Me or Et)

Compound	Group	$\nu^{is}CH^{a}/cm^{-1}$	r_0CH/Å	HCH/°	$D°_{298}$ (C–H)/kJ mol^{-1}
$[TiMe(cp)Cl_2]$	Methyl CH^a	2958	1.095_6	107.5(10) (H^aCH^a)	421
	CH^s	2918	1.100_0	108.9(10) (H^aCH^s)	406
$[TiEt(cp)Cl_2]$	Methyl CH^a	2942	1.097_2	110(2) (H^aCH^a)	415
	CH^s	2907	1.100_8	108(2) (H^aCH^s	402
	Methylene CH(1)[b]	2910	1.100_5	106.3(15)	403
	CH(2)[b]	2857	1.105_9		383

[a] ν_{obs} (CCl_4 solution) + 10 cm^{-1}. [b] Calculated frequencies.

Table 13 Isolated CH stretching wavenumbers[a] (cm^{-1}) in methyltitanium compounds

Compound	$\nu^{is}CH^a$	$\nu^{is}CH^s$	$\Delta\nu^{is}$	$\nu^{is}CH$ (av.)	Ref.
$[TiMe(cp)Cl_2]$	2958	2918	40	2945	This work
$[TiMe_2(cp)_2]$	2932	2915	17	2926	6
$[TiMe_3(cp)]$[b]	2938	2901	37	2926	14
$[TiMe_3(cp)]$[c]	2905	2948	−43	2919	14
$[TiMeCl_3]$	2952				9
$[TiMe_2Cl_2]$	2948				14

[a] Corrected to gas phase. [b] Crystal. [c] Matrix.

The CH bond lengths, r_0CH, are related to ν^{is}CH by equation (6)[27] and are accurate to at least 0.001 Å. The bond dissociation energies $D°_{298}$(CH) are obtained from equation (7).[12]

$$r_0\text{CH (Å)} = 1.3982 - 0.000\,102\,3\ \nu^{is}\text{CH (cm}^{-1}) \quad (6)$$

$$D°_{298}\text{CH (kJ mol}^{-1}) = 0.375\ \nu^{is}\text{CH (cm}^{-1}) - 688 \quad (7)$$

The experimental data used to derive equation (7) refer to small organic molecules rather than organometallic compounds and overall the relationship is less precise than that between ν^{is}CH and r_0CH. Uncertainties in the absolute values of $D°_{298}$(CH) may be of the order of 3-4 kJ mol^{-1}, but are consistent over the whole calibration, so that the *differences* between the CH bond dissociation energies, particularly for bonds within the same alkyl group, should be reliable for processes leading to radicals having conformations appropriate to the particular bond broken.

The ν^{is}CH frequencies upon which the $\nu^{is}CH - r_0CH$ relationship is based were all obtained from gas-phase measurements.[3] Typically, ν^{is}CH rises by ≈10 cm^{-1} from solution to the gas phase.[28] The ν^{is}CH frequencies quoted in Table 12 are therefore our experimental values (CCl_4 solution), plus 10 cm^{-1}, and the r_0CH values are notional 'gas phase' bond lengths. Isolated CH stretching frequency data for all the methyl titanium compounds for which this information is available are listed in Table 13.

The separation $\nu^{is}CH^a - \nu^{is}CH^s$ (40 cm^{-1}) observed in the methyl group in $[TiMe(cp)Cl_2]$ is comparable with the largest yet found in methylmetal compounds and correlates with a difference of 15 kJ mol^{-1} (≈4%) between the in-plane and out-of-plane CH bonds. Assuming a staggered conformation [Fig. 3(*a*)], the CH^s bond will be *trans* to the cyclopentadienyl ligand, and the CH^a ones *trans* to chlorine. In aliphatic systems, there is increasing evidence that β-substituent effects tend to act on *gauche* CH (or SiH) bonds, rather than *trans* ones,[29] suggesting that the CH^s bond in $[TiMe(cp)Cl_2]$ being *gauche* to two chlorine atoms should be similar to the CH bonds in $[TiMeCl_3]$ [Fig. 3(*b*)] whereas the CH^a bonds may be different, depending on the β-effect of the cyclopentadienyl ligand, about which we have as yet no information. In the event, the $\nu^{is}CH^a$ frequency is very close to ν^{is}CH in $[TiMeCl_3]$, whereas $\nu^{is}CH^s$ s markedly lower. Conceivably, this could be indicative of ı weak agostic[1,2] $CH^s \cdots Ti$ interaction, although other xplanations may also be possible.

The data for the other methyltitanium compounds listed in Table 13 present a confusing picture. In $[TiMe_2(cp)_2]$,[6] the CH^a bonds will be *gauche* to methyl and cyclopentadienyl [Fig. 3(*c*)]. Methyl substituents in aliphatic systems tend to have a modest weakening effect on the *gauche* β-CH bonds,[3] and the $\nu^{is}CH^a$ frequency of 2932 cm^{-1} in $[TiMe_2(cp)_2]$ would be compatible with such an effect. However, if we interpret the low value of $\nu^{is}CH^s$ (2915 cm^{-1}) in the same way, we have to conclude that the β-effect of the cyclopentadienyl ligand must be very much stronger than that of methyl. There is no such evidence in the spectrum of $[TiMe(cp)Cl_2]$ where

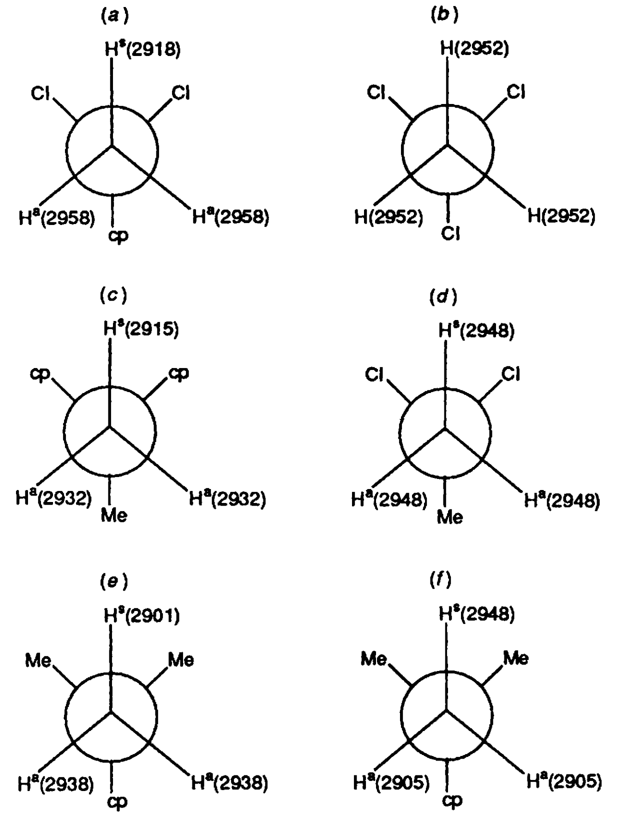

Fig. 3 Observed wavenumbers (cm^{-1}) for methyl CH bonds in (*a*) $[TiMe(cp)Cl_2]$, (*b*) $[TiMeCl_3]$, (*c*) $[TiMe_2(cp)_2]$, (*d*) $[TiMe_2Cl_2]$, (*e*) $[TiMe_3(cp)]$ (crystal) and (*f*) $[TiMe_3(cp)]$ (matrix)

Table 14 Isolated CH stretching wavenumbers (cm^{-1}) for [Ti(CD$_2$CHD$_2$)(cp)Cl$_2$],* CHD$_2$CD$_3$ and CHD$_2$CD$_2$X (X = F, Cl, Br or I)

Compound	ν^{is}CH^{a}	ν^{is}CH^{s}	$\Delta\nu^{is}$CH	ν^{is}CH (av.)	Ref.
[Ti(CD$_2$CHD$_2$)(cp)Cl$_2$]	2942	2907	35	2930	This work
CHD$_2$CD$_3$	2950				3
CHD$_2$CD$_2$F	2973	2957	16	2967	31
CHD$_2$CD$_2$Cl	2972	2945	27	2963	31
CHD$_2$CD$_2$Br	2971	2936	35	2959	31
CHD$_2$CD$_2$I	2968	2928	40	2954	31

* Bands in CCl$_4$ solution, + 10 cm^{-1}.

ν^{is}CH^{a}, *gauche* to cyclopentadienyl, is normal or even slightly high.

Further problems arise in the case of [TiMe$_2$Cl$_2$] [Fig. 3(*d*)][14] where only one ν^{is}CH band is observed, despite the very different β-substituent effects of methyl and chlorine in aliphatic systems. Finally, in the case of [TiMe$_3$(cp)] [Fig. 3(*e*) and (*f*)] the ν^{is}CH frequencies invert on change of phase, with ν^{is}CH^{a} > ν^{is}CH^{s} in the crystal, by 37 cm^{-1}, but ν^{is}CH^{s} > ν^{is}CH^{a} in a N$_2$ matrix, by 43 cm^{-1}. The origin of this inversion, or its relationship to the data for the other compounds, is far from obvious.

Overall, it is clear that substituent effects observed in relatively simple aliphatic systems cannot be extrapolated directly to the more complicated transition-metal compounds. Furthermore, there is no clear pattern even amongst the five methyltitanium compounds discussed here. It is necessary to bear in mind that these compounds are not necessarily directly comparable: the formal electron count for the titanium atom is eight for [TiMeCl$_3$] and [TiMe$_2$Cl$_2$], twelve for [TiMe(cp)Cl$_2$] and [TiMe$_3$(cp)] and sixteen for [TiMe$_2$(cp)$_2$]. Moreover, although all five compounds are formally tetrahedral, [TiMe(cp)Cl$_2$] and [TiMe$_3$(cp)] are perhaps better regarded as pseudo-octahedral, with the cyclopentadienyl ligand occupying three co-ordination sites, and [TiMe$_2$(cp)$_2$] by the same token would be eight-co-ordinate. There is no good *a priori* reason to expect all of them to behave in the same way. We can note, in passing, that [TiMe(cp)Cl$_2$] is the only one of these molecules in which a unique CH bond is in a position to interact with an appropriately oriented titanium orbital, and to this extent is perhaps the most likely compound to exhibit an agostic effect.

The *average* ν^{is}CH values for the various methyl titanium compounds show a progressive reduction as chlorine ligands are replaced by methyl or cyclopentadienyl, the latter two ligands appearing to have rather similar effects, as far as can be judged and bearing in mind the caveats mentioned above. The two very different sets of results for [TiMe$_3$(cp)], in the matrix and in the crystal, nevertheless yield very similar ν^{is}CH averages. In other series of methylmetal compounds [*e.g.* MMe$_2$ (M = Zn, Cd or Hg);[5] MMe$_4$ (M = C, Si, Ge, Sn or Pb);[5] [MMe(CO)$_3$] (M = Mn or Re)[8]] we have shown that ν^{is}CH is inversely related to the mean M–CH$_3$ bond energy, $D_{\text{M–CH}_3}$. Very roughly, a fall of 1 cm^{-1} in ν^{is}CH correlates with an increase of 4.2 ± 1.2 kJ mol^{-1} in $D_{\text{M–CH}_3}$. These results refer to isostructural compounds in which only the central metal atom is changed; we have no direct evidence to confirm that a similar relationship exists between ν^{is}CH and $D_{\text{M–CH}_3}$ for a given metal as the ligands in the co-ordination sphere are changed. Nevertheless it is not entirely unlikely that some such relationship will exist. If so, our results indicate that replacing the chlorine ligands in the [TiMeCl$_3$] with methyl or cyclopentadienyl leads to a measurable strengthening of the Ti–CH$_3$ bond.

Table 14 includes ν^{is}CH frequencies, bond length and bond energy data for [TiEt(cp)Cl$_2$], adjusted as before to notional 'gas-phase' values. Data for ethane and ethyl halides are also included in the Table. There is no evidence in the spectra to suggest the presence of more than one conformer of the ethyl group: we observe only one band for δ_{sym}CH$_3$ whereas compounds which contain two conformers (*i.e.* arising from rotations around the M–C bond) typically display a clearly split δ_{sym}CH$_3$ band, and two overtones.[30] As already discussed, the methyl group has well defined local C_s symmetry but there is no need to assume that this indicates, or derives from, overall C_s symmetry for the molecule; on the contrary, it is most unlikely that the methyl CH bonds experience significant γ-effects from groups beyond the titanium atom. We therefore draw no conclusions as to the *overall* symmetry of the molecule from our observations of the behaviour of the methyl group vibrations.

Comparison of the ν^{is}CH values for [Ti(CD$_2$CHD$_2$)(cp)Cl$_2$] with ν^{is}CH in ethane (2950 cm^{-1})[3] shows that the introduction of the β-titanium atom weakens all three methyl CH bonds, but particularly CH^{s}, which is *trans* to the titanium atom. Whether this is a general effect in ethylmetal systems, or one peculiar to titanium, remains to be seen. At the moment, our understanding of the *trans* and *gauche* effects of substituents is limited to the effects of halogen and methyl substitution in halogenoethanes and related molecules.[3,31]

The most striking feature of the [TiEt(cp)Cl$_2$] spectra, however, arises from the analysis of the stretching vibrations of the methylene group. It is clear that the νCH$_2$ and νCD$_2$ frequencies cannot be reconciled with a 'normal' methylene group containing two equivalent CH bonds. Our predicted ν^{is}CH values, even allowing for the inevitable uncertainties in the analysis, indicate a major difference in r_0CH between the two bonds; both are relatively weak and one of them (ν^{is}CH = 2857 cm^{-1}), is unusually so.

In a molecule with overall C_s symmetry, both methylene CH bonds would be *trans* to chlorine atoms and there would be no reason to expect them to differ from one another. By comparison with the CH^{a} bonds in [TiMe(cp)Cl$_2$], we would expect the ν^{is}CH values for the CH bonds in an unperturbed methylene group to be found up to ≈42 cm^{-1} lower, as a result of the usual α-effect of a substituent methyl group. The shifts required to produce the calculated ν^{is}CH frequencies of 2910 and 2857 cm^{-1} are 48 and 61 cm^{-1}, respectively. The former is only marginally outside the range expected for an α-Me effect, but the latter is substantially so. Given that the two methylene CH bonds are inequivalent, it is difficult to escape the conclusion that the ethyl ligand must be rotated around the Ti–CH$_2$ bond in such a way that one methylene CH bond interacts more strongly than the other with the metal atom. Such an interaction would also account for the observation of only one conformer of the compound. Alkyltitanium compounds have of course been a fertile source of postulated agostic interactions,[1,2,32,33] involving both α- and β-CH bonds. While not all of these have survived closer examination,[9,13–15] some certainly have, and the surprising differences between the methyl groups in [TiMe$_3$(cp)] in the matrix and in the crystal[14] provide us with a timely reminder of the complexity of alkyltitanium systems.

Finally, we note that if the methylene group is not in fact asymmetric, as we have inferred, the only other way in which we could account for the νCH$_2$ and νCD$_2$ frequencies would be by accepting a highly improbable stretch–stretch interaction constant f', or an HCH angle well outside the normally acceptable range, or both. Such a result would in itself be an indication of a major anomaly in the methylene group and would equally forcibly point to a strong interaction between the metal atom and the α-CH bonds. At this stage, we can only conclude that there are features of both the [TiMe(cp)Cl_2] and [TiEt(cp)Cl_2] spectra which can be interpreted in terms of a weak CH ··· Ti interaction involving the α-carbon atom, and that this effect appears to be stronger in the ethyl than in the methyl compound. For both compounds, the need for *ab initio* and neutron diffraction studies is obvious.

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