

Vibrational properties of ethyltitanium trichloride and its 1,2-bis(dimethylphosphino)ethane adduct: characterisation of isolated $\nu(\text{C-H})$ modes and implications for agostic bonding

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The IR spectra of normal and specifically deuteriated $[\text{CH}_3\text{CH}_2\text{TiCl}_3]$ show that coordination by $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ (dmpe) results in an unusually low stretching frequency for one of the $\beta\text{-C-H}$ bonds in the ethyltitanium fragment; the results are analysed for their relevance to the bonding in the β -agostic unit in the light of quantum chemical calculations.

Despite their potential significance,¹ so-called agostic interactions can be tormentingly difficult to pin down in transition-metal alkyls. Whilst the presence of $\text{M}\cdots\text{H-C}$ interactions ($\text{M} = \text{metal}$) may often be inferred from a distorted M-alkyl geometry, the true degree and nature of the effect are hard to ascertain. Diffraction with X-rays, if not with neutrons, and NMR and (particularly) vibrational spectroscopies have failed in most cases to afford clearcut results.

Vibrational studies of the coordinated alkyl group have mostly been impaired by the lack of any definitive analysis aimed at establishing the true natures of the various transitions. In principle, the C-H stretching modes should be a highly sensitive index to the bonding and geometry of the alkyl group: in practice, coupling with, or masking by, other modes, and notably $2 \times \delta_{\text{asym}}(\text{CH}_3)$, tends to cloud the picture. In an extensive study of small organic molecules, partial deuteration has been exploited to decouple C-H stretching fundamentals from other modes.² The 'isolated' C-H stretching modes [$\nu^{\text{is}}(\text{CH})$] thus identified provide an unusual insight into conformational, stereoelectronic and bonding effects, and prove to be an extremely sensitive measure of C-H bond strength. As part of a comprehensive, systematic enquiry into the nature of β -agostic interactions in transition-metal alkyls,³ we have investigated the IR spectra of the base-free molecule $[\text{EtTiCl}_3]$ **1** and its adduct **2** with $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ (dmpe), each incorporating either normal CH_3CH_2 or specifically deuteriated CHD_2CD_2 groups. Complex **2** has been deliberately chosen in view of its seminal rôle in relation to notions about β -agostic interactions, X-ray diffraction having identified a TiCH_2CH_3 fragment with a curiously tight TiCC angle (86°).⁴

The low volatility and thermal instability of $[\text{EtTiCl}_3]$ poses serious problems in the measurement and interpretation of the IR spectrum of the molecule in the gas phase. Notwithstanding these complications, we have obtained and assigned spectra for several isotopomers. The IR spectrum of the gaseous $[\text{CH}_3\text{CH}_2\text{TiCl}_3]$ molecule, **1**, [Fig. 1(a)] shows all the C-H stretching fundamentals to occur in the 'normal' region, *i.e.* $2800\text{--}3100\text{ cm}^{-1}$. The spectrum of the CHD_2CD_2 isotopomer, **1-h₁**, [Fig. 1(b)] shows just two proximal bands attributable to $\nu^{\text{is}}(\text{CH})$ modes and corresponding to conformers with the unique C-H bond disposed either out of or within the mirror plane of the C_s -symmetric molecule [$\text{C-H}''$ 2953 (A) or $\text{C-H}'$ 2927 cm^{-1} (B), respectively; Fig. 1(b), Scheme 1]. The spectra bear a close resemblance to those reported for $[(\eta\text{-C}_5\text{H}_5)\text{TiCl}_2\text{Et}]$ ⁵ and clearly imply a normal or an agostic

structure for **1**, in keeping with the findings of an electron diffraction study.³

By contrast, the IR spectrum of solid $[\text{CH}_3\text{CH}_2\text{TiCl}_3(\text{dmpe})]$ [Fig. 1(c)] exhibits, in addition to bands in the region $2800\text{--}3100\text{ cm}^{-1}$, a broad absorption centred at 2615 cm^{-1} (C). The spectrum of the CHD_2CD_2 isotopomer **2-h₁** [Fig. 1(d), Scheme 1] resembles that of **1-h₁** in containing just two features identifiable with $\nu^{\text{is}}(\text{CH})$ modes, but with frequencies of 2933 (D) and 2585 cm^{-1} (E) for the out-of-plane ($\text{C-H}''$) and in-plane

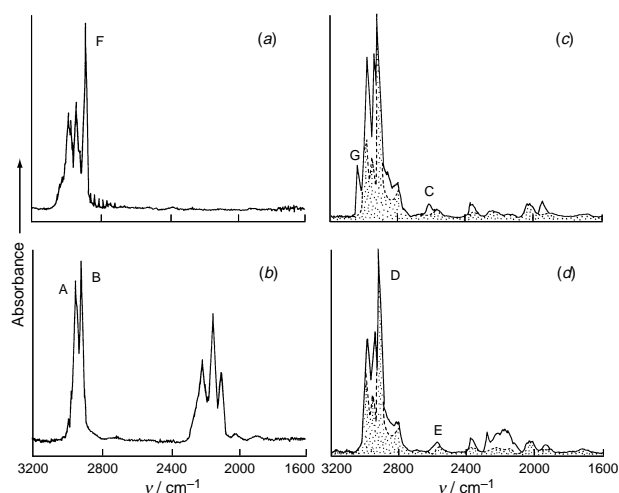
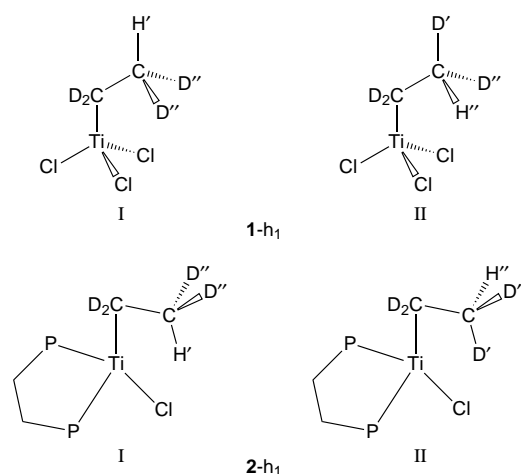


Fig. 1 IR spectra of **1** (a), **1-h₁** (b), **2** (c), and **2-h₁** (d) in the region corresponding to C-H(D) stretching vibrations. In (c) and (d) the spectrum of $[\text{TiCl}_4(\text{dmpe})]$ has been overlaid (stippled) to aid identification of the internal modes of the ethyl moiety.



Scheme 1

Table 1 Observed C–H(D) stretching frequencies (in cm⁻¹) for the ethyl groups of **1**, **1-h**₁ and **2-h**₁, and calculated scaled harmonic frequencies (in cm⁻¹) for **1**, **1-h**₁, **2a** and **2a-h**₁^a

Group	[CH ₃ CH ₂ TiCl ₃]			[CHD ₂ CD ₂ TiCl ₃]			[CH ₃ CH ₂ TiCl ₃ (diphosphine)]			[CHD ₂ CD ₂ TiCl ₃ (diphosphine)]		
	<i>v</i> _{obs}	<i>v</i> _{calc}	Assignment (local sym.)	<i>v</i> _{obs}	<i>v</i> _{calc}	Assignment (conformer) ^b	<i>v</i> _{obs} (2)	<i>v</i> _{calc} (2a)	Assignment (local sym.)	<i>v</i> _{obs} (2)	<i>v</i> _{calc} (2a)	Assignment (conformer) ^b
C _α H ₂	2933 ^c	2929	<i>v</i> _{as} (CH ₂ '') (a'')	2199(sh)	2192	<i>v</i> _{as} (CD ₂ '') (II)	3028(G) ^c	3028	<i>v</i> _{as} (CH ₂ '') (a'')	2275	2274	<i>v</i> _{as} (CD ₂ '') (I)
					2191	<i>v</i> _{as} (CD ₂ '') (I)				2273	2273	<i>v</i> _{as} (CD ₂ '') (II)
	2878(F) ^c	2879	<i>v</i> _s (CH ₂ '') (a')	2105	2112	<i>v</i> _s (CD ₂ '') (I)	2933	2960	<i>v</i> _s (CH ₂ '') (a')	2172	2169	<i>v</i> _s (CD ₂ '') (II) ^e
C _β H ₃	2980 ^d	2978	<i>v</i> _{as} (CH ₃) (a'')	2953(A) ^c	2953	<i>v</i> _{is} (CH'') (II)	2970	2964	<i>v</i> _{as} (CH ₂ '') (a'')	2933(D) ^c	2933	<i>v</i> _{is} (CH'') (II)
				2927(B) ^c	2927	<i>v</i> _{is} (CH') (I)						
	2963 ^d	2956	<i>v</i> _{as} (CH ₃) (a') ^e	2235(sh)	2230	<i>v</i> _{as} (CD ₂ '') (I)	ol ^f	2899	<i>v</i> _s (CH ₂ '') (a')	2225	2225	<i>v</i> _{as} (CD ₂ '') (I)
			2216	2217	<i>v</i> _{as} (CD'D'') (II) ^e				2172	2180	<i>v</i> (CD'') (II) ^e	
2878 ^d	2898	<i>v</i> _s (CH ₃) (a') ^e	2150	2147	<i>v</i> _s (CD ₂ '') (I)	2615(C)	2585	<i>v</i> (CH') (a')	2100	2125	<i>v</i> _s (CD ₂ '') (I)	
			2150	2139	<i>v</i> _s (CD'D'') (II) ^e				2585(E) ^c	2585	<i>v</i> _{is} (CH') (I)	
									1929	1907	<i>v</i> (CD') (II)	

^a Scale factors: [EtTiCl₃], methyl, CH'' 0.951, CH' 0.968; methylene, 0.971; [EtTiCl₃(H₂PCH₂CH₂PH₂)], methyl, CH'' 0.930, CH' 0.917; methylene, 0.953. The very small differences between the two CH'' bonds in both the methyl and methylene groups have been ignored. Calculated *v*(CD) values have been multiplied by 1.011 to offset anharmonicity. ^b Conformers specified by I and II as in Scheme 1. ^c Frequency used for scaling the DFT force field. ^d Likely to be affected by Fermi resonance. ^e These descriptions are approximate. ^f ol signifies overlap by features arising from the dmpe ligand.

(C–H') modes, respectively; the separation between them is an order of magnitude greater than that found for **1-h**₁. These observations point unmistakably to the presence of two chemically distinct types of C–H bond attached to the β-carbon atom of the ethyl ligand in **2** [*viz.* two terminal (C–H'') and one agostic (C–H')]. For the C–H' bond in **2-h**₁, *v*_{is}(CH) thus has a frequency comparable with those reported for the normal (coupled) *v*(CH) modes in other β-agostic complexes.³ To our knowledge, the *v*_{is}(CH) frequency of 2585 cm⁻¹ in **2-h**₁ is the first to be determined in a complex whose β-agostic structure has been verified by diffraction methods. It is remarkable for being some 200 cm⁻¹ lower than that of any *v*_{is}(CH) reported hitherto (*cf.* 2799 cm⁻¹ in NMe₃ where the C–H bonds are weakened through interaction with the antiperiplanar lone pair²).

Drawing on the empirical equations developed elsewhere^{2,6} leads from the values of *v*_{is}(CH) displayed by **2-h**₁ to the following estimates of spectroscopic bond length (*r*₀ in pm) and adiabatic bond dissociation enthalpy (*D*₀ in kJ mol⁻¹): *r*₀(C–H'') = 109.8, *D*₀(C–H'') = 410; *r*₀(C–H') = 113.4, *D*₀(C–H') = 280. At face value, therefore, the results imply that, as the β-CH₃ unit of the ethyl group approaches the Ti centre, the in-plane C–H' bond suffers an appreciable weakening, being 3.6 pm longer and having a dissociation enthalpy 130 kJ mol⁻¹ smaller than its out-of-plane (C–H'') counterparts.[†] However, there is no suggestion of significant chemical activation of the C–H' bond, nor of any significant degree of alkene hydride character to the ethyl unit on the evidence of ²H NMR measurements on samples of **2** in the presence of D₂, CD₄ and C₂D₄.

There is a second noteworthy feature of the IR spectra. Coordination of [EtTiCl₃] by dmpe results also in a significant increase in the frequencies of the *v*(CH) modes associated with the methylene portion of the ethyl ligand [from 2878 (F), 2933 cm⁻¹ in **1** to 2933, 3028 cm⁻¹ (G) in **2**]. A concomitant widening of the HCH angle can be inferred from the increase in the ratio *v*_{as}/*v*_s for the C_αH₂ unit. Complexation thus appears to give a methylene group with C–H bonds roughly 1.3 pm shorter and 20 kJ mol⁻¹ stronger than those in base-free [EtTiCl₃].⁷ Simultaneously the methylene ¹³C resonance of the solution species undergoes a substantial low-frequency shift, while ¹*J*(CH) increases from 134.3 to 147.3 Hz.^{1,3}

The interpretation of the IR spectra has been underpinned by density functional theory (DFT) calculations on [EtTiCl₃] and the model compound [EtTiCl₃(H₂PCH₂CH₂PH₂)] **2a**. Since optimisation yields equilibrium structures in good agreement

with those determined experimentally for **1** and **2**,^{3,4} replacement of the methyl groups in dmpe by hydrogen appears to have very little effect on the overall structure of the complex. Accordingly, the calculated (harmonic) frequencies of the EtTi group of **2a** may reasonably be expected, with due allowance for scaling, to approximate those determined by experiment for **2**. The results listed in Table 1 for the *v*(CH) and *v*(CD) modes of **1**, **2**, and **2a** bear out this expectation. Inspection of the calculated force field shows the normal mode characterising the C_β–H' stretching vibration to consist exclusively of a rectilinear motion almost perpendicular to the Ti–H directrix. Computational evidence indicates that the Ti–C_α bonding electrons are delocalised over both C_α and C_β atoms as well as over their appended H atoms, and that reduction of the TiCC valence angle allows the establishment of covalent bonding between Ti and C_β, and to a lesser extent, one of its H atoms.³ The spectroscopic evidence is fully consistent with such a model.

Footnotes and References

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† Against these quantitative estimates certain caveats need to be entered. Firstly, the empirical correlations between *v*_{is}(CH) and (*i*) bond length and (*ii*) bond enthalpy are founded on the assumptions of a C–H potential well whose curvature varies in a linear manner with the C–H distance and well depth, respectively. These conditions are likely to be met only for C–H bonds which are very similar in nature, with but small deviations from a 'norm'. Secondly, a low *v*_{is}(CH) frequency increases the likelihood of coupling of this mode, *e.g.* with the symmetric *v*(CD) mode of the terminal CHD₂ group (at *ca.* 2120 cm⁻¹), and so putting its vibrational isolation at risk.

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