INFRARED SPECTRA AND METHYL GROUP PROPERTIES IN DICYCLOPENTADIENYLDIMETHYL-TITANIUM(IV), -ZIRCONIUM(IV) AND -HAFNIUM(IV)

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Summary

Infrared spectra are reported for CH_3-, CD_3- and CHD_2-substituted Cp_2MMe_2 ($Cp = \eta^5$-C_5H_5, M = Ti, Zr, Hf) in CCl_4 solution. The isolated CH stretching frequencies, $\nu(^{is}CH)$, measured in the CHD_2 species are lower than any previously observed in methylmetal compounds and the methyl CH bonds in Cp_2HfMe_2 are predicted to be the longest and weakest such bonds yet to have been characterised by this method. The methyl groups in Cp_2ZrMe_2 and Cp_2HfMe_2 have all three CH bonds equal, but in Cp_2TiMe_2 each methyl group contains two strong CH bonds and one weak one. This may be the result of steric overcrowding effects around the relatively small titanium atom. The symmetric deformation $\delta_s(CH_3)$ rises with increasing atomic number of the metal atom, the reverse of the trend observed for methyl derivatives of Main Group elements.

Introduction

In earlier papers [1–4], we have shown that analysis of CH and CD stretching frequency data for CH_3-, CD_3- and CHD_2-substituted species of methylmetal compounds can yield much detailed information on methyl group geometry, on individual CH bond lengths and strengths, and on the existence or otherwise of barriers to internal rotation. In general, these results are derived from correlations of CH bond parameters with the 'isolated' CH stretching frequencies, $\nu(^{is}CH)$, observed in the CHD_2 species [5,6], from energy-factored force constant calculations [7] for the CH and CD stretching vibrations and from consideration of band profiles and of the effects of internal rotation energy barriers on the symmetries and activities of the vibrational modes [2,3]. A further empirical correlation with $\nu(^{is}CH)$ also appears to offer a promising method for the prediction of approximate M–CH_3 bond dissociation energies [1–4].

In extension of our earlier work on methyl-transition metal compounds in the manganese and chromium subgroups [$MeM(CO)_5$, M = Mn, Re] [3,4], [CpM-

$(CO)_3Me$, $Cp = \eta^5\text{-}C_5H_5$, $M = Cr$, Mo, W] [2], we now report the results of similar studies on the dicyclopentadienyldimethyl derivatives of the titanium group elements, Cp_2MMe_2 ($M = Ti$, Zr, Hf). Relevant previous work on these compounds includes a vibrational spectroscopic study below 600 cm^{-1} for the CH_3 species [8], crystal structure determinations [9] for Cp_2ZrMe_2 and Cp_2HfMe_2 which confirm the skeletal point group as C_{2v}, within the experimental error, and ^{13}C NMR data for Cp_2ZrMe_2 [10] indicating that the barrier to internal rotation of the methyl groups is greater than 6 kcal mol^{-1}.

Experimental

Preparative. The $(CH_3)_2$, $(CD_3)_2$ and $(CHD_2)_2$ species of the Cp_2MMe_2 compounds were obtained from the reactions of Cp_2MCl_2 ($M = Ti$, Zr, Hf) with the appropriate methyllithium in dry ether at $-78°C$ [11]. When the initial reaction was complete the ether was removed at room temperature and the resulting solid extracted with dry pentane. The desired products crystallised from the concentrated pentane extracts on standing overnight at $-78°C$. The zirconium and hafnium compounds were finally purified by sublimation in vacuo; the thermally less stable titanium compound was used without further purification. All operations were conducted in a dry nitrogen atmosphere, or on a vacuum line.

Spectroscopic measurements. Infrared spectra were recorded using a Nicolet 7199 FTIR spectrophotometer at a resolution of 1 cm^{-1}. All samples were run in dry CCl_4 solution (to avoid interferences in the CH stretching region) at various concentrations in a 0.5 mm cell. These solutions were opaque between 700 and 810 cm^{-1}. Traces of impurity in the zirconium and hafnium compounds probably arise from small amounts of hydrolysis products [11]. The spectra of the thermally unstable titanium compounds were recorded with minimum delay using solutions freshly prepared from newly crystallised material, but even so, invariably showed evidence of appreciable amounts of chemical and/or isotopic impurity (see discussion section below).

Results and Discussion

The IR spectra of the Cp_2MMe_2 compounds are illustrated in Figs. 1–3. In view of the reactivity of the compounds and the difficulty of obtaining rigorously pure specimens [9,11] and preserving them throughout the spectroscopic measurements we have made as complete an assignment as possible of the cyclopentadienyl as well as the methyl group vibrations, over the experimental frequency range (4000–810, 700–550 cm^{-1}), in order to distinguish genuine vibrations of the Cp_2MMe_2 species from the impurity bands which inevitably appear in some samples. Methyl group frequencies are listed in Table 1, and those ascribed to the cyclopentadienyl groups, in Table 2.

Cp_2HfMe_2. The pattern of the methyl CH_3 stretching bands is normal for an undistorted C_{3v} methyl group (Fig. 1a) with a slightly broadened $\nu_{as}(CH_3)$ band at 2918 cm^{-1} and the usual Fermi resonating pair associated with $\nu_s(CH_3)$ and $2\delta_{as}(CH_3)$ at 2867 and 2787 cm^{-1}. A fourth band at 2809 cm^{-1} is likely to be due to a $2\delta_{as}(CH_3)$ level with effective E rather than A_1 character. Neighbouring bands at 3104 and 2731 cm^{-1} clearly arise from the cyclopentadienyl groups and represent $\nu(CH(C_5H_5))$ and overtone (2×1368) modes, respectively.

TABLE 1

METHYL FREQUENCIES OBSERVED AND ANALYSED IN Cp_2MMe_2 COMPLEXES (cm^{-1})

		Cp_2TiMe_2		Cp_2ZrMe_2		Cp_2HfMe_2	
		obs.	calc.[a]	obs.	calc.[a]	obs.	calc.[a]
CH_3	ν_{as}	2953 / 2940	2951.6 / 2940.5	2924	2923.9	2918	2917.9
	ν_s	2882		2864		2867	
	ν_s^0(est.)[b]	(2855)	2852.2	(2838)	2824.5	(2840)	2825.0
	$2\delta_{as}(E)$[b]					2809	
	$2\delta_{as}$	2801		2778		2787	
	$2\delta_{as}^0$(est.)[b]	(2828)		(2804)		(2814)	
	δ_{as}	1419		1407		1412	
	δ_s	1119		1121		1144	
	ρ	554		624		635	
	$\Sigma\nu(CH_3)$[c]	8748		8686		8676	
CHD_2	ν^{is}	2922 / 2905	2923.7 / 2906.2	2894	2894.1	2890	2889.9
	$\nu_{as}(CD_2)$	2211	2210.9	2184	2189.3	2183	2184.8
	$\nu_s(CD_2)$	2116	2114.1	2106	2098.0	2105	2097.3
	$\delta(CH)$			1098		1106	
	$\delta(CD_2)$			942		952	
	$\Sigma\nu CH_3$[d]	8749		8682		8670	
CD_3	ν_{as}	2212 / 2200	2210.9 / 2202.3	2186.5	2189.3	2183	2184.8
	ν_s / $2\delta_{as}$	2099 / 2047	2076.0	2087 / 2046 / 2034	2057.2	2090 / 2036.5	2058.1
	δ_s			882.5		899	
	f[e]		4.674 / 4.617		4.578		4.556
	f'[e]		0.003			−0.009	−0.003
	HCH angle (assumed) (°)		106.3			105.6	105.4

[a] From 3×3 refinement. Output $\nu(CD)$ values ×1.011 to offset anharmonicity. Some frequencies predicted for the CH_2D group are 2923.9, 2861.3, 2141.7 cm^{-1} (Zr); 2917.9, 2859.2, 2139.2 cm^{-1} (Hf). [b] See text. [c] $\nu_{as}(1) + \nu_{as}(2) + \nu_s^0$(Ti); $2\nu_{as} + \nu_s^0$(Zr, Hf). [d] $2\nu(^{is}CH)(1) + \nu(^{is}CH)(2)$(Ti); $3\nu(^{is}CH)$(Zr, Hf). [e] mdyn $Å^{-1}$.

Bands at 1412 and 1144 cm^{-1} are readily assigned to $\delta_{as}(CH_3)$ and $\delta_s(CH_3)$, respectively. A weak band which appears at 635 cm^{-1} in the CH_3 species but disappears on deuteration is likely to be a $\rho(CH_3)$ mode.

In the CD_3 species (Fig. 1b) weak bands at $\sim$ 2960 and 2928 cm^{-1} are evidence of a small amount of a CH impurity. This does not arise from a CHD_2 group derived from CD_3 by proton exchange as the strong $\nu(^{is}CH)$ band in the CHD_2 compound is found at 2890 cm^{-1} (Fig. 1c). The same impurity is probably also present in the CHD_2 compound (weak shoulder $\sim$ 2961 cm^{-1}). We have observed

TABLE 2

FREQUENCIES ASSIGNED TO CYCLOPENTADIENYL GROUPS IN Cp_2MMe_2 SPECTRA

Cp_2TiMe_2	Cp_2ZrMe_2	Cp_2HfMe_2	Assignment [a]
3954w	3949mw	3953	
3942sh	3938sh	3941sh	
	3400vw, bd	3400vw, vbd	
3110mw	3104m	3104mw	ν(CH)(Cp)
		2960w	? (impurity?)
2739w	2729mw	2731w	2×1368
		2545vw	$1098 + 1444$?
2513vw	2506w	2507vw	$1068 + 1444$
2438vvw	2431w	2434vw	$1068 + 1368$
	2355vw	2360vw	$1098 + 1261$?
2332vw			
2288w	2280w	2280w	$1261 + 1017$?
	2260vw		
	2082mw	2084w, sp	$1068 + 1017$
1982vw	1965vw	1970vw	$1068 + 903$
1914vw	1909vw	1913vw	$\begin{cases} 1068 + 815 \\ 1017 + 903 \end{cases}$
1827mw, bd	1804m	1808mw, bd	$1018 + 792$
1734m, bd	1707ms, bd	1714m, bd	$903 + 812$
1637m, bd	1615ms, bd	1621m, bd	2×812
1448s	1443vs	1444s	ν(CC), E_1
1373w	1367w	1368w	ν(CC), E_2
1259w	1261w	1261w	δ_{ip}(CH), A_2
		1246vw	?
1132vw	1126sh	1128vw	ν(CC), A_1
	1098vw	1098vw	?
1069w	1067w	1068w	δ_{op}(CH), E_2
1018vs, as	1016vs	1017vs	δ_{ip}(CH), E_1
	958w	955w	
914w	904w	903w	δ_{ip}(CC), E_2
845sh		845sh	
b	b	825s	δ_{op}(CH), E_1
b	b	812vs	δ_{op}(CH), A_1
703vw	685w	691vw	
605vw	614w	616vw	

[a] Frequencies refer to Hf compound, assignments for C_{5v} local symmetry. [b] Obscured by solvent absorption.

similar weak absorptions near 2960 cm^{-1} in a number of other CD_3-substituted cyclopentadienylmethylmetal compounds [e.g. $CpMo(CO)_3CD_3$ (2b), $Cp_2Zr(CD_3)_2$ (see below)] with little or no frequency variation between compounds. The bands are very weak, or entirely missing, in the most stable compounds [e.g. $CpW(CO)_3CD_3$ (2), $CpFe(CO)_2CD_3$ (12)]. We conclude that a chemical impurity, rather than an isotopic one, must be responsible.

The ν(CD_3) fundamentals are associated with three bands in the CD_3 species at 2183 cm^{-1} (ν_{as}(CD_3)), 2090 and 2036.5 cm^{-1} (ν_s(CD_3)/$2\delta_{as}$(CD_3)), and the ν(CD_2) fundamentals in the CHD_2 species with frequencies of 2183 (ν_{as}(CD_2)) and 2105 cm^{-1} (ν_s(CD_2)). A shoulder at 2084 cm^{-1} on the 2105 cm^{-1} band is probably a C_5H_5-derived band seen more clearly in the spectrum of the CH_3 species (Table 2).
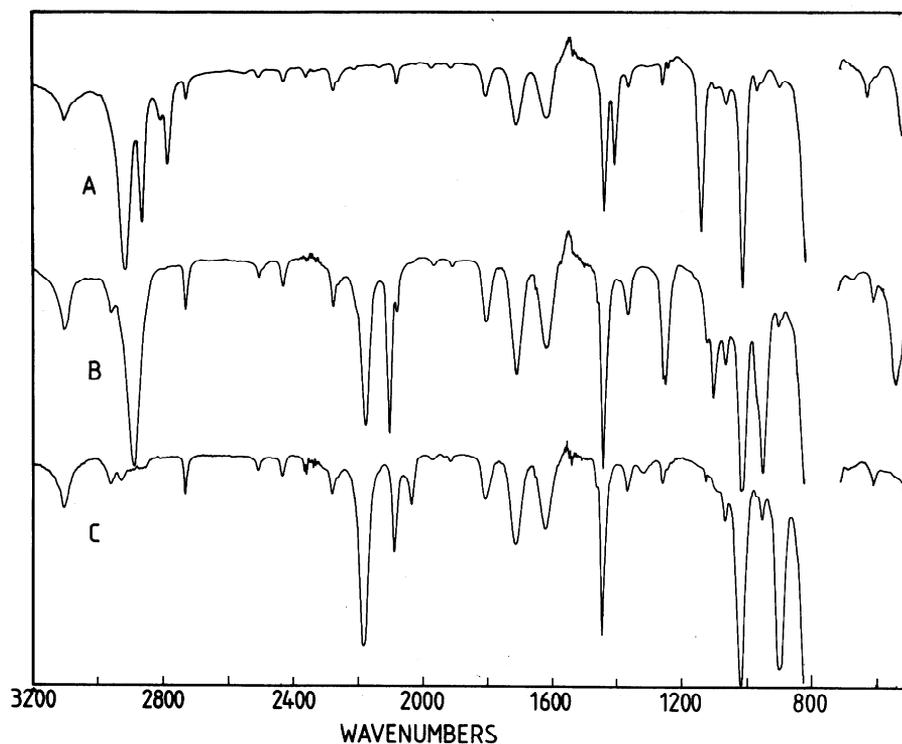
Fig. 1. Infrared spectra in CCl_4 solution of (A) $Cp_2Hf(CH_3)_2$, (B) $Cp_2Hf(CHD_2)_2$, (C) $Cp_2Hf(CD_3)_2$. (Strong solvent absorptions occur near 1560 and 1250 cm^{-1}).

There is no evidence of splitting either in the $\nu(^{is}CH)$ band at 2890 cm^{-1} or the $\nu_{as}(CD_3)$ band at 2183 cm^{-1} and so no variation in CH stretching force constant with bond orientation can be detected.

At lower frequencies in the CD_3 spectrum, a strong band at 899 cm^{-1} is readily assigned to $\delta_s(CD_3)$, yielding an acceptable CH_3/CD_3 frequency ratio of 1.273. The $\delta_{as}(CD_3)$ band must be submerged beneath the strong cyclopentadienyl band at 1017 cm^{-1}.

In the CHD_2 compound, bands at 1106 and 952 cm^{-1} are plausibly assigned to $\delta(CH)$ and $\delta(CD_2)$ modes, respectively. A medium intensity band at 1253 cm^{-1} has no counterpart in the CD_3 or CH_3 species but an apparently corresponding band is seen in $Cp_2Zr(CD_3)_2$. Assignment to a CHD_2 mode therefore seems unrealistic. The A_2 cyclopentadienyl in-plane CH deformation mode is expected near this frequency, but would normally be weak. An appropriate band appears at 1261 cm^{-1} in $Cp_2Hf(CH_3)_2$ (see below). It therefore appears to be necessary to attribute the 1253 cm^{-1} band in $Cp_2Hf(CHD_2)_2$ to a chemical impurity, even though there is little other evidence of impurity in this sample. There is a strong underlying solvent absorption near 1250 cm^{-1} which may affect intensity measurements in this part of the spectrum.

The Fermi resonance shift in the bending overtone $2\delta_{as}$ is calculated to be 27 cm^{-1}, on the assumption that $2 \times \delta_{as} - 2\delta_{as}° = 10$ cm^{-1}, where $2\delta_{as}°$ is the unperturbed overtone frequency. This in turn yields an unperturbed symmetric stretching

frequency, $\nu_s(^0CH_3)$, of 2855 cm^{-1}. The sum rule check, using this frequency, is very satisfactory ($\Sigma_3\nu(CH_3) - \Sigma_3\nu(^{is}CH) = 6$ cm^{-1}) (Table 1). The parameters and frequencies calculated in a 3×3 force constant refinement (i.e. for CH and CD stretching modes only) are also shown in the Table. The assumed HCH angle of 105.4° is taken from the $\nu(^{is}CH)$–HCH angle correlation [5], the observed $\nu(^{is}CH)$ solution frequency of 2890 cm^{-1} being increased by 10 cm^{-1} to allow for the usual solution-gas frequency shift and to give a hypothetical gasphase frequency of 2900 cm^{-1} for the purpose of the correlation. The low HCH angle stems from the low $\nu(^{is}CH)$ frequency and is also consistent with the $\nu_{as}(CH_3)/\nu_{as}(CD_3)$ frequency ratio. The very small value of the stretch-stretch interaction force constant f' (-0.003 mdyn Å^{-1}) is similar to those found in the CpM(CO)$_3$Me compounds [2].

The assignments for the cyclopentadienyl modes draw on previous work on ferrocene [13–18], Cp$_3$ZrH and Cp$_3$HfH [19] and various cyclopentadienylmetal compounds [2,20,21]. The observation of a weak band near 1370 cm^{-1}, with a probable overtone at 2730 cm^{-1}, in all three compounds (Ti, Zr, Hf), leads us to conclude that this must represent the E_2 ring stretching fundamental, in agreement with many workers on ferrocene [13–17] but not with the earlier major study of Lippincott and Nelson, who use the analogy with benzene to assign this vibration at 1560 cm^{-1} [18]. The very weak sharp band at 1128 cm^{-1} is certainly the corresponding A_1 mode.

If the medium intensity bands which appear near 1250 cm^{-1} in certain samples are accepted as arising from chemical impurity, the very weak bands which occur consistently at 1259–1261 cm^{-1} are obvious candidates for assignment to the A_2 $\delta_{ip}(CH)$ mode. An additional very weak band is seen at 1246 cm^{-1} in Cp$_2$Hf(CH$_3$)$_2$, but this has no detectable counterparts in Cp$_2$ZrMe$_2$ or Cp$_2$TiMe$_2$ and is less likely to be a fundamental mode.

The bands at 1068 and 1017 cm^{-1} are readily assigned to $\delta_{0p}(CH)(E_2)$ and $\delta_{ip}(CH)(E_1)$ modes, respectively. The weak band at 903 cm^{-1} probably represents the E_2 in-plane ring deformation. The exact frequencies of the E_1 and A_1 $\delta_{0p}(CH)$ bands at ~ 825 and 812 cm^{-1} are uncertain because of the onset of strong solvent absorption at this point.

The weak band seen at 616 cm^{-1} in the CH$_3$ compound has counterparts at 616 and 618 cm^{-1}, respectively, in the CD$_3$ and CHD$_2$ species. The latter two bands could conceivably be assigned to methyl rocking modes shifted from the 635 cm^{-1} frequency in the CH$_3$ compound. However the deuteration shift, on a methyl rock or a metal-methyl stretch, should be progressive in the order CH$_3$ > CHD$_2$ > CD$_3$; as it is not, and as absorption occurs at essentially the same frequency in all three species, we assign it to a cyclopentadienyl rather than a methyl vibration. Several authors [15–18] place the out-of-plane ring deformation modes in ferrocene near 600 cm^{-1} (ν_{28}, ν_{34}) but these have more recently been reassigned at 825 and 785 cm^{-1} [13]. The possibility that the bands near 616 cm^{-1} in the hafnium compounds are due to combinations or overtones cannot be excluded.

Cp$_2$ZrMe$_2$. The infrared spectrum of the CH$_3$ species (Fig. 2a) is very similar to that of the hafnium compound, except for an additional medium band at 1195 cm^{-1} and a few very weak bands attributed to chemical impurity.

The $\delta_{as}(CH_3)$ frequency (1407 cm^{-1}) is slightly lower than that in the hafnium compound (1412 cm^{-1}), leading to small decreases in $2\delta_{as}(CH_3)$ and $\nu_s(CH_3)$, through the usual Fermi resonance effects. The frequency of $\delta_s(CH_3)$ falls more
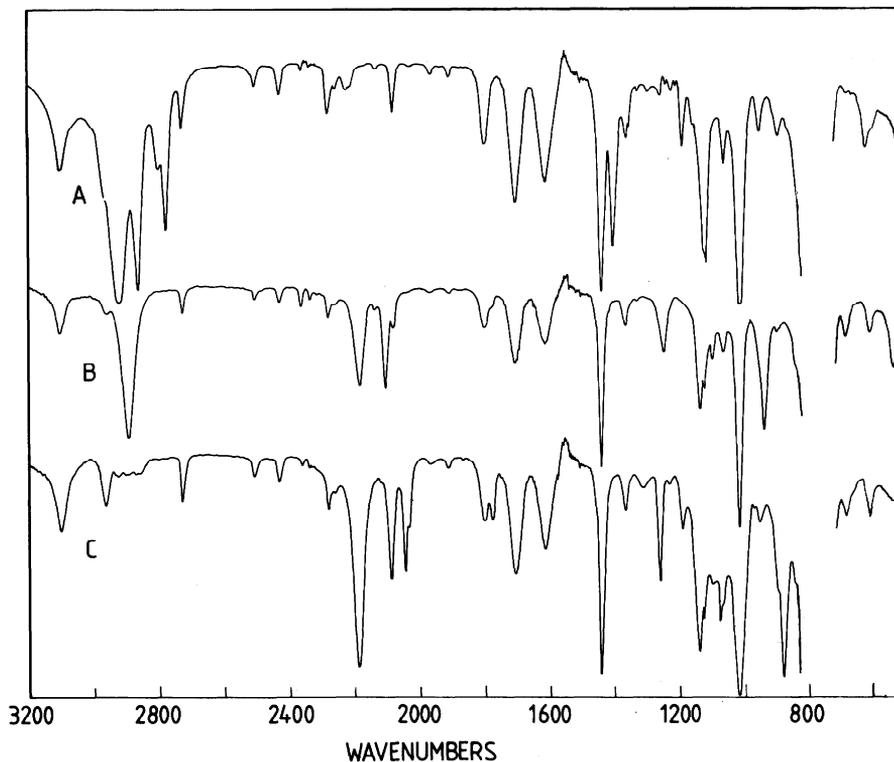
Fig. 2. Infrared spectra in CCl_4 solution of (A) $Cp_2Zr(CH_3)_2$, (B) $Cp_2Zr(CHD_2)_2$, (C) $Cp_2Zr(CD_3)_2$.

noticeably, from 1144 cm^{-1} (Hf) to 1121 cm^{-1} (Zr). The weak band at 624 cm^{-1} with a shoulder at ~610 cm^{-1}, probably arises from a $\rho(CH_3)$ mode comparable with the Hf mode at 635 cm^{-1}, the shoulder (which is seen clearly resolved in the spectra of the CD_3 and CHD_2 species at 614 cm^{-1}) being once again attributed to a cyclopentadienyl vibration.

The CD_3-substituted zirconium compound (Fig. 2c) appeared to contain somewhat more CH impurity than the hafnium compound, judging from the intensity of the band at 2963 cm^{-1}. Other extra bands at 1777, 1262, 1141 and possibly 687 cm^{-1} suggest that traces of more than one chemical impurity may be present. The shoulder at 1126 cm^{-1}, however, is seen in all three zirconium compounds and is certainly due to the A_1 ring stretching mode of the cyclopentadienyl groups.

The $\nu(CD_3)$ region of $Cp_2Zr(CD_3)_2$ is again quite free of any CHD_2 or CH_2D bands, and $\nu_{as}(CD_3)$ and a Fermi resonating $\nu_s(CD_3)/2\delta_{as}(CD_3)$ pair are readily assigned (Table 1). The $\delta_{as}(CD_3)$ mode is obviously overlapped by the cyclopentadienyl band at 1016 cm^{-1}, and $\delta_s(CD_3)$ is conspicuous at 883 cm^{-1} (CH_3/CD_3 ratio 1.27).

The CHD_2-zirconium compound (Fig. 2b) appears to be almost as isotopically pure as $Cp_2Hf(CHD_2)_2$, with a single $\nu(^{is}CH)$ band at 2893.8 cm^{-1}, an impurity shoulder at 2962 cm^{-1}, and just a trace of a $\nu(^{is}CD)$ band, arising from a CH_2D group, at 2139 cm^{-1} (the frequency predicted from the 3 × 3 refinement is 2142 cm^{-1}). Again there is no evidence of CH stretching force constant variation within
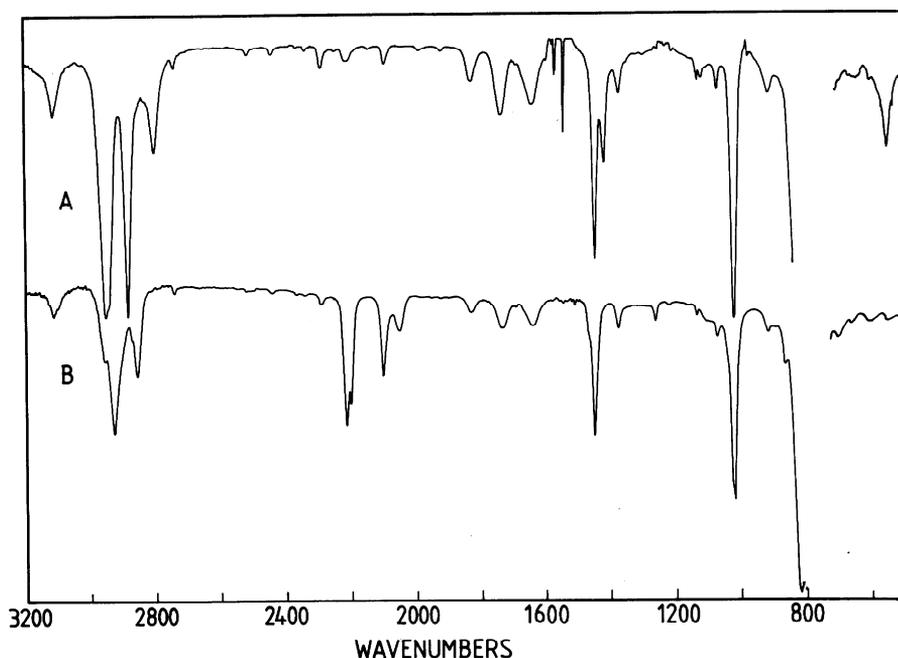
Fig. 3. Infrared spectra in CCl_4 solution of (A) $Cp_2Ti(CH_3)_2$, (B) $Cp_2Ti(CD_3)_2$.

the methyl group. Likely bending modes of the CHD_2 group occur at 1098 cm^{-1} ($\delta(CH)$) and 942 cm^{-1} ($\delta(CD_2)$): like the CH_3 and CD_3 bending modes, these are at somewhat lower frequencies than the corresponding vibrations in the hafnium compounds. The cyclopentadienyl frequencies listed in Table 2 are in general very like those in the hafnium compound.

Cp$_2$TiMe$_2$. The spectrum of $Cp_2Ti(CH_3)_2$ showed no detectable evidence of chemical impurity (Fig. 3a). The $\nu_{as}(CH_3)$ band at 2953 cm^{-1} is substantially broader than $\nu_s(CH_3)$ (2882 cm^{-1}) and is definitely asymmetric in shape, suggesting the presence of a weaker lower frequency component. The $\delta_{as}(CH_3)$ frequency at 1419 cm^{-1} is higher than in the hafnium or zirconium compounds, and only a weak band at 1119 cm^{-1} is available for assignment to $\delta_s(CH_3)$. The close correspondence between this and the $\delta_s(CH_3)$ frequency in $Cp_2Zr(CH_3)_2$ (1121 cm^{-1}) is repeated in the chromium group compounds [2], where $\delta_s(CH_3)$ occurs at 1167 cm^{-1} in $CpCr(CO)_3CH_3$ and 1168 cm^{-1} in $CpMo(CO)_3CH_3$ (see also Table 4).

The band at 554 cm^{-1} in our CCl_4 solution spectrum is evidently the same as that found at 557 cm^{-1} in a Nujol mull [8], and since it is clearly absent in the $Cp_2Ti(CD_3)_2$ spectrum (Fig. 3b), must be due to a methyl rocking mode. Since this is well below the $\rho(CH_3)$ bands observed in the zirconium and hafnium compounds, at 624 and 635 cm^{-1} respectively, it seems possible that the latter will possess additional unobserved rocking frequencies below 550 cm^{-1}, and that the titanium compound has another about 650 cm^{-1}. It would be quite normal for a considerable spread of methyl rocking frequencies to be found in any given compound.

The spectrum of $Cp_2Ti(CD_3)_2$ below 2000 cm^{-1} (Fig. 3b) is very similar to that of the CH_3 species, lacking only the bands at 1419, 1120 and 553 cm^{-1}, and having
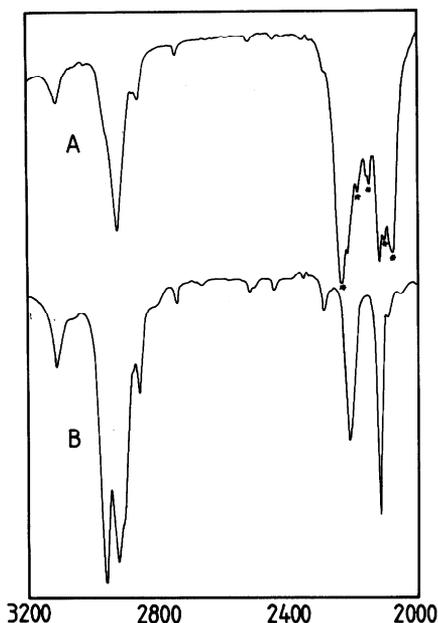
Fig. 4. Infrared spectra in CCl_4 solution of $Cp_2Ti(CHD_2)_2$, (A) prepared in $Et_2O\text{-}d_{10}$, with $\nu(CD)$ bands (*) from the latter, (B) prepared in $Et_2O\text{-}h_{10}$. (InSb detector, spectrum below 2000 cm^{-1} not recorded.)

an additional weak band at 1261 cm^{-1} and a very weak shoulder at 860 cm^{-1}. However the presence of a substantial amount of CH impurity is indicated by the bands near 2900 cm^{-1}, with intensities suggesting an isotopic abundance of about 35% hydrogen. Even with rapid sampling handling and spectroscopic measurement, it did not appear to be possible to improve on this degree of isotopic purity in carbon tetrachloride solution at room temperature. The strongest $\nu(CH)$ band, at 2925 cm^{-1}, could indeed derive from a CHD_2 group, as the best CHD_2 spectrum (Fig. 4a) shows a band centred at 2922 cm^{-1}. However, given the observed $\nu(CH)$ intensity, we would then expect also to observe the $\nu_s(CD_2)$ mode of the CHD_2 group at 2116 cm^{-1}, but this is definitely not present in the experimental $Cp_2Ti(CD_3)_2$ spectrum. Instead, we observe a split $\nu_{as}(CD_3)$ band (2212, 2200 cm^{-1}) and a normal $\nu_s(CD_3)/2\delta_{as}(CD_3)$ pair at 2099 and 2047 cm^{-1}. These $\nu(CD_3)$ bands are unchanged even in samples with much higher levels of CH impurity (indicated by more intense $\nu(CH)$ bands near 2900 cm^{-1}). We therefore again conclude that the $\nu(CH)$ bands must arise from a chemical impurity and not from internal exchange reactions involving the CD_3 group.

In order to test the possibility of interference from the solvent used in the preparative reaction, samples of $Cp_2Ti(CH_3)_3$ and $Cp_2Ti(CD_3)_2$ were prepared in diethyl ether-d_{10}. The CH_3 compound so prepared contained no $\nu(CD)$ bands and the CD_3 compound again had a high proportion of CH impurity. Exchange with the solvent therefore appears to be eliminated and the $\nu(CH)$ impurity bands must presumably arise from thermal decomposition products.

Samples of $Cp_2Ti(CHD_2)_2$ prepared in diethyl ether-h_{10} all showed evidence of substantial amounts of CH impurity in the form of $\nu(CH)$ bands of variable intensity at 2963 and 2855 cm^{-1}. Once again the $\nu(CD)$ region is simple in all cases,

TABLE 3

$\nu(^{is}CH)$ VALUES AND PREDICTIONS OF $r_0(CH)$, HCH ANGLE AND $D(C-H)$

	$\nu(^{is}CH)$ (cm^{-1})	$r_0(CH)$ (Å)	HCH (°)	$D^0(C-H)298$ (kcal mol^{-1})
Cp$_2$TiMe$_2$	2932 [a]	1.098$_3$	106.7 [b]	98.1
	2915 [a]	1.100$_3$		96.6
Cp$_2$ZrMe$_2$	2904 [a]	1.101$_1$	105.6	95.6
Cp$_2$HfMe$_2$	2900 [a]	1.101$_5$	105.4	95.3
CpCr(CO)$_3$Me [c]	2976 [a]	1.093$_8$	108.6 [b]	101.8
	2963 [a]	1095$_1$		100.7
CpW(CO)$_3$Me [c]	2966 [a]	1094$_8$	107.8 [b]	101.1
	2943 [a]	1.097$_1$		99.0
MeMn(CO)$_5$ [d]	2955	1.095$_9$	108.0	100.0
MeRe(CO)$_5$ [d]	2935	1.098$_0$	107.1	99.3

[a] Solution frequencies + 10 cm^{-1}. [b] Average values. [c] Ref. 2. [d] Ref. 3.

with just the two expected bands at 2211 ($\nu_{as}(CD_2)$) and 2116 cm^{-1} ($\nu_s(CD_2)$) (Fig. 4b). The CH impurity bands are greatly reduced in samples prepared in deuterated ether (Fig. 4a). A band at 2922 cm^{-1}, with a shoulder at 2905 cm^{-1}, is common to all of the samples and is the predominant feature of the spectrum of the material prepared in diethyl ether-d_{10}. We are confident that this represents the $\nu(^{is}CH)$ band of the genuine CHD$_2$ compound. The 3 × 3 refinement (Table 1) converges successfully using these frequencies and confirms that the chosen $\nu(CH)$ and the $\nu(CD)$ frequencies are compatible with each other.

The evidence for two types of CH bond in the methyl group is then good: the relative intensities suggest that two of these are strong and one weak and this assumption is confirmed by the sum rule calculation (Table 1).

Frequencies associated with the cyclopentadienyl group are listed in Table 2 and need no further comment.

Chemical significance. Estimates of methyl CH bond lengths, bond dissociation energies and HCH angles in Cp$_2$TiMe$_2$, Cp$_2$ZrMe$_2$ and Cp$_2$HfMe$_2$ are listed in Table 3. The CH bond parameters are derived from the usual correlations [5,6] of $\nu(^{is}CH)$ with $r_0(CH)$, $D(C-H)$ and HCH angle, the observed $\nu(^{is}CH)$ solution frequencies being increased by 10 cm^{-1} in each case to take account of the probable shift from solution to the gas phase. Data for other methyl-transition metal compounds are included in Table 3.

The $\nu(^{is}CH)$ frequencies in the titanium group compounds fall from an average value of 2916 cm^{-1} in Cp$_2$TiMe$_2$ to 2890 cm^{-1} in Cp$_2$HfMe$_2$, another example of the general tendency [2–4] for CH bonds in methyl-transition metal compounds to become progressively longer and weaker down each group. The difference of 26 cm^{-1} between the titanium and hafnium frequencies may be compared with 16 cm^{-1} between CpCr(CO)$_3$Me and CpW(CO)$_3$Me [2], or 20 cm^{-1} between MeMn(CO)$_5$ and MeRe(CO)$_5$ [3,4]. The weakening effect on the CH bonds is thus most clearly evident in the Cp$_2$TiMe$_2$ - Cp$_2$ZrMe$_2$ - Cp$_2$HfMe$_2$ sequence. More strikingly, however, all of the $\nu(^{is}CH)$ frequencies in the titanium group compounds are lower than any yet found elsewhere for methyl derivatives of d-block or p-block metals. The higher of the two Cp$_2$TiMe$_2$ $\nu(^{is}CH)$ frequencies (2922 cm^{-1}) is 11 cm^{-1} below the lowest previously observed value (2933 cm^{-1} for $\nu(^{is}CH_a)$) in

CpW(CO$_3$)Me in CCl$_4$ solution) [2] and the frequencies in the zirconium and hafnium compounds are respectively 26 and 32 cm^{-1} lower still. The parameters derived from these frequencies confirm that the methyl CH bonds in Cp$_2$ZrMe$_2$ and particularly, Cp$_2$HfMe$_2$, are significantly longer and weaker than the corresponding bonds in any other methylmetal compounds for which $\nu(^{is}CH)$ data are available. At the other end of the scale, the highest reported $\nu(^{is}CH)$ frequency in a methylmetal compound occurs in PbMe$_4$ (2977.9 cm^{-1}) [22]: the difference between this and the $\nu(^{is}CH)$ frequency in Cp$_2$HfMe$_2$ corresponds to a difference of ~ 8% in CH bond dissociation energy.

The unusually low HCH angles in Cp$_2$ZrMe$_2$ and Cp$_2$HfMe$_2$ follow directly from the lengthening of the CH bonds and the reduction in the repulsive interaction between them.

In our earlier work [1–4], we have established a simple correlation between $\nu(^{is}CH)$ and M–CH$_3$ bond dissociation energy, with the former increasing as the latter decreases. The correlation appears to be nearly linear within each group, although it is not directly transferable from group to group and absolute values for D(M–CH$_3$) can be predicted only if thermochemical data are already available for at least one or two compounds within the group. As a general rule, however, a decrease of 1 cm^{-1} in $\nu(^{is}CH)$ appears to reflect an increase of 1.0 ± 0.3 kcal mol^{-1} in the M–CH$_3$ bond dissociation energy, the exact amount varying from group to group. Application of this rule to the Cp$_2$MMe$_2$ compounds predicts an increase of 18–34 kcal mol^{-1} (76–143 kJ mol^{-1}) in D(M–CH$_3$) from Cp$_2$TiMe$_2$ to Cp$_2$HfMe$_2$. Comparisons with the chromium [2] and manganese [3,4] group compounds suggest that an increase of 70–80% in the M–CH$_3$ bond energy from titanium to hafnium is by no means improbable. This marked increase in bond energy is of course entirely consistent with experimental observations of the relative thermal stabilities of the two compounds. As no independent thermochemical data are available, there is no way in which we can estimate the absolute value of D(Hf–CH$_3$), but it is clear from these results that the Hf–CH$_3$ bond must be unusually strong compared with most other transition metal–carbon σ-bonds.

The barrier to internal rotation of the methyl groups in Cp$_2$ZrMe$_2$, estimated from ^{13}C relaxation time (T_1) data to be > 6 kcal mol^{-1} [10], must arise primarily from the short non-bonded H $\cdots$ H contacts which develop between the two methyl groups and the methyl and cyclopentadienyl groups in the course of the rotational motion. This steric effect will be the same in Cp$_2$HfMe$_2$ as in Cp$_2$ZrMe$_2$, the considerably greater in Cp$_2$TiMe$_2$. Internal rotation barriers greater than about 1 kcal mol^{-1} are usually sufficient to cause conformationally inequivalent methyl CH bonds to give rise to separate $\nu(^{is}CH)$ bands in the infrared spectrum. Thus in Cp$_2$TiMe$_2$, the higher-frequency $\nu(^{is}CH)$ band is readily assigned to the two CH bonds *trans* to cyclopentadienyl ligands, and the lower-frequency band to the CH bond *trans* to the second methyl group. However, if we attribute the frequency difference between these two bands simply to the different *trans*-influences of the cyclopentadienyl and methyl ligands, we are left with the problem of accounting for the non-appearance of similar pairs of $\nu(^{is}CH)$ bands in the spectra of the hafnium and zirconium compounds. Even if the difference between the two ligands is less well developed in the latter two complexes, we might still reasonably expect to see some sign of it in the vibrational spectra. (In the neighbouring CpM(CO)$_3$Me series, all three compounds display two $\nu(^{is}CH)$ bands with the frequency separation

TABLE 4

COMPARISON OF $\delta_s(CH_3)$ AND $\nu(MH)$ FREQUENCIES (cm^{-1})

M	Cp_2MMe_2 $\delta_s(CH_3)$	Cp_3MH $\nu(MH)$ [a]	M	$CpM(CO)_3Me$ $\delta_s(CH_3)$ [b]	$CpM(CO)_3H$ $\nu(MH)$ [c]	· M	$MeM(CO)_5$ $\delta_s(CH_3)$ [d]	$HM(CO)_5$ $\nu(MH)$ [e]
Ti:	1119	-	Cr:	1167		Mn	1191	1783
Zr:	1121	1608	Mo:	1168	1790			
Hf:	1144	1669	W:	1191	1845	Re	1212	1832

[a] Ref. 19. [b] Ref. 2. [c] Ref. 24. [d] Refs. 3, 4. [e] Ref. 25.

increasing from Cr to W [2]). An alternative and possibly more satisfactory explanation for the observed spectra may be that the cyclopentadienyl and methyl ligands have very similar or (in these compounds) negligible *trans*-influences and that the splitting of the $\nu(^{is}band)$ is Cp_2TiMe_2 arises from a purely physical distortion of the methyl group in this undoubtedly more crowded molecule. We should perhaps re-emphasise here that the evidence for two inequivalent types of methyl CH bond in Cp_2TiMe_2 comes not only from the observation of two $\nu(^{is}CH)$ bands but also from the splitting of $\nu_{as}(CH_3)$ and $\nu_{as}(CD_3)$: none of these effects are observed in the spectra of the zirconium or hafnium compounds.

In the methyl derivatives of the Main Group elements the symmetric deformation frequency $\delta_s(CH_3)$ decreased down each group and correlates empirically with a decrease in $\nu(MH)$ in the analogous hydride [23]. In the transition series (Table 4) similar correlations are observed but this time $\delta_s(CH_3)$ and $\nu(MH)$ in each group increase with increasing atomic number of the metal atom. These results are further evidence of the general tendency for metal–ligand σ-bond strengths to increase down the transition groups but to decrease down the main groups. (The dialkyls of Zn, Cd and Hg constitute an intermediate case). A particularly striking feature in the spectrum of Cp_2TiMe_2 is the unusually low intensity of $\delta_s(CH_3)$, compared with the strong bands found in the chromium and manganese group compounds. The $\delta_{as}(CH_3)$ frequency in $Cp_2Ti(CH_3)_2$ is normal, at about 1429 cm^{-1} in the gas phase, and contrasts with the abnormal value of 1375 cm^{-1} found in $MeTiCl_3$ [26], where there is much evidence for an unusual geometry of the methyl group [27].

Acknowledgements

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