Isolated CH Stretching Frequencies, Methyl Group Geometry, and Methyl CH Bond Lengths and Strengths in Tricarbonyl(η^5-cyclopentadienyl)methyl-chromium(II), -molybdenum(II), and -tungsten(II)†

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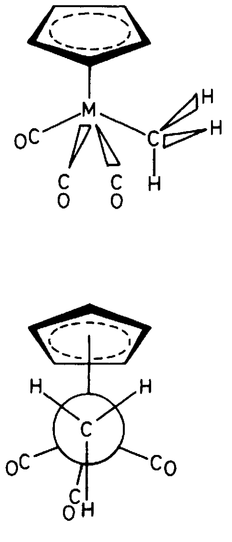
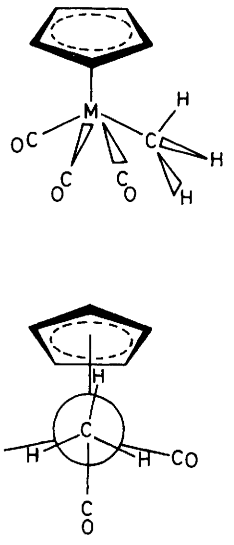
'Isolated' methyl CH stretching frequencies, $\nu(CH^{is})$, are reported for $[M(CHD_2)(\eta^5\text{-}C_5H_5)(CO)_3]$ (M = Cr, Mo, or W) and are used to predict CH bond lengths, bond-dissociation energies, and mean HCH angles. The methyl groups are subject to appreciable internal rotation energy barriers and each contain two different types of CH bond, with non-equivalent orientations in the molecule and with significantly different bond lengths and strengths. The CH bond strengths decrease in the order Cr > Mo > W, reflecting a corresponding increase in metal–carbon bond strength estimated to be of the order of 55—70% from Cr to W. The methyl groups in $[Cr(CHD_2)(\eta^5\text{-}C_5H_5)(CO)_3]$ and $[Cr(CD_3)(\eta^5\text{-}C_5H_5)(CO)_3]$ are affected by extensive H/D exchange, probably with the 1,2-dimethoxyethane solvent used in the preparative reaction.

The properties of methyl groups bound to transition elements are most often investigated using nuclear magnetic resonance spectroscopy, occasionally supplemented by diffraction experiments. Although the n.m.r. studies provide a wealth of information on the local environment of the methyl group and on its interaction with the remainder of the molecule, they do not usually yield precise internal geometries. In particular, the n.m.r. data do not readily provide accurate estimates of individual CH bond lengths or bond-dissociation energies. In principle, these CH bond parameters should be accessible from vibrational frequency measurements, but until very recently[1-5] the formidable interpretative problems have precluded any systematic use of vibrational spectroscopy for this purpose.

Specifically, for CH_3 compounds, the vibrational spectrum in the CH stretching frequency region is complicated by the appearance of bending overtones which not only pose potential assignment problems but also severely perturb the stretching fundamentals [particularly $\nu_{sym}(CH_3)$] by strong Fermi-resonance effects. Even when the unperturbed group frequencies are accurately established, there are difficulties in relating them to individual CH bond properties, and the situation is further complicated in low-symmetry environments, where the CH bonds are not all equivalent.



(I)



(II)

Most of these difficulties disappear in partially deuteriated (*i.e.*, CHD_2 substituted) compounds.[1,2] The bending overtones no longer appear in the CH stretching region and the observed CH stretching modes, $\nu(CH^{is})$, now arise from the 'isolated' stretching motions of individual CH bonds. If the CH bond length remains constant in all orientations, a single i.r. absorption band is observed,[3] but if it varies with orientation, as is usually the case in molecules with significant barriers to internal rotation, two or three $\nu(CH^{is})$ bands appear, associated with individual CH bonds in specific non-equivalent positions in the minimum energy structure.[4] Moreover, as these vibrations are virtually unaffected (< 5 cm^{-1}) by coupling with other modes, the observed $\nu(CH^{is})$ frequencies are linearly correlated with the CH bond lengths,[1,2] yielding estimates of $r_0(CH)$ reliable to ± 0.0005 Å for precisely determined frequencies in the gas phase. It is thus possible not only to determine individual CH bond lengths routinely with an accuracy unattainable by other techniques, but also to detect very small variations in CH bond length within a single methyl group. Further correlations with $\nu(CH^{is})$ lead to estimates of the CH bond-dissociation energy and (for symmetrical methyl groups) of the HCH angle.[1]

The behaviour of $\nu(CH^{is})$ in methyl groups with free internal rotation is treated in detail elsewhere.[5] In this paper we discuss the spectra of the partially deuteriated compounds $[M(CHD_2)(\eta^5\text{-}C_5H_5)(CO)_3]$ (M = Cr, Mo, or W) as examples of molecules with appreciable barriers to internal rotation. In the case of $[Mo(CHD_2)(\eta^5\text{-}C_5H_5)(CO)_3]$, the barrier has been estimated as >6 kcal mol^{-1}, from ^{13}C n.m.r. data,[6] and is attributed to steric interactions between the methyl and cyclopentadienyl CH bonds. To the extent that this barrier is purely steric in origin, we expect to find a comparable one in the tungsten compound, and a larger one in the chromium compound. Assuming ideal C_s molecular symmetry, steric interferences will be minimised in structure (**I**). The methyl group appears to be more effectively staggered, relative to the remainder of the molecule, in this than in the alternative conformation (**II**) although this depends to some extent upon the way in which the metal–cyclopentadienyl interaction is represented.

We distinguish two methyl CH bond environments, desig-

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† *Non-S.I. units employed:* cal = 4.184 J, dyn = 10^{-5} N.

Table 1. I.r. frequencies (cm^{-1}) and assignments in the $\nu(CH)$ and $\nu(CD)$ regions of $[MMe(\eta^5\text{-}C_5H_5)(CO)_3]$ (CCl_4 solution) (sp = sharp, br = broad)

Me Species	M = Cr	M = Mo	M = W	Assignment
CH_3	3 119vw	3 115vw	3 115vw	$\nu(CH)(C_5H_5)$
	2 992w,br	2 984w,br	2 974w,br	$\nu_{asym}(CH_3)$
	2 911m,sp[a]	2 904mw,sp[a]	2 902m,sp[a]	$\nu_{sym}(CH_3)$
	2 829vw	2 814vw	2 821w,sp	$2\delta_{asym}(CH_3)$
	2 011vs,sp	~2 018vs,sp	2 018.5vs,sp	$\nu_{sym}(CO)$
	1 935vs,br	~1 930vs,br	1 927vs,br	$\nu_{asym}(CO)$
CD_3[b]	3 119w	3 118w	3 116w	$\nu(CH)(C_5H_5)$
	2 239m	2 240w 2 234w	2 232w 2 223w	$\nu_{asym}(CD_3)$
	2 118mw,sp	2 117w	2 118w	$\nu_{sym}(CD_3)$
	2 066 (sh), sp	2 061 (sh)	2 065vw	$2\delta_{asym}(CD_3)$
		2 020.6vs,sp	2 017.5vs,sp	$\nu_{sym}(CO)$
		1 936vs,br	1 927vs,br	$\nu_{asym}(CO)$
CHD_2[b]	3 119w	3 115w	3 116w	$\nu(CH)(C_5H_5)$
	2 966 (sh)	2 964 (sh)	2 956 (sh)	$\nu(CH)$ $[\nu(CH_s^{is})]$
	2 953mw	2 946mw	2 933w	$\nu(CH)$ $[\nu(CH_a^{is})]$
	2 239 (sh)	2 229w	2 223vw	$\nu_{asym}(CD_2)$
	2 145m,sp	2 145m	2 141w	$\nu_{sym}(CD_2)$
		2 021vs,sp	2 018vs,sp	$\nu_{sym}(CO)$
		1 936vs,br	1 927vs,br	$\nu_{asym}(CO)$

[a] Unperturbed values estimated assuming $W = 34\ cm^{-1}$ are: Cr, 2 893, Mo, 2 888, and W, 2 884 cm^{-1}. [b] Frequencies for Cr compounds obtained from experimental data listed in Table 2.

Table 2. CH and CD stretching frequencies (cm^{-1}) in '$[Cr(CD_3)(\eta^5\text{-}C_5H_5)(CO)_3]$' and '$[Cr(CHD_2)(\eta^5\text{-}C_5H_5)(CO)_3]$' ($CCl_4$ solution)

'$[Cr(CD_3)(\eta^5\text{-}C_5H_5)(CO)_3]$'		'$[Cr(CHD_2)(\eta^5\text{-}C_5H_5)(CO)_3]$'	
2 966 (sh)	$\nu(CH^{is})$ (CHD_2)	2 988w	$\nu_{asym}(CH_3)$, $\nu_{asym}(CH_2)$ (CH_2D)
2 953mw	$\nu(CH^{is})$ (CHD_2)	2 963mw	$\nu_{asym}(CH_2)$ (CH_2D), $\nu(CH)$ (CHD_2)
2 939 (sh)	$\nu_{sym}(CH_2)$ (CH_2D)		
2 910 (sh)	$\nu_{sym}(CH_3)$	2 939mw	$\nu_{sym}(CH_2)$ (CH_2D)
2 863vw,br	$2\delta_{sym}(CH_2)$ (CH_2D)	2 911mw	$\nu_{sym}(CH_3)$
		2 860vvw,br	$2\delta_{sym}(CH_2)$ (CH_2D)
2 239m,br	$\nu_{asym}(CD_2)$ (CHD_2), $\nu_{asym}(CD_3)$	2 830vvw,br	$2\delta_{asym}(CH_3)$
2 198w	$\nu(CD)$ (CH_2D)	2 238vw	$\nu_{asym}(CD_2)$ (CHD_2)
2 145m,sp	$\nu_{sym}(CD_2)$ (CHD_2)	2 198w	$\nu(CD)$ (CH_2D)
2 118m,sp	$\nu_{sym}(CD_3)$	2 144m,sp	$\nu_{sym}(CD_2)$ (CHD_2)
2 066mw,sp	$2\delta_{asym}(CD_3)$		

nated as CH_s for the bond lying in the symmetry plane and CH_a, for the two bonds lying out of the plane. The spectra of the CH_3-, CHD_2-, CD_3- and (for the chromium compound) CH_2D-substituted molecules are reported in the following sections.

Experimental

Preparative.—The methyl compounds were prepared by standard methods,[7,8] from the reactions of the appropriately deuteriated methyl iodides with the potassium salts of the tricarbonyl(η^5-cyclopentadienyl)metal(II) ions in 1,2-dimethoxyethane solution. The products were purified by careful sublimation *in vacuo*. All operations were carried out in an atmosphere of dry nitrogen, or on a vacuum line.

Spectra.—The i.r. spectra were obtained in CCl_4 solution with 2-cm^{-1} resolution using a Nicolet 7199 FTIR spectrophotometer. The molybdenum and tungsten compounds are relatively stable and the spectroscopic measurements presented no experimental problems, but the chromium compound began to decompose detectably after 15—30 min in CCl_4 solution at room temperature. Decomposition was indicated by the development of a green colour in the initially yellow solution, by the appearance of new CO stretching bands, possibly associated with $[Cr(\eta^5\text{-}C_5H_5)(CO)_3Cl]$, at 2 045, 1 980, and 1 965 cm^{-1}, and by changes in the profiles of the CH stretching absorptions. The frequencies quoted in Table 1 refer to new solutions prepared from freshly-sublimed samples, and were measured in all cases before any of these signs of decomposition became evident.

Results and Discussion

The i.r. spectra of the CH_3-, CHD_2-, and CD_3-substituted compounds are illustrated in Figures 1—3, and the relevant frequency data are listed in Tables 1 and 2. The cyclopentadienyl CH stretching modes occur in the range 3 115—3 120 cm^{-1}, well clear of the methyl CH stretching region. A medium-intensity band observed at 2 966 cm^{-1} in solid $[W(CH_3)(\eta^5\text{-}C_5H_5)(CO)_3]$ does not appear in the spectrum of the CD_3-substituted compound and clearly should be assigned to $\nu_{asym}(CH_3)$ rather than to a ring CH stretching mode, as has been previously suggested.[9]

Assignments.—$[MoMe(\eta^5\text{-}C_5H_5)(CO)_3]$ *and* $[WMe(\eta^5\text{-}C_5H_5)(CO)_3]$. Assignments for the methyl CH and CD stretch-

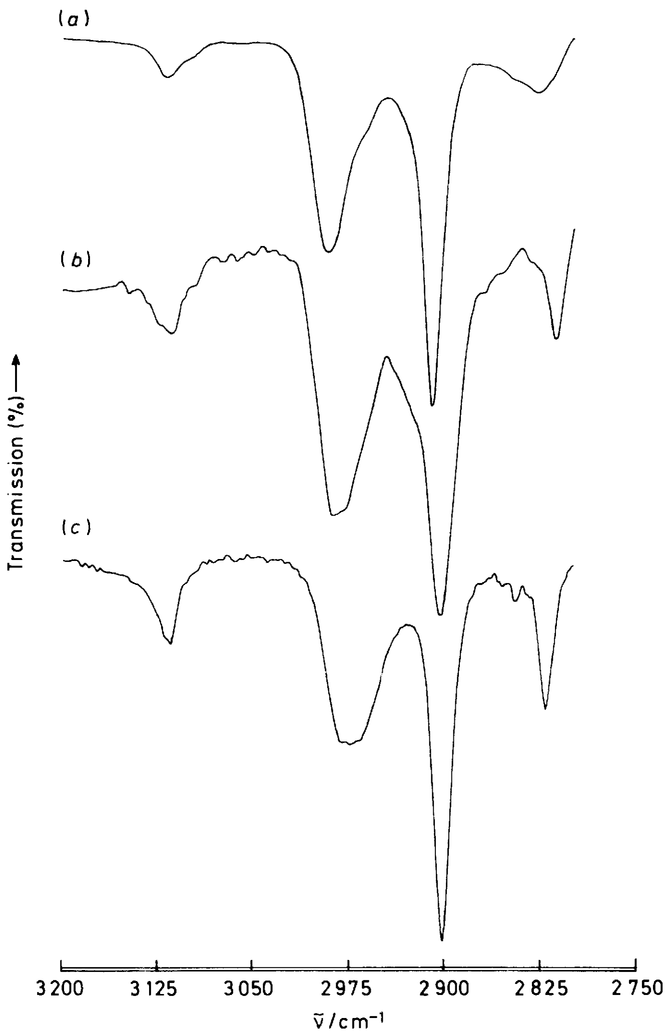


Figure 1. CH stretching region for [M(CH$_3$)(η^5-C$_5$H$_5$)(CO)$_3$] [M = Cr (*a*), Mo (*b*), or W (*c*)] [saturated CCl$_4$ solutions, arbitrary transmittance scale. Strongest ν(CH) or ν(CD) bands are typically 50—60% transmission in 0.1-mm cell]

ing modes in the Mo and W compounds are straightforward. The presence of two types of methyl CH bond is confirmed by the appearance of two ν(CH^{is}) bands in the CHD$_2$ species, by the splitting of ν_{asym}(CD$_3$) in the CD$_3$ species, and by the broad profile of ν_{asym}(CH$_3$) in the CH$_3$ species. The relative intensities of the ν(CH^{is}) absorptions, with the stronger band at lower frequency, suggest that two of the CH bonds (CH$_a$) are (relatively) weak, and one (CH$_s$) strong. This prediction is supported by sum rule calculations for the Mo compound. Using a *W* (Fermi-resonance shift) value[10] of 34 cm^{-1} for the Fermi-resonance interaction between ν_{sym}(CH$_3$) and $2\delta_{asym}$(CH$_3$), the frequency sum [$\Sigma\nu$(CH$_3$) = ν_{sym}(CH$_3$) + $2\nu_{asym}$(CH$_3$)] is 8 856 cm^{-1}; the corresponding ν(CH^{is}) sum, $\Sigma\nu$(CH^{is}), assuming two weak bonds (2 946 cm^{-1}) and one strong one (2 964 cm^{-1}) is also 8 856 cm^{-1}. For two strong bonds and one weak one the sum is 8 874 cm^{-1}. The situation in the Mo compound is therefore clear cut, but corresponding calculations for the W compound are more ambivalent. In this case $\Sigma\nu$(CH$_3$) is 8 832 cm^{-1}; $\Sigma\nu$(CH^{is}) for two weak bonds and one strong one is 8 822 cm^{-1} and for two strong bonds and one weak it is 8 845 cm^{-1}. However, if an additional small correction of 3 cm^{-1} is applied for a resonance with $2\delta_{sym}$(CH$_3$), the sums move convincingly in favour of two weak bonds and one strong one.

The assignments are further supported by so-called '3 × 3' force constant calculations (*i.e.*, energy-factored normal coordinate treatments of the CH and CD stretching frequencies),[11] the results of which are shown in Table 3. In these calculations the ν(CH^{is}) frequencies define the individual CH bond-stretching force constants, while the stretch–stretch interactions derive from the separation of ν(CH^{is}) from the ν_{asym}(CH$_3$) frequencies. As the splitting of ν_{asym}(CH$_3$) could not be determined directly, but only inferred from the breadth of the absorption band, the stretch–stretch interaction constants, f', had to be constrained equal. The fit to the observed CH and CD frequencies is generally satisfactory, except for the rather low calculated values of ν_{asym}(CH$_3$). A striking feature of the results is the very small or negative value of f', which in previous studies of methyl groups in the gas phase has usually been found to be *ca.* 0.03 mdyn Å^{-1}. The small values of f' here reflect the unusually large spacings of 25—40 cm^{-1} between ν(CH^{is}) and ν_{asym}(CH$_3$), compared with 20—25 cm^{-1} in most other compounds.

[CrMe(η^5-C$_5$H$_5$)(CO)$_3$]. The ν_{sym}(CH$_3$) and ν_{asym}(CH$_3$) vibrations in [Cr(CH$_3$)(η^5-C$_5$H$_5$)(CO)$_3$] occur at marginally higher frequencies than those in the corresponding molybdenum compound, but the band profiles and general appearance of the spectra are otherwise very similar (Figure 1). However, the spectra of the chromium compounds containing deuteriated methyl groups are quite different from those of their molybdenum and tungsten analogues, in both the CH and CD stretching regions (Figure 2) and show evidence of extensive methyl H/D exchange, most probably with the solvent used in the preparative reaction (see below). Thus the sample of '[Cr(CD$_3$)(η^5-C$_5$H$_5$)(CO)$_3$]' freshly prepared from CD$_3$I has five peaks or shoulders in the methyl CH stretching region, three of which can be directly assigned to CH$_3$ or CH$_2$D species. The CH$_3$ and CH$_2$ bending overtones are also evident (Table 2). The spectrum of the sample prepared from CHD$_2$I shows the presence of a high proportion of CH$_3$ groups and the ν(CD) band from the CH$_2$D group can be identified at 2 198 cm^{-1}. The identification of the CH$_3$ and CH$_2$D contributions to the spectra is supported by the 3 × 3 force constant calculations (Table 3), which also confirm the assignment of the bands at 2 966 and 2 953 cm^{-1} to ν(CH^{is}) modes in the CHD$_2$ species. These are slightly higher than the ν(CH^{is}) frequencies in the molybdenum–CHD$_2$ species, consistent with the trend observed for ν_{sym}(CH$_3$) and ν_{asym}(CH$_3$) in the chromium- and molybdenum-CH$_3$ species.

The frequency sum, $\Sigma\nu$(CH^{is}), assuming two weak bonds and one strong one, is 8 872 cm^{-1}, in good agreement with the sum of 8 877 cm^{-1} calculated for the resonance-corrected ν(CH$_3$) frequencies. We should emphasise that all these frequencies and assignments refer to freshly prepared samples with no detectable evidence of decomposition: the exchange reaction is quite independent of the thermal and photochemical decomposition reactions of the molecule.

Chemical Significance.—The CH bond parameters derived from the ν(CH^{is}) frequencies are listed in Table 4. The correlations[1] used to determine CH bond lengths, bond-dissociation energies, and HCH angles employ frequencies determined in the gas phase whereas the frequencies in the present study were measured in solution and are likely to be *ca.* 10 cm^{-1} lower than their gas-phase values. The solution frequencies have accordingly been adjusted by this amount before making the predictions given in Table 4, which therefore refer to the hypothetical gaseous molecules and are directly comparable with data for other gaseous methyl compounds. The bond lengths and bond-dissociation energies

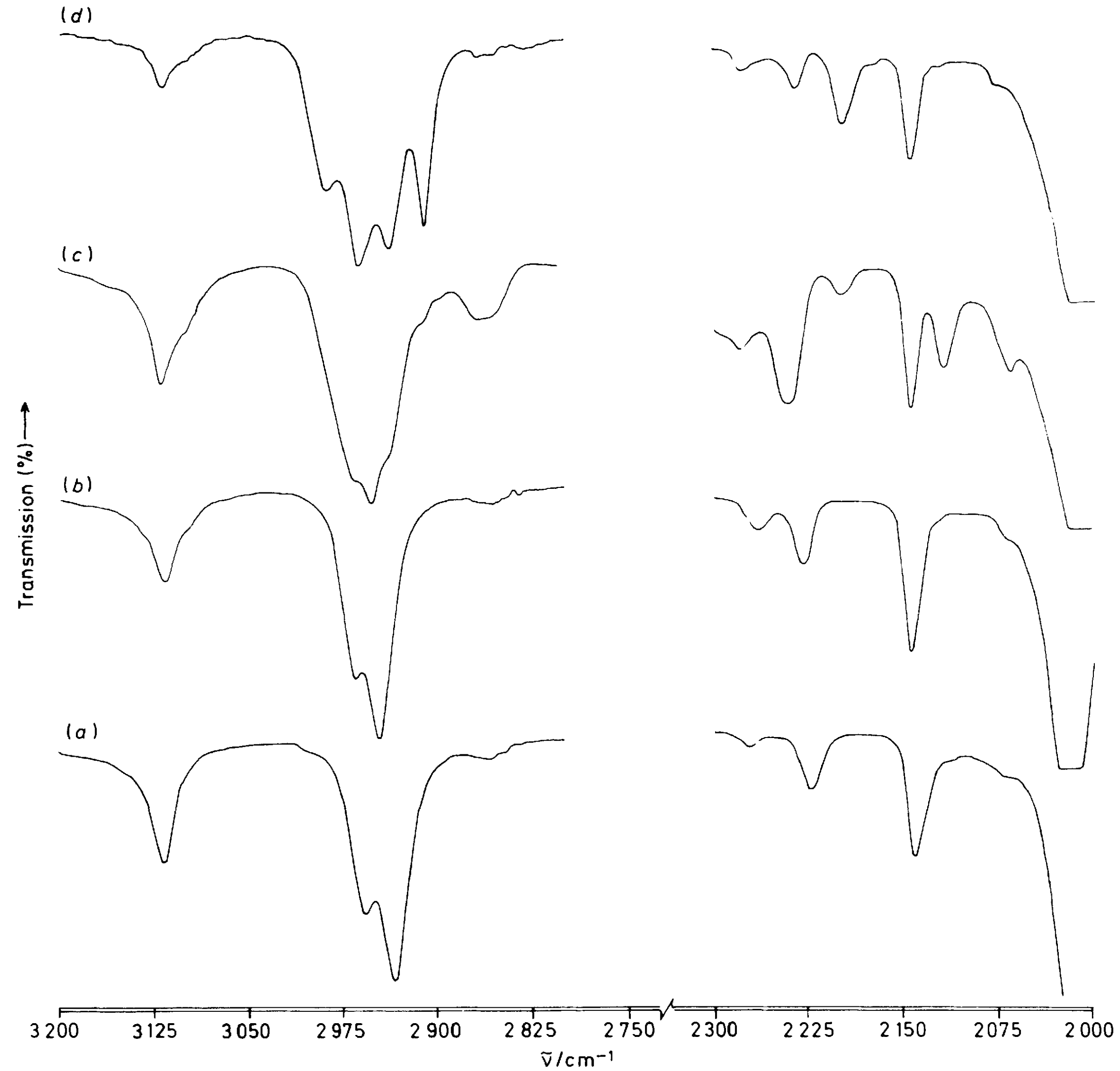


Figure 2. CH and CD stretching regions for $[M(CHD_2)(\eta^5\text{-}C_5H_5)(CO)_3]$ [M = W (*a*) or Mo (*b*)] and for (*c*) '$[Cr(CD_3)(\eta^5\text{-}C_5H_5)(CO)_3]$' and (*d*) $[Cr(CHD_2)(\eta^5\text{-}C_5H_5)(CO)_3]$ (saturated CCl_4 solutions)

in solution would then be, respectively, 0.001 Å greater and 0.9 kcal mol^{-1} less than the values quoted in Table 4.

The observation of two distinct $\nu(CH^{is})$ bands in each methyl group confirms the existence[6] of relatively high internal rotational energy barriers in all three molecules. There is no evidence in the spectrum to indicate the directions of the weak and strong bonds [this would normally be deduced from analysis of the $\nu(CH^{is})$ band shapes in the gas-phase spectra] but if we accept that structure (**I**) is inherently more probable than (**II**), the strong CH bond, CH_s, would be *trans* to the cyclopentadienyl group, and the weaker bonds, CH_a, approximately *trans* to carbonyl groups.

The observed $\nu(CH^{is})$ frequencies decrease in the order Cr > Mo > W, the differences between the chromium and molybdenum compounds being very much smaller than those between molybdenum and tungsten. The drop in frequency is more marked for $\nu(CH_a{}^{is})$ than for $\nu(CH_s{}^{is})$, so that the separation between the two vibrations increases from 13 cm^{-1} in the chromium compound to 23 cm^{-1} in the tungsten compound, reflecting, in the latter case, a difference of about 2% in the CH bond strengths. In our earlier studies[3,5] of methyl derivatives of Group 2B, 4A, and 7B elements, we have observed a clear connection between $\nu(CH^{is})$ and the metal–carbon bond-dissociation energy, $\bar{D}$(M–C). In Groups 2B and 4A,[3] the relationship is virtually linear, with $\nu(CH^{is})$ increasing as $\bar{D}$(M–C) decreases down each Group. Data for Group 7A compounds are available only for $[MnMe(CO)_5]$ and $[ReMe(CO)_5]$; in this case $\nu(CH^{is})$ decreases[5] and $\bar{D}(M\text{–}CH_3)$ increases[12,13] down the Group. Very broadly, over all these Groups, an increase of 1 cm^{-1} in $\nu(CH^{is})$ correlates with a decrease of 1.0 ± 0.3 kcal (4.2 ± 1.2 kJ) mol^{-1} in D(M–C). These results refer to compounds with free internal rotation and hence with only one $\nu(CH^{is})$ frequency, and are not necessarily directly transferable to systems with hindered internal rotation and more complex $\nu(CH^{is})$ spectra. However, if we use the mean $\nu(CH^{is})$ values for the Cr, Mo, and W complexes the data suggest an increase of 5.0 ± 1.5 kcal (21 ± 6 kJ) mol^{-1} in $D(M\text{–}CH_3)$ from chromium to molybdenum and a further increase of 9.0 ± 2.7 kcal (38 ± 11 kJ) mol^{-1} from molybdenum to tungsten. Alternatively, the $\nu(CH_a{}^{is})$ frequencies in $[Cr(CHD_2)(\eta^5\text{-}C_5H_5)(CO)_3]$ and $[W(CHD_2)(\eta^5\text{-}C_5H_5)(CO)_3]$ are virtually identical with $\nu(CH^{is})$ in $[Mn(CHD_2)(CO)_5]$ (2 955 cm^{-1}) and $[Re(CHD_2)(CO)_5]$ (2 935 cm^{-1}) respectively.[5] The metal–methyl carbon bond-dissociation energies in the latter two compounds

Table 3. 3 × 3 refinements for CH and CD stretching vibrations (ν/cm⁻¹)

Me Species	Cr Obs.	Cr Calc.[a]	Mo Obs.	Mo Calc.[a]	W Obs.	W Calc.[a]
CH_3	2 992	2 997 2 987	2 984	2 990 2 977	2 974	2 983 2 965
	2 911[b]	2 874	2 904[b]	2 877	2 902[b]	2 862
CD_3	2 239	2 247 2 240	2 240 2 234	2 242 2 233	2 232 2 223	2 236 2 222
	2 118[b]	2 086	2 117[b]	2 088	2 118[b]	2 080
CHD_2	~2 966	2 966	2 964	2 964	2 956	2 956
	~2 239	2 240	2 229	2 233	2 223	2 222
	2 145[b]	2 131	2 145[b]	2 130	2 141[b]	2 121
CHD_2	~2 953	2 953	2 946	2 946	2 933	2 933
	~2 239	2 245	2 229	2 240	2 223	2 233
	~2 145[b]	2 136	2 145[b]	2 136	2 141[b]	2 127
CH_2D	~2 988	2 995	—	2 988	—	2 979
	~2 939[b]	2 920	—	2 919	—	2 906
	2 198	2 183	—	2 179	—	2 169
CH_2D	~2 963	2 987	—	2 977	—	2 965
	~2 939[b]	2 914	—	2 911	—	2 898
	2 198	2 193	—	2 192	—	2 186
f_s	4.806		4.801		4.775	
f_a	4.762		4.743		4.741	
f'	−0.008		0.003		−0.006	
$HCH_{assumed}$	108.5°		108.5°		107.8°	

[a] ν(CD) (calc.) × 1.011 to offset anharmonicity effects. [b] Uncorrected for Fermi resonance.

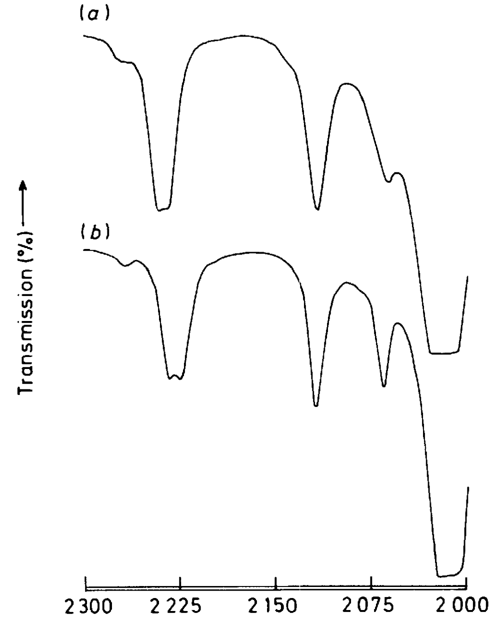


Figure 3. CD stretching region for [M(CD_3)(η^5-C_5H_5)(CO)$_3$] [M = Mo (*a*) or W (*b*)] (saturated CCl_4 solutions)

are 27.9 or 30.9 kcal (117 or 127 kJ) mol⁻¹ for M = Mn, and 53.2 kcal (223 kJ) mol⁻¹ for M = Re.[12,13] Using these figures as a basis for comparison, we would predict an increase of *ca.* 65% in the metal–carbon bond-dissociation energy from chromium to tungsten.

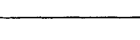
There is of course no way in which we can use the ν(CH^{is}) data to predict absolute values for M–CH_3 bond-dissociation energies. The only relevant thermochemical data at present available are for WMe_6,[13] for which *D*(M–CH_3) is 38 kcal (159 kJ) mol⁻¹. For tungsten in the formal +II oxidation state in [W(CH_3)(η^5-C_5H_5)(CO)$_3$] the W–CH_3 bond-dissociation energy would probably be somewhat greater than this. The ν(CH^{is}) frequencies indicate a relatively small change in *D*(M–CH_3) from chromium to molybdenum, followed by a much larger change from molybdenum to tungsten. This result is broadly consistent with the results of force-field calculations for the metal hexacarbonyls,[14] which yield very similar metal–carbon stretching force constants for the chromium and molybdenum compounds, but a substantially higher one for the tungsten compound.

The cyclopentadienyl CH stretching frequencies, unlike those in the methyl groups, are virtually insensitive to changes in the metal atom. The solitary bands observed in these compounds in the range 3 115—3 120 cm⁻¹ will of course represent several C_5H_5 group vibrations (A_1 + E_1, assuming C_{5v} local symmetry) and are not ν(CH^{is}) modes. However, by analogy with C_6H_6 and C_6D_5H,[15] we would expect to find the ν(CH^{is}) frequencies within 10 cm⁻¹ of the C_5H_5 frequencies. On this basis, we predict a cyclopentadienyl CH bond length of 1.07_9 Å, with a bond-dissociation energy of 114 kcal (477 kJ) mol⁻¹. The comparable figures for benzene are 1.084 Å and 109.5 kcal (448 kJ) mol⁻¹.

Table 4. $\nu(CH^{is})$ values and predicted CH bond lengths and dissociation energies

	$\nu(CH^{is})/cm^{-1}$				
	Solution	'Gas'	$r_0(CH)/Å$	Mean HCH/°	$D^0_{298}(C-H)$/kcal mol^{-1}(kJ mol^{-1})
Cr	2 966	2 976	1.093_8	108.6	101.8 (426.1)
	2 953	2 963	1.095_1		100.7 (421.5)
Mo	2 964	2 974	1.094_0	108.4	101.7 (425.7)
	2 946	2 956	1.095_8		100.1 (419.0)
W	2 956	2 966	1.094_8	107.8	101.1 (422.8)
	2 933	2 943	1.097_1		99.0 (414.0)

Exchange Reaction.—The H/D exchange in $[Cr(CD_3)(\eta^5\text{-}C_5H_5)(CO)_3]$ and $[Cr(CHD_2)(\eta^5\text{-}C_5H_5)(CO)_3]$ clearly occurs at an earlier stage than the thermal or photochemical decomposition reactions and we have found no evidence to suggest that the two processes are related. The exchange reaction could be intramolecular, between the methyl and cyclopentadienyl groups, or intermolecular, between the methyl groups and the 1,2-dimethoxyethane solvent used in the preparative reaction. The former process would lead to partial deuteriation of the cyclopentadienyl group, the latter would not. There are no detectable cyclopentadienyl $\nu(CD)$ absorptions in the spectra of the exchanged species, and the profiles of the cyclopentadienyl $\nu(CH)$ bands are not significantly different from those in $[Cr(CH_3)(\eta^5\text{-}C_5H_5)(CO)_3]$. The cyclopentadienyl CH stretching absorptions are intrinsically very much weaker than those associated with the methyl groups, so that small amounts of deuterium in the cyclopentadienyl ligand could conceivably escape detection; however, the experimental data indicate very extensive H/D exchange and hence very strongly suggest an intermolecular exchange process involving the 1,2-dimethoxyethane solvent.

The mechanism of the exchange reaction is not yet clear. A plausible scheme could involve an initial α-hydride transfer to form a carbene intermediate,  $Cr(D){=}CD_2$, followed by hydrogen abstraction from the solvent to generate the $Cr\text{-}CHD_2$ species. Mechanisms involving α-hydride transfers have been proposed in a number of related systems,[16–18] and the dicarbonyl carbene hydride $[Cr(CH_2)H(\eta^5\text{-}C_5H_5)(CO)_2]$ has been prepared in a CO matrix at 12 K.[19] As yet, we are aware of no other evidence to suggest that this or similar species may also be formed under more 'normal' conditions at room temperature. Whatever the mechanism, the reaction appears to be exclusive to the chromium compound: we have found no evidence, of any kind, to indicate that similar exchange processes may occur in the molybdenum and tungsten compounds.

Conclusions

(*a*) The internal rotation energy barrier in $[M(CH_3)(\eta^5\text{-}C_5H_5)(CO)_3]$ molecules leads to the presence of two types of methyl CH bond, with appreciably different CH bond lengths and dissociation energies. (*b*) The metal–methyl carbon bond-dissociation energies increase in the order Cr < Mo < W, probably by 55—70% from Cr to W. (*c*) The chromium compound $[Cr(CH_3)(\eta^5\text{-}C_5H_5)(CO)_3]$, but not the molybdenum or the tungsten analogues, undergoes extensive methyl proton exchange during the preparative reaction.

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