Partial Deuteration Studies, Ethyl-group Geometries and C–H Bond Properties in [MEt(cp)(CO)$_2$] (M = Fe or Ru) and [MEt(cp)(CO)$_3$] (M = Mo or W) (cp = η^5-C$_5$H$_5$)†

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Vibrational spectra have been obtained for the CH_3CH_2, CH_3CD_2, CD_3CH_2, CHD_2CD_2 and (for Fe and Mo) CHD_2CHD isotopomers of [MEt(cp)(CO)$_2$] (M = Fe or Ru) and [MEt(cp)(CO)$_3$] (M = Mo or W) (cp = η^5-C$_5$H$_5$). The isolated CH stretching frequencies ν^{is}(CH), observed in the spectra of the CHD_2CD_2M isotopomers, show that the terminal methyl groups in all four compounds are significantly asymmetric, with one weak and two equivalent stronger C–H bonds [ν^{is}(CH) Mo, 2885, 2941; W, 2888, 2936; Fe, Ru, 2877, 2927 cm^{-1}]. These differences in ν^{is}(CH) indicate differences of about 0.005 Å in bond length, or 20 kJ mol^{-1} in bond-dissociation energy, between the weaker and stronger C–H bonds in each methyl group. The effect of the metal atom substituents is to weaken all three β-C–H bonds (relative to ethane), the *gauche* bonds by a relatively small amount but the *trans* bonds by as much as 25 kJ mol^{-1}. These bonds are amongst the weakest yet identified in non-agostic alkyltransition-metal compounds. The methylene (α-C–H) bonds are also weakened relative to ethane, although to a lesser extent than the *trans*-β-C–H bonds, and are weaker than the methyl C–H bonds in the corresponding methylmetal compounds. There is no evidence to suggest that the methylene C–H bonds are inequivalent, as appears to be the case in [TiEt(cp)Cl$_2$]. The ethyl groups occur in two conformations, C_s and C_1, but the methyl C–H bond properties are unaffected by the differences in orientation.

In an earlier paper[1] we discussed the vibrational spectrum of the ethyltitanium compound [TiEt(cp)Cl$_2$] (cp = η^5-C$_5$H$_5$) using frequency data for the CH_3CH_2, CH_3CD_2, CD_3CH_2 and CHD_2CD_2 isotopomers to explore the local geometries of the methyl and methylene groups and to estimate individual C–H bond lengths and H–C–H angles. Although we have made extensive use of partial deuteration techniques to investigate methyl group geometries and C–H bond properties in methylmetal compounds,[2–7] we had not previously extended this approach to molecules containing ethyl or larger alkyl groups. Assignment problems are markedly more severe in the ethylmetal compounds, and the ubiquitous Fermi resonances between the C–H or C–D stretching fundamentals and the corresponding bending overtones create additional difficulties in the crucial C–H and C–D stretching regions. Accurate assessments of the resonance shifts in turn require reliable estimates of the frequencies of the unperturbed bending fundamentals. The recent appearance of a definitive force field for chloroethane[8] has provided a much-needed reference point and our assignments for [TiEt(cp)Cl$_2$], particularly in the lower-frequency parts of the spectrum, draw heavily on the chloroethane data.

The methylene C–H stretching frequencies observed for [TiEt(cp)Cl$_2$] lead to the unexpected conclusion that the group must be asymmetric,[1] suggesting a structure in which the methylene C–H bonding pairs interact unequally with low-lying unoccupied metal orbitals. This compound is formally a 12-electron system and is not necessarily a typical example of an ethylmetal compound; for purposes of comparison, and further to explore the implications of the results obtained for the ethyltitanium compound, data for other ethylmetal derivatives are badly needed. In this paper we report the results of partial deuteriation studies of the dicarbonyl compounds [MEt(cp)(CO)$_2$] (M = Fe or Ru) and the tricarbonyl compounds [MEt(cp)(CO)$_3$] (M = Mo or W), all of which have formal electron counts of 18. These ethyl compounds are additionally interesting because the corresponding methyl compounds are surprisingly different from each other. In the chromium group compounds, [MMe(cp)(CO)$_3$] (M = Cr, Mo or W), the methyl groups are subject to a substantial barrier to internal rotation and the methyl C–H bond lengths and stretching frequencies vary significantly with orientation. In the iron and ruthenium compounds, [MMe(cp)(CO)$_2$], in contrast, the methyl groups appear to be more or less freely rotating,[2] with at best only a small variation of the C–H bond length with the rotational angle.

In this work we have been able to make use of a small sample of CHD_2CHDBr, which has enabled us to prepare the corresponding isotopomers of the iron and molybdenum compounds. This material was not available at the time of the titanium study. Details of the theoretical treatment of the spectroscopic data are given in earlier papers[1,9] and will not be repeated here.

Experimental

All operations were carried out under strictly anhydrous conditions, using inert-atmosphere (N$_2$) or vacuum-line techniques. The compounds CH_3CH_2I, CH_3CD_2I, CD_3CH_2I and CD_3CD_2I were obtained commercially; CHD_2CD_2Br and CHD_2CHDBr were prepared at the University of Caen.[10]

[MEt(cp)(CO)$_2$] (M = Fe *or* Ru).—These compounds were prepared from the reactions of the sodium salts, Na[M(cp)(CO)$_2$], with the appropriate ethyl halide, using the method of Piper and Wilkinson.[2,11] The products were obtained as almost colourless oils and were purified by fractionation, *in vacuo*, through an ice-cooled trap. The ^{1}H NMR and IR spectra were consistent with those expected for the desired products, showing no evidence of significant impurity or of proton exchange in the partially deuteriated species.

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† *Non-SI units employed:* mmHg ≈ 133 Pa, dyn = 10^{-5} N.

Table 1 Infrared bands (cm^{-1}) in the 650–450 cm^{-1} region for [$FeEt(cp)(CO)_2$] and [$RuEt(cp)(CO)_2$][a]

	$\Delta_4(B_1)$	$\Delta_2(A_2)$	$\Delta_3(B_2)$	$\Delta_1(A_1)$	S_1[b]
CH_3CH_2Fe	638vs	603 (sh)	592vs	580vs 569 (sh)	515m
CH_3CD_2Fe	639vs	604 (sh)	590vs	554m	
CD_3CD_2Fe	639vs	604 (sh)	≈584 (100%)		≈532w
CH_3CH_2Ru	612.3s	601.3s	572.4vs	525.1vs	≈509 (sh) 462w
CH_3CD_2Ru	612.0ms	604.0 (sh)	575.2s	524.9s	≈511 (sh)
CD_3CH_2Ru	612.1s	600.8s	572.4vs	524.1vs	510.1s 463w 459m
CHD_2CD_2Ru	612.2s	603.3s	573.3vs 544 (sh)	524.8vs	508.8ms 494.3m

[a] Notation as in ref. 12. [b] Involves M–C stretching.

Table 2 Cyclopentadienyl and carbonyl fundamentals above 600 cm^{-1}

ν_{obs}[a]		
[$MoEt(cp)(CO)_3$]	[$EtW(cp)(CO)_3$]	Assignment
3117w	3116w	$\nu(CH)\ a_1, e_1$
2016.9vs	2014.5vs	$\nu_{asym}(CO)\ e$
1929.4vs	1922.1vs	$\nu_{sym}(CO)\ a_1$
1427 (sh) 1423.1m	1426 (sh) 1422.3ms	$\nu(CC)\ e_1$
1356.1vw	1355.6vw	$\nu(CC)\ e_2$
(1261)[b]	(1261)[b]	$\delta_{ip}(CH)\ a_2$
1111.1w	1110.5w	$\nu(CC)\ a_1$
1064w	1064.0m	$\delta_{op}(CH)\ e_2$
1013.6ms[c] 1006.4ms[c]	1012.2ms 1006.0ms	$\delta_{ip}(CH)\ e_1$
≈915w	917.4w	$\delta_{ip}(CC)\ e_2$
—	845 (sh)	$\delta_{op}(CH)\ e_1$
—	≈825vs	$\delta_{op}(CH)\ a_1$
617 (sh) 608 (sh)	610 (sh)	$\delta(CCC)\ e_2$

[a] In CCl_4 solutions. [b] Inferred from split combination bands near 2270 cm^{-1}, involving $\delta_{ip}(CH)$, e_1 (Mo, 2275, 2268; W, 2273, 2267 cm^{-1}). [c] From the CHD_2 species.

[$MEt(cp)(CO)_3$] (M = Mo *or* W).—The molybdenum and tungsten compounds were prepared from the reactions of the anions [$M(cp)(CO)_3$]$^-$ with the required ethyl halide, using the method first described by Piper and Wilkinson,[11] as modified by Jolly.[12] A solution of K(cp), prepared by treatment of freshly distilled cyclopentadiene (1.3 cm^3) with powdered KOH (4 g) in 1,2-dimethoxyethane (12 cm^3) was filtered to remove unreacted KOH and [$Mo(CO)_6$] (3.6 g) or [$W(CO)_6$] (4.8 g) added. The reaction mixture was refluxed under nitrogen for 12 h, cooled, and ethyl iodide added dropwise with stirring. The mixture was left to stir at room temperature for 5 h (longer when ethyl bromides were used) after which the solvent was removed *in vacuo* and the product separated from the residue by sublimation at 50 °C. Traces of the hexacarbonyls, [$M(CO)_6$], obtained with the sublimate were removed by pumping (< 0.1 mmHg) at room temperature. The products were yellow-orange crystalline solids in both cases. Their purity was confirmed spectroscopically as before.

[$CrEt(cp)(CO)_3$].—Attempts to prepare the chromium compound using the above procedure yielded a brown crystalline material which clearly contained the desired product. However, CCl_4 solutions decomposed too rapidly for meaningful spectroscopic studies (IR, NMR) and solutions in C_6D_6 also invariably contained impurities and decomposition products which created strong interferences in the C–H stretching region. Preparations of the partially deuteriated isotopomers were not attempted.

Spectroscopy.—Infrared spectra were recorded for freshly prepared CCl_4 solutions, at room temperature, using a Nicolet 7199 FTIR instrument at 1 cm^{-1} resolution. The solutions began to show signs of decomposition (colour change, appearance of impurity peaks) after 30–60 min: all such solutions were discarded.

Results and Assignments

Cyclopentadienyl and Carbonyl Vibrations.—The vibrations of the cyclopentadienyl ligands in the ethyl-iron and -ruthenium compounds are identical, to within ± 1 cm^{-1}, with those in the corresponding methyl compounds[2] and are not repeated here. The only marginal exception is $\delta_{ip}(CC)$ (e_2) (ip = in plane) which is found at 919.6 cm^{-1} for [$FeEt(cp)(CO)_2$] and 909.4 cm^{-1} for [$RuEt(cp)(CO)_2$], 1.9 and 2.6 cm^{-1}, respectively, below the values for the methyl compounds.

The ν(CO) modes in the iron and ruthenium compounds [$\nu_{asym}(CO)$, a″, 2004 (Fe), 2015.9 (Ru); $\nu_{sym}(CO)$, a′, 1949 (Fe), 1954.2 (Ru); $\nu(^{13}CO)$, 1919.6 (Fe), 1925.5 cm^{-1} (Ru)] are 4–5 cm^{-1} below the corresponding values for the methyl compounds. In the δ(MCO) region (Table 1) the frequencies are again generally very similar to those for the methyl compounds. The Δ_1 (a_1) mode (using the Manning[13] notation) in [$FeEt(cp)(CO)_2$] is noticeably sensitive to deuteriation of the methylene group in the ethyl ligand, suggesting that a $\rho(CD_2)$ mode must occur in this region. No comparable effect is observed in the ruthenium compound.

The frequencies of the cyclopentadienyl and carbonyl fundamentals above 600 cm^{-1} for the molybdenum and tungsten compounds are listed in Table 2. Broadly speaking, whereas the cyclopentadienyl frequencies of [$RuEt(cp)(CO)_2$] tend to be 5–15 cm^{-1} lower than those of [$FeEt(cp)(CO)_2$], those of [$MEt(cp)(CO)_3$] (M = Mo or W) are found within 1–2 cm^{-1} of each other and in most cases lie between the iron and ruthenium frequencies. Only one cyclopentadienyl ν(CH) band is detectable in the spectra of the molybdenum and tungsten compounds, whereas two (a_1, e), separated by about 18 cm^{-1}, are observed for the iron and ruthenium compounds. The e_1 ν(CC) and $\delta_{ip}(CH)$ modes are split by 4–7. cm^{-1} in the [$MEt(cp)(CO)_3$] compounds, compared with 13–15 cm^{-1} in [$MEt(cp)(CO)_2$]. No splitting is observed in these modes in [$TiEt(cp)Cl_2$].[1] The δ(MCO) modes in the molybdenum and tungsten compounds are not well resolved but there is no evidence that any significant shifts are caused by deuteriation of the ethyl ligand.

Ethyl-group Vibrations.—The spectra of the CH_3CH_2, CH_3CD_2, CD_3CH_2, CHD_2CD_2 and CHD_2CHD isotopomers of [$MEt(cp)(CO)_2$] (M = Fe or Ru) and [$MEt(cp)(CO)_3$] (M = Mo or W) in the C–H and C–D stretching regions are illustrated in Figs. 1–4. Wavenumbers for these compounds are

Table 3 Infrared bands above 900 cm^{-1} assigned to the CH_3CH_2 group in CH_3CH_2M compounds

$[M(C_2H_5)(cp)(CO)_2]$		$[M(C_2H_5)(cp)(CO)_3]$			
M = Fe	Ru	M = Mo	W	Assignment	Mode
2957.6s	2957.5s	2970.6ms	2966.0ms	$\nu_{asym}(CH_3)$ a″	12
2937.0s	2938.3s	2948.2ms	2946.3ms	$\nu_{asym}(CH_3)$ a′	1
2914.6s	2916.7s	2921.5ms	2918.5ms	$\nu_{sym}(CH_2)$, $2\delta_{asym}(CH_3)$ A′	2
2887 (sh)	2886.9m	2892.7m	2896 (sh)	$2\delta_{asym}(CH_3)$, A′, A″	
2854.5s	2852.5vs	2860.8ms	2863.0ms 2846 (sh)	$\nu_{sym}(CH_3)$ a′	3
2725.0 (sh)	2725 (sh)	2737.4ms	2737.5vw	$2\delta_{sym}(CH_3)$ A′	
2715.6w	2716w	2724.0vw	2724.4vw		
1451.4ms	1450.3ms	1456.5ms	1458.3ms	$\delta_{asym}(CH_3)$ a′, a″	4, 14
		1439.6w	1447 (sh) 1440.3w	$\delta_{sym}(CH_2)$ a′	5
1374.0m	1372.8 (sh)	1380.0mw	1380.7mw	$\delta_{sym}(CH_3)$ a′	6
1369.4ms	1368.7m	1373.5m	1373.5m	(2 conformers)	
1230.9vw	1236.0vw	≈1234vw	1242vw	$\rho(CH_3)/\tau(CH_2)$ a″	15
1214.9vvw				impurity ?	
1155.4vs	1172.6vs	1146.3s	1161.5s	$\omega(CH_2)$ a′	7
		≈1040 (sh)	1038.6w		
967.3w	973.7w	965.6m	969.6m	$\rho(CH_3)/\nu(CC)$ a′	8
930.0w	949.9w	935vw	≈952w	$\tau(CH_2)/\rho(CH_3)$ a″	16

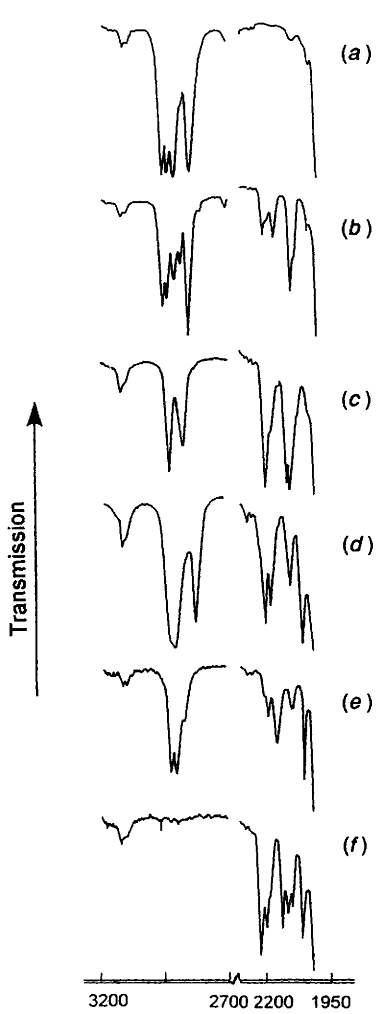


Fig. 1 The C–H and C–D stretching vibrations for isotopomers of $[FeEt(cp)(CO)_2]$: (a) C_2H_5, (b) CH_3CD_2, (c) CHD_2CD_2, (d) CD_3CH_2, (e) CHD_2CHD and (f) CD_3CD_2 (CCl_4 solutions, maximum feasible concentrations, pathlengths 0.05–0.2 mm)

listed in Tables 3–8. The CHD_2CHD isotopomers were prepared for the iron and molybdenum compounds only.

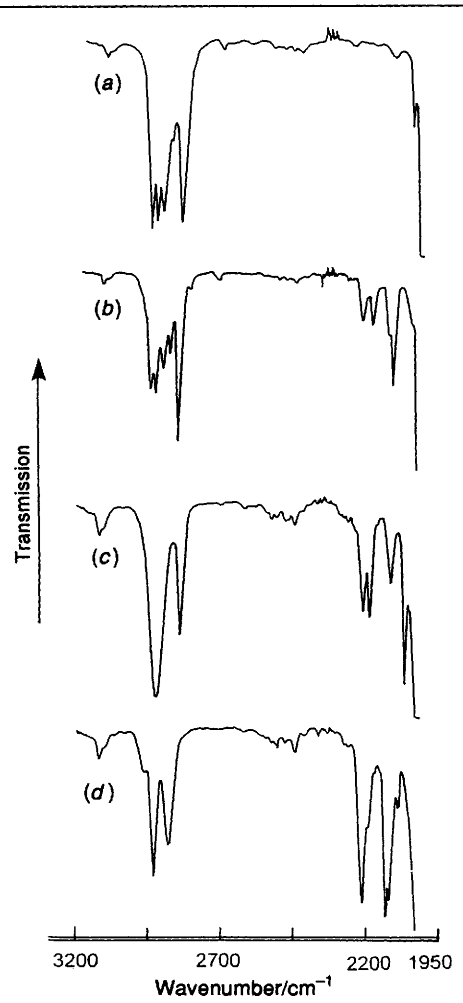


Fig. 2 The C–H and C–D stretching vibrations in isotopomers of $[RuEt(cp)(CO)_2]$: (a) CH_3CH_2, (b) CH_3CD_2, (c) CD_3CH_2 and (d) CHD_2CD_2. Conditions as in Fig. 1

In assigning the various bands we use the same terminology as in the earlier paper:[1] the symmetry labels refer to the local symmetry of the ethyl group and the mode numbering is that appropriate to an EtX system, the numbers in each symmetry

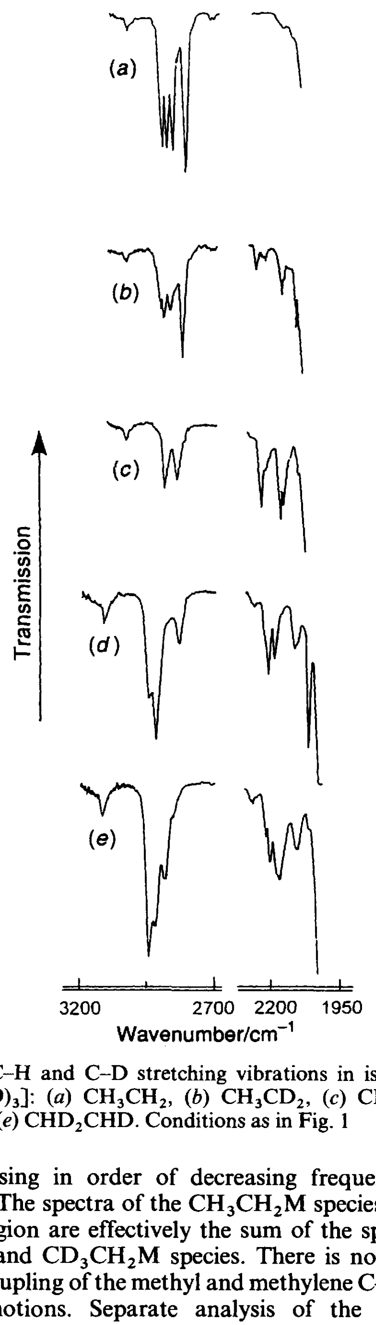


Fig. 3 The C–H and C–D stretching vibrations in isotopomers of [MoEt(cp)(CO)$_3$]: (*a*) CH_3CH_2, (*b*) CH_3CD_2, (*c*) CHD_2CD_2, (*d*) CD_3CH_2 and (*e*) CHD_2CHD. Conditions as in Fig. 1

block increasing in order of decreasing frequency in each isotopomer. The spectra of the CH_3CH_2M species in the C–H stretching region are effectively the sum of the spectra of the CH_3CD_2M and CD_3CH_2M species. There is no evidence of significant coupling of the methyl and methylene C–H (or C–D) stretching motions. Separate analysis of the methyl and methylene vibrations is therefore justified.

Methyl vibrations. The absorptions associated with the vibrations of the methyl groups are readily identified by comparing the spectra of the CH_3CD_2M and CD_3CH_2M species. The spectra clearly demonstrate that the methyl groups in all four compounds, like that in [TiEt(cp)Cl$_2$],[1] have C_s rather than C_{3v} symmetry. For the CHD_2CD_2M species we observe two well separated isolated ν^{is}(CH) absorptions, arising from the stretching of isolated C–H bonds lying in (C–H^s) and out (C–H^a) of the local symmetry plane, and the $\nu_{asym}(CH_3)$ and $\nu_{asym}(CD_3)$ modes in the CH_3 and CD_3 species are split into well resolved a′ and a″ components. A preliminary sum-rule calculation,[1,9] using the observed frequencies, indicates that in each case the methyl group contains two strong C–H^a bonds and a significantly weaker C–H^s bond. Subsequent calculations using the resonance-corrected frequencies (see below) confirm this prediction.

The patterns of the methyl C–H stretching bands of the carbonyl complexes are very similar to that of [TiEt(cp)Cl$_2$]. However, at lower frequencies the $\delta_{sym}(CH_3)$ bands, near 1370 cm^{-1}, and their overtones are all split, with a higher-frequency component roughly half as intense as the lower one. No corresponding splittings are observed for the ethyltitanium compound. The appearance of two $\delta_{sym}(CH_3)$ bands is clear evidence for the presence of two conformers which can only differ in the orientation of the methyl group relative to the cyclopentadienyl and carbonyl ligands (Scheme 1), confirming the earlier conclusion drawn from the observation of additional ν(CO) bands in the spectrum of [FeEt(cp)(CO)$_2$].[14,15] The simplest interpretation of the relative intensities is that the lower-frequency band arises from the C_1 conformer, the higher-frequency band from the C_s conformer and that the free energies of the two conformers, apart from the *RT*ln 2 term, are very similar. Molecular mechanics calculations[15] estimate the C_1 form to be more stable than the C_s form by 4.6 kJ mol^{-1}, suggesting an abundance of about 7% for the C_s form, whereas our observations of the [FeEt(cp)(CO)$_2$] spectrum suggest about 37%, assuming the intrinsic intensities of the two bands of the two conformers to be identical. (The ratios of the peak

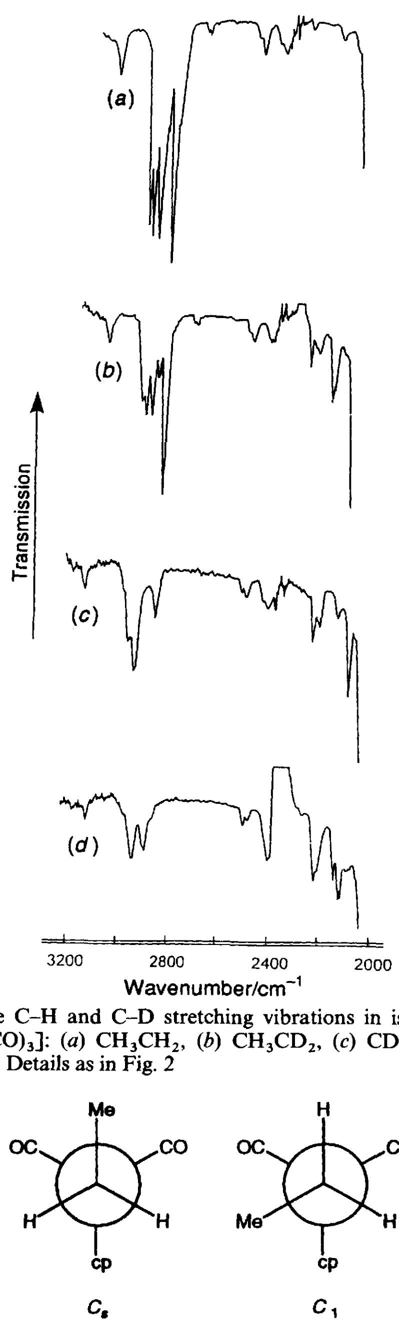
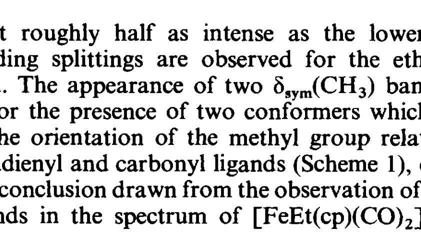


Fig. 4 The C–H and C–D stretching vibrations in isotopomers of [WEt(cp)(CO)$_3$]: (*a*) CH_3CH_2, (*b*) CH_3CD_2, (*c*) CD_3CH_2 and (*d*) CHD_2CD_2. Details as in Fig. 2



Scheme 1

Table 4 Infrared absorption bands above 900 cm^{-1} assigned to the CH_3CD_2 group in CH_3CD_2M compounds

$[M(CD_2CH_3)(cp)(CO)_2]$		$[M(CD_2CH_3)(cp)(CO)_3]$			
M = Fe	Ru	M = Mo	W	Assignment	Mode
2953.2ms	2951.8ms	2965m	2960mw	$\nu_{asym}(CH_3)$ a″	12
2934.9ms	2934.5ms	2944.5m	2940.7mw	$\nu_{asym}(CH_3)$ a′	1
2905.9m	2906.5m	2912.4m	2916.2mw	$2\delta_{asym}(CH_3)$ A′*	
2884.5m	2884.8m	≈2890 (sh)	2888.5w	$2\delta_{asym}(CH_3)$ A″*	
2852.3s	2852.7s	2858.7m	2859.8ms	$\nu_{sym}(CH_3)$ a′	2
2814 (sh)	2822, 2815 (sh)		≈2820 (sh)	$\delta_{asym} + \delta_{sym}(CH_3)$ A′	
2726 (sh)	2725 (sh)	≈2740vvw	2740vvw	$2\delta_{sym}(CH_3)$ A′	
2717.2vw	2717vw	≈2730vvw	2728vvw		
2222.4m	2218.9m	2229.1w	2222.7w	$\delta_{sym}(CD_2) + \nu_{15}$ A″	
2209 (sh)					
		≈2204 (sh)	2199 (sh)		
2181.0m	2181.5m	2190w	2185w	$\nu_{asym}(CD_2)$ a″	13
2117.1ms	2125 (sh)	2123.7mw	2121.1mw	$\nu_{sym}(CD_2)$ a′	3
2107 (sh)	2110.5ms	2111(sh)	2109.9mw	$2\nu_7$	
			≈2073vw		
1448.2ms	1448.8m	1453.6m	1455.6m	$\delta_{asym}(CH_3)$ a′, a″	4, 14
		1450 (sh)			
1374.6mw	≈1375 (sh)	1380.9w	1381.2w	$\delta_{sym}(CH_3)$ a′	5
1369.9m	1370.0m	1374.0mw	1374.4m	(2 conformers)	
	1121 (sh)			$\delta_{sym}(CD_2)$	6
≈1095 (sh)	1097m	1097.5mw	1098.0w	$\rho(CH_3)$ a″	15
≈1080 (sh)	≈1069 (sh)				
1061.5s	1064.6s	1062.6m	1067.3m	$\rho(CH_3)$ a′	7
1053.7s	≈1058 (sh)	1050.6m	1053.5m	(2 conformers)	
954.5w	964.5mw	954w	960w	$\delta_{sym}(CD_2)$, $\nu(CC)$ a′	8
		947w	954 (sh)	?	
		935w		?	

* The $2\delta_{asym}(CH_3)$ (A′) levels derive from $2\delta_{asym}(CH_3)$ (A_1) and $2\delta_{asym}(CH_3)$ (E) of the C_{3v} methyl group; $2\delta_{asym}(CH_3)$ (A″) derived from $2\delta_{asym}(CH_3)$ (E) not observed.

Table 5 Infrared bands (cm^{-1}) assigned to the CD_3CH_2 group in CD_3CH_2M compounds

$[M(CH_2CD_3)(cp)(CO)_2]$		$[M(CH_2CD_3)(cp)(CO)_3]$			
M = Fe	Ru	M = Mo	W	Assignment	Mode
2914.5vs (br)	2921s (br)	2949.8m	2941m	$\nu_{asym}(CH_2)$ a″	12
		2921.6m	2915.0m	$\nu_{sym}(CH_2)$ a′	1
2834.1s	2840.2ms	2837.9mw	2835.9mw	$2\delta_{sym}(CH_2)$ A′	
2716vw	2699vvw				
≈2235 (sh)	2236 (sh)	≈2225 (sh)		? $2\delta_{sym}(CD_3)$ A′	
2205.4s	2208.2ms	2213.2mw	2212.7w	$\nu_{asym}(CD_3)$ a″	13
2186.4s	2184.6ms	2189.9mw	2186.4vw	$\nu_{asym}(CD_3)$ a′	2
≈2177 (sh)					
≈2157 (sh)					
2109.7ms	2112.5m	2119.7mw	2120 (sh)	$2\delta_{asym}(CD_3)$ A′	
			2115vw		
2064.5vs	2065.8s	2070.0m	2070.4mw	$\nu_{sym}(CD_3)$ a′	3
≈1436vw	≈1431vw	≈1433vw	—	$\delta_{sym}(CH_2)$	4
1284 (sh)		1292vw			
1176.7ms	1183.7wm	1128.6m	1146.7m	$\tau(CH_2)$ a″	14
1126.7vs	1148.6vs	1113.7ms	1133.8m	$\omega(CH_2)$ a′	5
	1103.1 (sh)			$\delta_{sym}(CD_3)$ a′	6
1064 (sh)		1064 (sh)		$\delta_{asym}(CD_3)$ a′, a″	7, 15
1051.0s	1053.6ms	1054.6m	1056.1m		
	≈1050 (sh)?				
920ms	925w	933 (sh)	921w	$\nu(CC)/\delta_{sym}(CD_3)$ a′	8
		920wm			
687w	675vw			? $\rho(CD_3)/\rho(CH_2)$	16

absorbances for the EtW and EtFe compounds are 2.2:1 and 1.7:1 respectively.)

In principle, all the ethyl bands might be expected to split as a result of the presence of two conformers, but the only case [apart from $\delta_{sym}(CH_3)$] in which a possible duplication can be identified is found in the 1050–1060 cm^{-1} region of the CH_3CD_2M species, where we assign a pair of bands to the $\rho(CH_3)$ (a′) mode ν_7. In particular there is no evidence for any duplication of the $\nu(CH)$ and $\nu(CD)$ bands, which is important when we come later to consider the source of the asymmetry of the methyl group.

In assembling the data required for the assessment of Fermi resonances the only uncertain fundamental position is that of $\delta_{sym}(CD_3)$ (a′), ν_6, in the CD_3CH_2M species. This band is expected in the 1100–1150 cm^{-1} region, and is probably masked by the stronger band ascribed to the $\omega(CH_2)$ (a′) mode ν_5.

Table 6 Infrared bands (cm^{-1}) assigned to the CHD_2CD_2 group in CHD_2CD_2M compounds

$[M(CD_2CHD_2)(cp)(CO)_2]$		$[M(CD_2CHD_2)(cp)(CO)_3]$		
M = Fe	Ru	M = Mo	W	Assignment
2927.5m	2927.4m	2941.3mw	2935.7mw	$\nu^{is}(CH^a)$
2877.3m	2877.3m	2884.8mw	2887.9mw	$\nu^{is}(CH^s)$
2208.4ms	2208.3ms	2219.4mw	≈2216mw	$\nu_{asym}(CD^aD^a)$
2187 (sh)	2187 (sh)	2196 (sh)		$\nu_{asym}(CD^aD^s)$
2164 (sh)	2165 (sh)	2185 (sh)		*a*
2129.6ms	2130.5ms	2136.2mw	≈2137mw	$\nu_{sym}(CD_aD_a)$
2114.7ms	2118.9ms	2122mw	≈2120mw	$\nu_{sym}(CD^aD^s)$
			≈2113mw	*b*
2091 (sh)	2087.2m	2095 (sh)	2095w	*b*
		2070 (sh)	2070 (sh)	*b*
2054 (sh)		2058 (sh)	≈2050 (sh)	*b*
	1290 (sh)		≈1297 (sh)	
1285.0m	1283.5m	1289.9mw	≈1292w	δ(CH)
	1272 (sh)	1272.4 (sh)	1279 (sh)	
1264.4mw	1267.0m	1265.6w	≈1270vw	
1109.9m		1104 (sh)	≈1105 (sh)	*b*
1050.8w	1064m		1067mw	*b*
968.9s	983.2ms	963.9w	965w	*b*
934.7s	952.4s	955.6w	958w	*b*
		925.3m	≈940m	*b*
		919 (sh)		*b*
695.3w				$\rho(CD_2)/\rho(CH_2)$

[a] Origin uncertain. [b] Ethyl-group vibrations. Individual assignments not possible because of the presence of several conformers associated with C–H bond orientation and rotation around the M–C bond.

Table 7 Infrared bands (cm^{-1}) assigned to the CHD_2CHD group in CHD_2CHDM compounds

$[Fe(CHDCHD_2)(cp)(CO)_2]$	$[Mo(CHDCHD_2)(cp)(CO)_3]$	
2930.5mw	2943m	$\nu^{is}(CH^a)$
2907.1m	2917.2m	$\nu^{is}(CH^{methylene})$
2878.9m	2885.5mw	$\nu^{is}(CH^s)$
2211w	2218.2w	*a*
2195w	2201.5mw	*a*
	2177 (sh)	*a*
2159.7mw	2168.3mw	*a*
2105w	2108w	*a*
1325.7w	1326.2w	*b*
1308vw	1307.6vw	*b*
1291 (sh)	1290m	
1281.3mw	1285m	δ(CH)
	1274mw	
1263.8mw		
	1268mw	
1102m	1122 (sh)	
1072.7m	1071.5mw	*a*
1068 (sh)		*a*
999ms	992.3ms	*a*
958.7w	955.1mw	*a*

[a] Ethyl-group vibrations. Individual assignments not possible because of the presence of several conformers arising from C–H orientations and rotation around the M–C bond. [b] Origin uncertain.

Methyl group: Fermi-resonance corrections and harmonic local-mode force-field calculations. For the $\nu(CH_3)$ region of the CH_3CD_2M species we have used the same local mode/normal mode model as was employed for $[TiEt(cp)Cl_2]$.[1] This borrows 'standard' Fermi-resonance parameter[16] values for W_{155}, W_{455} and W_{122} of 32, 20 and 40 cm^{-1}, respectively, from the methyl halides,[17,18] W_{455} being reduced by $2^{-\frac{1}{2}}$ to take into account the lifting of the degeneracy of $\nu_{asym}(CH_3)$. Five parameters $\lambda_{a,s}$, $\lambda_{a,a}$, $2\delta^{o}_{asym}(A_1)$, $2\delta^{o}_{asym}(E)$ and $2\delta^{o}_{sym}(A_1)$ were refined,[1] as shown in Table 9. The resonance shifts were obtained by repeating the calculation with the refined values of λ, but with all $W_{ijk} = 0$. The resulting values in Table 9 show that the largest shift, 12–14 cm^{-1}, is expected on $\nu_{asym}(CH_3)$ (a′), that on $\nu_{sym}(CH_3)$ (a′) being smaller because of the opposing effects of the resonances with $2\delta_{sym}(CH_3)$ (A′), below it, and $2\delta_{asym}(CH_3)$ (A′), above. These calculated shifts were then applied to the observed frequencies to obtain estimated unperturbed values for the stretching fundamentals for input to the full harmonic local-mode force-field refinement the results of which are set out in Table 10.

The data available for a similar treatment of the $\nu(CD_3)$ vibrations are less extensive. The major resonance in the $\nu(CD)$ region appears to be that between $2\delta_{asym}(CD_3)$ and $\nu_{sym}(CD_3)$. The position of $2\delta^{o}_{asym}(CD_3)$ was fixed by assigning a conventional value of -7 cm^{-1} to $2(x_{5,5} - g_{5,5})^1$ and the resulting resonance shift calculated for $2\delta_{asym}(CD_3)$ applied to $\nu_{sym}(CD_3)$, giving the $\nu^{o}_{sym}(CD_3)$ values in Table 10. Uncertainties of ± 5 cm^{-1} were associated with all data except the $\nu^{is}(CH)$ frequencies, where the usual ± 1 cm^{-1} was employed.

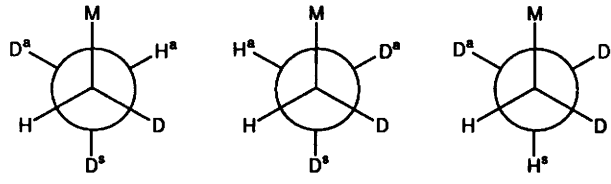
Various H–C–H angles were used in trial refinements. The angles calculated from the $\nu_{asym}(CH_3)/\nu_{asym}(CD_3)$ ratios, using the corrected $\nu_{asym}(CH_3)$ data,[1] lie in general between 102 and 106°. The lowest angles give the lowest values for the interaction force constants $f'_{a,a}$ and $f'_{a,s}$. In the event, we prefer angles which yield f' values similar to those for the methyl groups in CH_3CD_3[19] and CH_3CD_2Cl,[8] in the range 0.050–0.056 mdyn Å^{-1}. The $f'_{a,a}$ and $f'_{a,s}$ values should be very similar: this can be achieved by setting the angle H^a–C–H^s 0.5–1.5° larger than H^a–C–H^a. A difference of this order in the H–C–H angles is not unreasonable, given the inequality of the C–H^a and C–H^s bonds.

The results in Table 10 are based on the foregoing considerations. The H–C–H angles chosen (108–109.5°) are reasonable in comparison with chloroethane,[8] where the *ab initio* 6-31G* geometry gives H^a–C–H^a 108.51°, H^a–C–H^s 108.46° and the microwave spectroscopy values are 108.2 and 109.2°, respectively.[20] A general feature of the refinements is a tendency for the ν(CD) values to be calculated too high (ε_v negative) while $\nu_{asym}(CH_3)$ (a″) is too low (ε_v positive), particularly for the molybdenum and tungsten compounds. This may reflect error in the factor 1.011 used to modify the observed ν(CD) values, before refinement, as a compensation for anharmonicity. Judging from the reproduction of the $\nu_{asym}(CD_2)$ and $\nu_{sym}(CD_2)$ frequencies of the CHD_2 group (Table 10) to within 6–10 cm^{-1}, it is as likely to result from inadequate resonance corrections in the CD_3 group, possibly involving unrecognised overtone or combination levels.

Table 8 Infrared bands (cm^{-1}) assigned to the C_2D_5 group in $[Fe(C_2D_5)(cp)(CO)_2]$

ν_{obs}	Assignment	Mode
2217.5vs	$\nu_{asym}(CD_2)$ a″	12
2199.5s	$\nu_{asym}(CD_3)$ a″	13
2185 (sh)	$\nu_{asym}(CD_3)$ a′	1
2136.1s	combination/overtone?	
2116.0ms	$\nu_{sym}(CD_2)$ a′	2
2100.8ms	combination/overtone?	
2062.0vs	$\nu_{sym}(CD_3)$ a′	3
1126.7m	$\delta_{sym}(CD_3)$/ν(CC) a′	4
1055.7ms	$\delta_{asym}(CD_3)$ a′, a″	5, 14
968.8w	a′	6
932.9vs	$\omega(CD_2)$ a′, a″	7, 15
679.8ms	a′	9

Methylene group vibrations. In contrast with the methyl-group vibrations, there are marked difficulties in interpreting the ν(CH) and ν(CD) vibrations in the methylene group. There is also a clear difference between the iron and ruthenium compounds, on the one hand, and the molybdenum and tungsten compounds on the other. In both cases the methylene ν(CH) bands differ significantly from those of $[TiEt(cp)Cl_2]$, from which it was inferred that the CH_2 group was asymmetric.[1] In the iron and molybdenum compounds we have the advantage of data for the CHD_2CHDM species, yielding more direct evidence for $\nu^{is}(CH)$ in the methylene group than was available in the $[TiEt(cp)Cl_2]$ study. In each CHD_2CHDM species there are three conformers in which the solitary methylene C–H bond may be *trans* to a methyl C–H^a bond or *gauche* to C–H^a, or *gauche* to C–H^s (Scheme 2). The three coupling shifts involved may be estimated using the scaled *ab initio* interaction force constants determined for chloroethane;[8] in the case of the iron compound these are +0.8, −0.5 and +0.2 cm^{-1}, respectively, for the three possibilities listed above. The shifts observed in the CHD_2 frequencies from CHD_2CD_2M to CHD_2CHDM (3.0, 1.6 cm^{-1}) must arise from other causes, such as band overlap. We therefore take 2907.5 and 2917.5 cm^{-1} as the $\nu^{is}(CH)$ values of the methylene groups in $[FeEt(cp)(CO)_2]$ and $[MoEt(cp)(CO)_3]$, respectively.



Scheme 2

Table 9 Fermi-resonance estimates for the CH_3 group in MEt compounds

	$[M(CD_2CH_3)(cp)(CO)_2]$		$[M(CD_2CH_3)(cp)(CO)_3]$	
	M = Fe	Ru	M = Mo	W
Standard *W* values[a]				
ν_{calc} $\nu_{asym}(CH_3)$ a″	2950.6	2949.2	2964.6	2959.2
$\nu_{sym}(CH_3)$ a′	2931.8	2932.0	2943.5	2939.8
$2\delta_{asym}(CH_3)$ A′[b]	2908.7	2908.8	2915.8	2917.0
$2\delta_{asym}(CH_3)$ A″[b]	2887.7	2888.2	2891.1	2890.9
$2\delta_{asym}(CH_3)$ A′	2884.2	2884.5	2888.8	2888.5
$\nu_{sym}(CH_3)$ a′	2850.7	2851.7	2858.9	2859.3
$2\delta_{sym}(CH_3)$ A′	2717.3	2716.1	2728.2	2728.0
$\lambda_{a,s}$	−17.99	−17.08	(−18.75)[c]	−18.75
$\lambda_{a,a}$	−21.83	−20.98	(−22.51)[c]	−22.51
$2\delta^{o}_{asym}(A_1)$	2894.5	2894.9	(2902.3)[c]	2902.3
$2\delta^{o}_{asym}(E)$	2891.1	2891.6	(2894.0)[c]	2894.0
$2\delta^{o}_{sym}(A_1)$	2728.4	2727.0	(2739.4)[c]	2739.4
All *W*'s = 0[d]				
$\nu_{asym}(CH_3)$ a″	2947.3	2946.4	2961.8	2956.2
$\nu_{asym}(CH_3)$ a′	2918.6	2918.1	2931.3	2927.9
$\nu_{sym}(CH_3)$ a′	2860.3	2861.6	2868.3	2869.1
Fermi-resonance shifts ($\nu - \nu_{calc}$)[e]				
$\nu_{asym}(CH_3)$ a″	−3.3	−2.8	−2.8	−3.1
$\nu_{asym}(CH_3)$ a′	−13.2	−13.9	−12.2	−11.9
$\nu_{sym}(CH_3)$ a′	9.6	9.9	9.4	9.9

[a] See footnote to Table 4. [b] $W_{155} = 32$, $W_{455} = 20$, $W_{122} = 40$ cm^{-1}, nomenclature as for methyl halides.[1] Calculation refines $\lambda_{a,s}$, $\lambda_{a,a}$ and unperturbed overtone levels to values which give best fit to experimental frequencies. [c] Constrained. [d] Calculation of theoretical unperturbed frequencies using $\lambda_{a,a}$, $\lambda_{a,s}$ and $2\delta^{o}_{asym}$, $2\delta^{o}_{sym}$ values from above. [e] Shifts applied to observed frequencies.

Table 10 Harmonic local-mode force field for methyl CH and CD stretching vibrations

	$[MEt(cp)(CO)_2]$				$[MEt(cp)(CO)_3]$			
	M = Fe		Ru		M = Mo		W	
	ν_{obs}[a]	ε_v[b]	ν_{obs}[a]	ε_v[b]	ν_{obs}[a]	ε_v[b]	ν_{obs}[a]	ε_v[b]
CH_3	2949.9	3.6	2949.0	2.0	2962.2	2.2	2956.9	1.4
	2921.7	0.1	2920.6	0.3	2932.3	−0.7	2928.8	0.5
	2861.9	2.3	2862.6	2.7	2868.1	−1.1	2869.7	−0.4
CD_3	2205.4	−3.4	2208.2	−2.3	2213.2	−6.4	2212.7	−4.7
	2186.4	1.3	2184.6	0.6	2189.9	−2.4	2186.4	−3.8
	2079.2	−1.6	2078.1	−2.5	2087.5	−1.5	2085.0	−2.2
CH^sD_2	2877.3	−0.1	2877.3	−0.1	2884.8	0.1	2887.9	0.1
	—	(2209)	—	(2211)	—	(2220)	—	(2217)
	—	(2131)	—	(2130)	—	(2141)	—	(2135)
CH^aD_2	2927.5	−0.1	2927.4	0.0	2941.3	0.2	2935.7	0.2
	—	(2193)	—	(2193)	—	(2202)	—	(2199)
	—	(2110)	—	(2110)	—	(2117)	—	(2117)
$H^a–C–H^a/°$	108.5		109.0		108.5		109.5	
$H^a–C–H^s/°$	108.0		108.0		108.0		108.0	
f_s	4.5328		4.5330		4.5563		4.5663	
f_a	4.6926		4.6922		4.7364		4.7183	
$f'_{a,s}$	0.0508		0.0523		0.0533		0.0540	
$f'_{a,a}$	0.0514		0.0516		0.0521		0.0538	
ΣWSE[c]	1.52		0.91		2.26		1.77	

[a] After Fermi-resonance corrections to ν_1', ν_2, ν_3 of CH_3, ν_3 of CD_3. Uncertainties in ν_{obs} ± 5 cm^{-1} [$\nu(CH_3)$, $\nu(CD_3)$], ± 1 cm^{-1} (ν^{is}). [b] $\varepsilon_v = \nu_{obs} - \nu_{calc}$; ν_{calc} in parentheses. [c] Sum of weighted squares of errors.

In the CH stretching region in $[Fe(CH_2CD_3)(cp)(CO)_2]$ we observe a broad asymmetric strong band centred at 2914.5 cm^{-1} and a moderately intense narrow band at 2834.1 cm^{-1}. The latter is clearly $2\delta_{sym}(CH_2)$, in close resonance with $\nu_{sym}(CH_2)$, causing $\nu_{sym}(CH_2)$ and $\nu_{asym}(CH_2)$ to overlap in the band at 2914.5 cm^{-1}. The $\delta_{sym}(CH_2)$ fundamental lies under a cyclopentadienyl band near 1430 cm^{-1}. A difficult subtraction using species with no CH_3 or CH_2 groups present suggests a centre at about 1436 cm^{-1}. Using a conventional anharmonicity constant, *x*, of −5.0 cm^{-1} for the $\delta_{sym}(CH_2)$ mode, the calculated resonance shift on $2\delta_{sym}(CH_2)$ is 28 cm^{-1}, which puts $\nu^{\circ}_{sym}(CH_2)$ at 2886.5 cm^{-1}. As the $\nu^{is}(CH)$ value must lie midway between the unperturbed values of $\nu_{sym}(CH_2)$ and $\nu_{asym}(CH_2)$, we deduce the position of $\nu_{asym}(CH_2)$ to be 2928.5 cm^{-1}, corresponding to a $\nu^{\circ}_{asym}(CH_2) - \nu^{\circ}_{sym}(CH_2)$ split of 42 cm^{-1}. The *W* value of 38.3 cm^{-1} implied by the Fermi-resonance correction is acceptable.

The spectrum of $[Ru(CH_2CD_3)(cp)(CO)_2]$ is very like that of the iron compound, but with both observed bands [*i.e.* the overlapping $\nu_{sym}(CH_2)/\nu_{asym}(CH_2)$ band, and $2\delta_{sym}(CH_2)$] 6–7 cm^{-1} higher than for the latter. In the absence of CHD_2CHDRu data, we estimate $\nu^{is}(CH)$ for the methylene group to be 2912 ± 2 cm^{-1}, about 5 cm^{-1} higher than for the iron compound, comparable with the rise in $\nu^{is}(CH)$ observed from $[Fe(CHD_2)(cp)(CO)_2]$ to $[Ru(CHD_2)(cp)(CO)_2]$.[2]

Turning to the molybdenum and tungsten compounds, the CH stretching region of $[Mo(CH_2CD_3)(cp)(CO)_3]$ contains three bands, with $\nu_{asym}(CH_2)$ and $\nu_{sym}(CH_2)$ being more clearly separated than was the case for the iron or ruthenium compounds. From the value of $\nu^{is}(CH)$ (2917 cm^{-1}) with $\nu_{asym}(CH_2)$ 2949.8 cm^{-1}, $\nu^{\circ}_{sym}(CH_2)$ is predicted to lie at 2885.2 cm^{-1}. The Fermi-resonance shift on $\nu_{sym}(CH_2)$ is then 36.4 cm^{-1}, in turn placing $2\delta^{\circ}_{sym}(CH_2)$ at 2847.3 cm^{-1} and $\delta_{sym}(CH_2)$ near 1440 cm^{-1} for the CH_3CH_2Mo isotopomer. In this case, coupling with $\delta_{asym}(CH_3)$ is likely to depress $\delta_{sym}(CH_2)$ by about 3 cm^{-1}, making the most likely estimate for $\delta_{sym}(CH_2)$ of the CD_3CH_2Mo isotopomer to be 1443 cm^{-1}. The resulting value of the anharmonicity constant *x* is −5.85 cm^{-1}, close to that assumed for the iron compound. The close approach of $\nu^{\circ}_{sym}(CH_2)$ and $2\delta^{\circ}_{sym}(CH_2)$ (10.9 cm^{-1}) is compatible with the observed intensity distribution, and the associated *W* value (41.5 cm^{-1}) is within acceptable limits.

There is a modest increase in $\nu^{is}(CH)$ (10 cm^{-1}) from the iron to the molybdenum compound, and a marked increase in the $\nu_{asym}(CH_2) - \nu_{sym}(CH_2)$ separation, from 42 (Fe) to 64.6 cm^{-1} (Mo).

In the case of the tungsten compound we have no information from a CHD_2CHD isotopomer, and $\delta_{sym}(CH_2)$ of $[W(CH_2CD_3)(cp)(CO)_3]$ is obscured by a cyclopentadienyl band. The $\nu_{sym}(CH_2) - 2\delta_{sym}(CH_2)$ separation is 79.1 cm^{-1}, so the resonance shift cannot be more than 39.6 cm^{-1}, for exact coincidence of $\nu^{\circ}_{sym}(CH_2)$ and $2\delta^{\circ}_{sym}(CH_2)$, giving a minimum value for $\nu^{\circ}_{sym}(CH_2)$ of 2875.5 cm^{-1}. The separation $\nu_{asym}(CH_2) - \nu^{\circ}_{sym}(CH_2)$ is then $\leqslant$65.5 cm^{-1} and the average of $\nu_{asym}(CH_2)$ and $\nu^{\circ}_{sym}(CH_2)$, which will give $\nu^{is}(CH)$, is $\geqslant$2908 cm^{-1}. A value of about 2910 cm^{-1} for $\nu^{is}(CH)$ for the methylene group in $[WEt(cp)(CO)_3]$, about 8 cm^{-1} below the corresponding value for the molybdenum compound, would be compatible with the differences observed between the methyl $\nu^{is}(CH)$ frequencies of $[MoMe(cp)(CO)_3]$ and $[WMe(cp)(CO)_3]$.[3]

The $\nu(CD_2)$ modes in the CH_3CD_2M isotopomers are more difficult to analyse. The iron and ruthenium compounds have three major bands in this region, with additional weak features, and a similar complexity is found for the molybdenum and tungsten compounds. In Table 11(*a*) we show the values of $\nu^{\circ}_{sym}(CD_2)$ and $\nu^{\circ}_{asym}(CD_2)$ for $[Fe(CD_2CH_3)(cp)(CO)_2]$ calculated from a harmonic local-mode force field using the $\nu_{asym}(CH_2)$ and $\nu^{\circ}_{sym}(CH_2)$ frequencies from the CD_3CH_2Fe isotopomer, for various H–C–H angles from 102 to 110°. A band observed at 2117 cm^{-1} in the experimental spectrum is close to the predicted values for $\nu_{sym}(CD_2)$ and is therefore not likely to be seriously affected by resonance. The major interaction appears to be between the two higher bands, at 2222 and 2181 cm^{-1}, which must involve $\nu_{asym}(CD_2)$ and an A″ combination level. The centre of this doublet, 2202 cm^{-1}, lies about 9 cm^{-1} above the predicted $\nu_{asym}(CD_2)$ value for H–C–H 106°. Unfortunately the fundamentals responsible for an A″ combination near 2210 cm^{-1} are hard to locate. The only suitable A″ mode appears to be $\rho(CH_3)$, ν_{15}, to which a shoulder or band near 1095 cm^{-1} is assigned for all four compounds. The necessary A′ fundamental would then have to

Table 11 Harmonic local-mode predictions of $\nu_{asym}(CD_2)$ and $\nu_{sym}(CD_2)$

H–C–H/°	F_{as}	F_s	f'	$\nu_{asym}(CD_2)$	$\nu_{sym}(CD_2)$	$\Delta\nu$
	mdyn $Å^{-1}$			cm^{-1}		
(*a*) $[Fe(CD_2CH_3)(cp)(CO)_2]$[a]						
102	4.6234	4.6388	0.0077	2188.5	2127.6	60.9
104	4.6115	4.6513	0.0200	2190.9	2125.1	65.8
106	4.5997	4.6637	0.0322	2193.2	2122.6	70.6
108	4.5880	4.6760	0.0440	2195.5	2120.1	75.4
110	4.5766	4.6883	0.0559	2197.7	2117.6	80.1
(*b*) $[Mo(CD_2CH_3)(cp)(CO)_3]$[b]						
102	4.6909	4.6346	−0.0280	2204.5	2126.7	77.8
104	4.6788	4.6471	−0.0158	2206.8	2124.1	82.7
106	4.6668	4.6595	−0.0037	2209.1	2121.6	87.5
108	4.6550	4.6718	0.0084	2211.4	2119.1	92.3
110	4.6434	4.6841	0.0203	2213.7	2116.6	97.1

[a] Based on $\nu_{asym}(CH_2)$ 2928.5, $\nu_{sym}(CH_2)$ 2886.5, $\Delta\nu$ 42 cm^{-1}. [b] Based on $\nu_{asym}(CH_2)$ 2949.8, $\nu_{sym}(CH_2)$ 2885.2, $\Delta\nu$ 64.6 cm^{-1}.

Table 12 Carbon–hydrogen bond lengths and angles in $[MEt(cp)(CO)_2]$ and $[MEt(cp)(CO)_3]$

Methyl groups		$\nu^{is}(CH)$[a]/cm^{-1}	$r_0(C–H)$[b]/Å	H–C–H[c]/°
$[Fe(CD_2CHD_2)(cp)(CO)_2]$	CH^a	2927	1.097_7	108.0, 108.5
	CH^s	2877	1.102_9	
$[Ru(CD_2CHD_2)(cp)(CO)_2]$	CH^a	2927	1.097_7	108.0, 109.0
	CH^s	2877	1.102_9	
$[Mo(CD_2CHD_2)(cp)(CO)_2]$	CH^a	2941	1.096_3	108.0, 108.5
	CH^s	2885	1.102_0	
$[W(CD_2CHD_2)(cp)(CO)_2]$	CH^a	2936	1.096_8	108.0, 109.5
	CH^s	2888	1.101_7	
Methylene groups				
$[Fe(CHDCHD_2)(cp)(CO)_2]$		2907	1.099_8	$\leqslant 106$[d]
$[Ru(CHDCHD_2)(cp)(CO)_2]$		≈ 2912[e]	1.099_3	
$[Mo(CHDCHD_2)(cp)(CO)_3]$		2917	1.098_8	$\approx 108?$[d]
$[W(CHDCHD_2)(cp)(CO)_3]$		≈ 2910[e]	1.099_5	

[a] Measured in CCl_4 solution. [b] From $r_0(C–H) = 1.3982 - 0.000\,102\,3\,[\nu^{is}(CH)_{obs} + 10]$.[20] [c] H^a–C–H^s, H^a–C–H^a. [d] See text. [e] Estimated.

lie just above 1095 cm^{-1}. The missing fundamental, $\delta_{sym}(CD_2)$, ν_6 (a′) should be found here.

The results in Table 11(*a*) show that the fit of the calculated to the observed $\nu_{sym}(CD_2)$ frequency (2117 cm^{-1}) improves as the H–C–H angle increases, but the value of the interaction constant f' also increases in this direction. Given that f' values in methylmetal compounds are usually low (typically < 0.03 mdyn $Å^{-1}$) an H–C–H angle $\leqslant 106°$ is probably to be preferred.

Table 11(*b*) shows the results of force-field calculations for $[Mo(CD_2CH_3)(cp)(CO)_3]$ analogous to those in Table 11(*a*). An H–C–H angle of 104–106° gives a $\nu_{sym}(CD_2)$ frequency close to the observed band at 2124 cm^{-1}, while a resonance shift of only about 20 cm^{-1} would be required to fit $\nu_{asym}(CD_2)$ to the band at 2229 cm^{-1}. There is however a striking change in the range of f' values, from −0.03 to 0.02 mdyn $Å^{-1}$ in the molybdenum compound for H–C–H 102–110°, to 0.01 to 0.06 mdyn $Å^{-1}$ in the iron compound, for the same range of angles. This arises from the greatly increased $\nu_{asym}(CH_2) - \nu_{sym}(CH_2)$ separation $\Delta\nu$, from 42 (Fe) to 64.6 cm^{-1} (Mo). For $[Ti(CH_2CD_3)(cp)Cl_2]$[1] a $\nu_{asym}(CH_2) - \nu_{sym}(CH_2)$ separation of 85 cm^{-1} was interpreted as indicating the presence of an asymmetric methylene group, with two inequivalent C–H bonds. The separation of 64.6 cm^{-1} for $[Mo(CH_2CD_3)(cp)(CO)_3]$ might suggest a smaller but similar effect. However a simple calculation makes this rather improbable. The maximum displacement of $\nu_{sym}(CH_2)$ can only be 41.9 cm^{-1}, for exact coincidence of $\nu^{\circ}_{sym}(CH_2)$ and $2\delta^{\circ}_{sym}(CH_2)$, so that the maximum sum $\nu_{asym}(CH_2) + \nu^{\circ}_{sym}(CH_2)$ is 5829.6 cm^{-1}. With one $\nu^{is}(CH)$ already identified at 2917.5 cm^{-1}, the second could only be 2912.1 cm^{-1}, at the lowest, virtually identical with the first. In addition of course we see no evidence for two methylene $\nu^{is}(CH)$ bands in the spectrum of the CHD_2CHDMo isotopomer. We conclude that the CH_2 group is symmetrical, but that it differs markedly from that in the iron compound, either in its f' value, or in the H–C–H angle, or both.

The spectra of the CH_3CD_2 isotopomers of the ruthenium and tungsten compounds are generally very similar to those of their iron or molybdenum analogues, and require little further comment, other than to note that $\nu_{sym}(CD_2)$ of $[Ru(CD_2CH_3)(cp)(CO)_2]$ is about 7 cm^{-1} below the corresponding frequency of $[Fe(CD_2CH_3)(cp)(CO)_2]$ whereas the small increase in $\nu^{is}(CH)$, for the methylene group, from iron to ruthenium suggests it should be slightly higher. The resonances affecting $\nu_{sym}(CD_2)$ in the ruthenium compound appear to be rather stronger than those occurring in the iron compound.

$[Fe(C_2D_5)(cp)(CO)_2]$.—This isotopomer is not directly relevant to the C–H bond study, but the frequencies in Table 8 are included for completeness. The proposed assignments and numbering system are based on those for C_2D_5Cl.[9]

Discussion

In Table 12 we list the $\nu^{is}(CH)$ frequencies, calculated bond lengths, $r_0(C–H)$, and H–C–H angles for the ethyl C–H bonds in the iron, ruthenium, molybdenum and tungsten compounds, together with those previously determined for $[TiEt(cp)Cl_2]$.[1] As before, the $r_0(C–H)$ values are derived from the standard $r_0(C–H)$–$\nu^{is}(CH)$ correlation for the gas phase,[21] the observed $\nu^{is}(CH)$ frequencies for CCl_4 solution being increased by 10 cm^{-1} to allow for the normal solution–gas frequency shift. In

Table 13 Frequencies ν^{is}(CH) (cm^{-1}) for some organometallic[a] and organic molecules

		ν^{is}(CH)	ν^{is}(CH)$_{av}$	ν^{is}(CH^a) − ν^{is}(CH^s)	Ref.
(*a*) Methyl groups in EtX and MeCOR compounds					
CHD_2CD_3		2950			
[FeEt(cp)(CO)$_2$]	CH^a	2937	2920	50	9
	CH^s	2887			
[RuEt(cp)(CO)$_2$]	CH^a	2937	2920	50	*b*
	CH^s	2887			
[MoEt(cp)(CO)$_3$]	CH^a	2951	2932	56	*b*
	CH^s	2895			
[WEt(cp)(CO)$_3$]	CH^a	2946	2930	48	*b*
	CH^s	2898			
[TiEt(cp)Cl$_2$]	CH^a	2942	2930	35	1
	CH^s	2907			
EtF	CH^a	2973	2967	16	10, 22
	CH^s	2957			
EtI	CH^a	2969	2955	41	10, 22
	CH^s	2928			
EtCN		2973			23
MeCHO	CH^a	2945	2964	−57	23
	CH^s	3002			
MeCOF	CH^a	2980	2995	−45	23
	CH^s	3025			
MeCOCl	CH^a	2979	2987	−25	23
	CH^s	3004			
MeCOBr	CH^a	2978	2984	−17	23
	CH^s	2995			
MeCOI		2978			23
MeCOMe	CH^a	2946	2965	−58	23
	CH^s	3004			
(*b*) Methylene groups					
[FeEt(cp)(CO)$_2$]		2917			*b*
[RuEt(cp)(CO)$_2$]		2922			*b*
[MoEt(cp)(CO)$_3$]		2927			*b*
[WEt(cp)(CO)$_3$]		2920			*b*
[TiEt(cp)Cl$_2$]		2910			1
		2857			
EtF		2950			10
EtI		2998			10
(*c*) Methylmetal compounds					
[FeMe(cp)(CO)$_2$]		2945			2
[RuMe(cp)(CO)$_2$]		2950			2
[CrMe(cp)(CO)$_3$]	CH^a	2963	2967	−13	3
	CH^s	2976			
[MoMe(cp)(CO)$_3$]	CH^a	2956	2962	−18	3
	CH^s	2974			
[WMe(cp)(CO)$_3$]	CH^a	2943	2951	−23	3
	CH^s	2966			
[TiMe(cp)Cl$_2$]	CH^a	2958	2945	40	1
	CH^s	2918			

[a] For the organometallic compounds observed CCl_4 solution frequencies were increased by 10 cm^{-1} for comparison with gas-phase data for organic compounds. [b] This work.

Table 13 we include ν^{is}(CH) values for other ethyl compounds, and for selected methyl compounds.

The most striking feature to emerge from the spectra of all four compounds is the very marked asymmetry of the terminal methyl group, indicated by the appearance of well separated ν^{is}(CH^a) and ν^{is}(CH^s) bands and the splitting of the $\nu_{asym}(CH_3)$ and $\nu_{asym}(CD_3)$ levels. The differences ν^{is}(CH^a) − ν^{is}(CH^s) are in the range 48–56 cm^{-1} and are comparable with the largest separations found for purely 'organic' ethyl or acetyl compounds.[9,10,22–24] The corresponding ν^{is}(CH^a) − ν^{is}(CH^s) splittings for asymmetric methyl groups directly bound to metal atoms rarely approach these values. A reduction of 50 cm^{-1} in ν^{is}(CH) corresponds to a decrease of about 18.0 kJ mol^{-1} in the C–H bond-dissociation energy,[9] implying that the C–H^s bonds in the terminal methyl groups of the ethylmetal compounds are about 4.5% weaker than the C–H^a bonds in the same groups. [From D°_{298}(C–H) = 0.3605 ν^{is}(CH) − 646.8 kJ mol^{-1}.[9]]

One obvious conclusion arising from the observation of separate methyl ν^{is}(CH^a) and ν^{is}(CH^s) levels is that the methyl groups must be subject to a substantial barrier to internal rotation. Typically, these barriers in sterically unhindered alkyl groups are about 12 kJ mol^{-1}, and there is no need to assume that those in the ethylmetal compounds are significantly different, either in nature or in magnitude.

The absence of any frequency doubling in the C–H and C–D stretching regions, despite the clear evidence for the presence of C_s and C_1 conformers, indicates that the methyl C–H bonds are unaffected by their orientation relative to the cyclopentadienyl and carbonyl ligands. We therefore need look no further than the metal atom for the cause of the asymmetry in the methyl group, and can treat the system essentially as CH_3CH_2X. The other ligands will of course exert a more general non-directional effect to the extent that they may modify the effective electronegativity of the metal atom and hence influence the strength of its overall interaction with the methyl group. This is in very marked contrast to the situation in methylmetal compounds, where the ligands attached to the metal atom are β to the methyl C–H bonds and have direct *trans* or *gauche* effects on the properties of individual bonds.

It is clear from the ν^{is}(CH) data in Table 13 that the substituent effects of electropositive metal atoms are very different from those of halogens or other electronegative atoms or groups. Taking ν^{is}(CH) for ethane (CHD_2CD_3, 2950 cm^{-1}) as an initial point of reference, it is evident that the primary effect of the metal atom is sharply to weaken the β-C–H bond *trans* to it ($C–H^s$), with an accompanying but much smaller effect on the *gauche* bonds ($C–H^a$). In non-organometallic compounds substituent effects tend to be more variable and have been discussed in detail elsewhere.[9] In the ethyl halides the halogen atoms consistently strengthen the β-C–H bonds *gauche* to them ($C–H^a$) but have different effects on the *trans* bonds, from a small increase in $\nu^{is}(CH^s)$ for EtF to a rather larger decrease for EtI.[9,10] The net result is to produce an asymmetric methyl group of the same type as in the ethylmetal compounds, with $\nu^{is}(CH^a) > \nu^{is}(CH^s)$, but by a very different route. In the acetyl compounds, in contrast,[23] the asymmetry of the methyl group is in the opposite sense, with $\nu^{is}(CH^a) < \nu^{is}(CH^s)$. However, one point which emerges very clearly from the average ν^{is}(CH) values in Table 13 is that the overall effect of metal atom substituents is to weaken the β-C–H bonds whereas electronegative substituents strengthen them.

The origin of the very strong *trans* effect of the metal atom on the β-$C–H^s$ bond is not obvious, but if the metal–carbon bond has a significant degree of ionic character in the sense $C^-–M^+$ this might assist an effect similar to that found in CH_3–N and CH_3–O systems, whereby lone-pair electron density is relocated into a σ* orbital in the *trans* C–H bond, producing a marked weakening effect.[9]

Given the well established tendency of ethylmetal compounds to decompose *via* β-hydride-transfer pathways, it is interesting that our data do show that one β-C–H bond is particularly weak. We must add, of course, that the five ethylmetal compounds studied {including [TiEt(cp)Cl_2]} all have staggered conformations (C_s or C_1) whereas for an intramolecular β-hydride transfer the ethyl group would have to adopt an eclipsed (or almost eclipsed) conformation. There is no evidence to suggest that the C–H bond lengths and strengths we predict from our spectra would be unchanged in an eclipsed structure even though they are apparently unaffected by the less drastic change from a C_s to a C_1 conformation. Also, although the methyl $C–H^s$ bonds are noticeably weaker than the $C–H^a$ bonds, and are about 10% weaker than the C–H bonds in methane, in absolute terms they are still relatively strong [$D°_{298}$(CH) ≈395 kJ mol^{-1}]. The problem here is to identify a 'threshold' ν^{is}(CH) frequency and C–H bond length at which one might reasonably speculate that the C–H bond reactivity (*i.e.* the likelihood that the bond might be broken) may be measurably enhanced. It is worth adding that reactions do not necessarily have to proceed by an intramolecular route, and the $C–H^s$ bonds, in either the C_s or the C_1 conformation, will be readily accessible for intermolecular attack.

For the methylene groups, the ν^{is}(CH) frequency of [Fe($CHDCD_3$)(cp)$(CO)_2$] is 28 cm^{-1} below that of the methyl compound [Fe(CHD_2)(cp)$(CO)_2$],[2] and the corresponding frequency of [Mo($CHDCD_3$)(cp)$(CO)_3$] is 29 cm^{-1} below $\nu^{is}(CH^a)$ of [Mo(CHD_2)(cp)$(CO)_3$].[3] The calculated methylene ν^{is}(CH) frequencies of the ethyl-ruthenium and -tungsten compounds are similarly shifted, by ≈28 and ≈23 cm^{-1}, respectively from the analogous ν^{is}(CH) frequencies of the methyl compounds. These shifts are well within the range of the normal α effect of methyl substitution.[9]

Although the methylene ν^{is}(CH) frequencies of the iron and molybdenum compounds are not greatly different, the force-field calculations (Table 11) do suggest that the two molecules are not directly comparable. There are very marked differences between the corresponding methyl compounds, [FeMe(cp)$(CO)_2$] and [MoMe(cp)$(CO)_3$], with apparently free methyl-group rotation in the former but a substantial barrier in the latter.[2] We have tentatively attributed this to the steric problems which arise in the more crowded tricarbonyl molecule. If this is correct, differences between the methylene C–H bonds in the ethyl-iron and -molybdenum compounds are not unexpected. In the force-field calculation these differences can be accounted for either by assuming that the H–C–H angle is noticeably larger in the molybdenum than in the iron compound, or that the interaction force constant f' is anomalously low in the molybdenum compound. If the methylene group in the ethylmolybdenum compound is significantly more crowded than the corresponding group in the ethyliron compound, as seems very likely, an increase in the H–C–H angle would be a natural consequence. Accordingly, we feel that the best interpretation of the force-field data is to assume ≈108° for the methylene H–C–H angle in [MoEt(cp)$(CO)_3$], with a 'normal' small positive value for the stretch–stretch interaction constant.

Finally, the results obtained for the [MEt(cp)$(CO)_2$] and [MEt(cp)$(CO)_3$] complexes tend to support our earlier conclusions[1] concerning the structure of [TiEt(cp)Cl_2]. The methyl group in the titanium compound is broadly similar to those in the other four ethylmetal compounds, albeit with a rather smaller $\nu^{is}(CH^a) - \nu^{is}(CH^s)$ separation. There is no evidence of a β-agostic effect analogous to those reported for certain other ethyltitanium compounds.[25–28] However, there are two salient points of difference between [TiEt(cp)Cl_2] and the [MEt(cp)$(CO)_2$] and [MEt(cp)$(CO)_3$] compounds. First, the ethyl group in the titanium compound clearly is present in only one conformation, with no evidence of the C_s–C_1 isomerism observed in the other molecules. Secondly, the CH_2 and CD_2 stretching-frequency data can only be satisfactorily accounted for if we assume that the methylene group contains two inequivalent C–H bonds. Our estimated ν^{is}(CH) frequencies for these bonds are 2910 and 2858 cm^{-1}. The higher frequency is comparable with ν^{is}(CH) for the methylene groups in [FeEt(cp)$(CO)_2$] or [MoEt(cp)$(CO)_3$] and thus presumably represents a 'normal' methylenic C–H bond. The lower frequency, however, is markedly abnormal, as the results for the iron and molybdenum compounds show, and we have attributed this to a weak α-agostic interaction with the titanium atom. Such an interaction would of course tend to inhibit rotation about the Ti–C bond and hence could account for the observation of only one conformer (C_1) in the titanium compound. Comparable interactions are not to be expected in the 18-electron iron and molybdenum compounds and hence there is no effective barrier, in these compounds, to C_s–C_1 isomerism.

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