Methyl Group Geometries, C–H Bond Properties and Internal Rotation in Dicarbonyl(η^5-cyclopentadienyl)methyl-iron(II) and -ruthenium(II), [MMe(η^5-C_5H_5)$(CO)_2$] (M = Fe or Ru)†

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Vibrational spectra have been recorded for the CH_3, CD_3 and CHD_2 isotopomers of [MMe(cp)$(CO)_2$] (M = Fe or Ru; cp = cyclopentadienyl). The effects of Fermi resonance were considered in detail and the resonance-corrected CH and CD stretching frequencies used to predict methyl group geometries. Only one 'isolated' CH stretching absorption, ν^{is}CH, is observed in each CHD_2 isotopomer. The results are not consistent with a model in which the methyl groups are subject to an effective barrier to internal rotation, with significant variation of CH bond length with orientation. The spectra are best interpreted in terms of an essentially freely rotating methyl group in which the individual CH bonds undergo a small variation in bond length with rotational angle. The larger barriers which occur in the tricarbonyl compounds [MMe(cp)$(CO)_3$] (M = Cr, Mo or W) are likely to be primarily steric in origin, whereas that in [TiMe(cp)Cl_2] may arise from an interaction between a CH bonding pair and an unoccupied titanium orbital. The Ru–CH_3 bond appears to be slightly weaker than the Fe–CH_3 bond, in contrast with results for earlier groups in the d block, in which M–CH_3 bond strengths increase down each group.

In earlier papers[1–10] we have used CH and CD stretching frequency data for the CH_3, CD_3 and CHD_2 isotopomers of methyl–metal compounds to predict methyl CH bond lengths, bond dissociation energies and HCH angles, to make qualitative estimates of metal–carbon bond strengths,[2,4] and to explore the effects of internal rotation.[5,6,8,10] In the d block, we have used this approach to establish the geometries of methyl derivatives of elements in the titanium,[1,2] chromium[4] and manganese[5–7] groups, and of dimethyl-zinc, -cadmium and -mercury.[3]

The spectra of the CHD_2 isotopomers of the titanium compounds {*e.g.*, [$TiMe_2(cp)_2$],[2] [TiMe(cp)Cl_2][1] and also [TiMe$(cp)_3$],[11] cp = η^5-C_5H_5} and of the chromium group compounds [MMe(cp)$(CO)_3$][4] (M = Cr, Mo or W) each display two well-resolved 'isolated' CH stretching absorptions, ν^{is}CH, indicating that the methyl group is subject to a significant barrier (> 4 kJ mol^{-1}, approx.) to internal rotation, and that the methyl CH bonds are not all equivalent in the minimum energy conformations. The groups have local C_s, rather than C_{3v} symmetry, and the observed ν^{is}CH bands are associated with bonds lying in (CH^s) or out of (CH^a) the symmetry plane. The $\nu_{asym}CH_3$ and $\nu_{asym}CD_3$ bands in the spectra of the CH_3 and CD_3 isotopomers correspondingly split into a' and a'' components.

The manganese and rhenium compounds [MMe$(CO)_5$] (M = Mn or Re), in contrast, display only one ν^{is}CH band,[5] even though it is not possible to write a structure for these molecules in which the three methyl CH bonds are formally equivalent. The gas-phase and solution spectra can only be understood in terms of a methyl group with free internal rotation. Initial studies of the gas-phase spectra appeared to suggest an appreciable variation in CH bond length and stretching force constant with the rotational angle,[5] but more recent matrix-isolation results indicate that any such variation must be very small[7]

Iron compounds of the type [FeL(cp)$(CO)_2$] have attracted wide attention because of their relative stability and because a variety of ligands L may be attached to the Fe(cp)$(CO)_2$ moiety. In the methyl compound [FeMe(cp)$(CO)_2$], the barrier to internal rotation of the methyl group has been estimated to be 22 ± 9 kJ mol^{-1} from ^{13}C NMR studies,[12] or *ca.* 12 kJ mol^{-1}, from a theoretical treatment.[13] More recently, the NMR data have been reanalysed to give an estimated maximum barrier height of 12 kJ mol^{-1} while a molecular mechanics (MMX) treatment suggests a lower value still ($\approx$5 kJ mol^{-1}).[14] The theoretical study[13] also suggests that the CH bonds lying in (CH^s) and out of (CH^a) the molecular symmetry plane (*i.e. trans* to cyclopentadienyl or *trans* to carbonyl) are likely to be appreciably different. As the barrier to internal rotation would need to be less than about 4 kJ mol^{-1} for inequivalent CH bonds to become indistinguishable in the vibrational spectrum, we would expect the spectrum of the CHD_2 isotopomer [Fe(CHD_2)(cp)$(CO)_2$] to resemble those of the [M(CHD_2)(cp)$(CO)_3$] species (M = Cr, Mo or W) with two well-resolved ν^{is}CH absorptions. In this paper we report a study of the CH_3, CD_3 and CHD_2 isotopomers of [FeMe(cp)$(CO)_2$], and of their ruthenium analogues.

Experimental

[MMe(cp)$(CO)_2$) (Me = CH_3, CD_3 or CHD_2; M = Fe *or* Ru).—The iron and ruthenium compounds were prepared using adaptations of earlier methods [equations (1) and (2)].[15,16]

$$[\{M(cp)(CO)_2\}_2] \xrightarrow{Na/Hg} 2Na[M(cp)(CO)_2] \quad (1)$$

$$Na[M(cp)(CO)_2] \xrightarrow{MeI} [MMe(cp)(CO)_2] \quad (2)$$

All operations were carried out in a dry nitrogen atmosphere, or on a vacuum line; all solvents were dried before use.

[FeMe(cp)$(CO)_2$].—The compound [{Fe(cp)$(CO)_2$}$_2$] (2 g) in tetrahydrofuran (thf) was stirred with a 4.2% Na/Hg amalgam (1.25 g Na in 30 g Hg) for 12 h. The resulting solution

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

of Na[Fe(cp)$(CO)_2$] was decanted, transferred to a vacuum line, degassed and treated with the appropriate methyl iodide (1.6 g). The reaction mixture was stirred for 3 h, during which a precipitate of NaI appeared. (Note: This precipitate is only obtained if a slight excess of MeI is used; without an excess of MeI, no precipitate forms.) The pale cream products were separated by sublimation at 60–70 °C onto an ice-cooled probe. The ^1H NMR spectra revealed no detectable impurities.

[RuMe(cp)$(CO)_2$].—This compound is more difficult to prepare than its iron analogue and a number of alternative methods have been suggested.[17,18] Nevertheless, despite reports to the contrary,[18] we have found the original method of Davidson, McCleverty and Wilkinson[16] to give satisfactory results. The compound [{Ru(cp)$(CO)_2$}$_2$] was obtained from the reaction of [{Ru$(CO)_3Cl_2$}$_2$] (Strem) (1g) with K(cp) in 1,2-dimethoxyethane.[19] The reaction mixture was refluxed for 12 h, the solvent removed *in vacuo* and the product separated as bright orange crystals by sublimation at 140–160 °C (0.1 mmHg) (55%).

A solution of [{Ru(cp)$(CO)_2$}$_2$] in thf was stirred with a large excess of 4.2% Na/Hg amalgam for 18 hours. The resulting dark red-brown solution of Na[Ru(cp)$(CO)_2$] was removed to the vacuum line and treated with MeI, as before. The reaction mixture was allowed to stir at 45 °C for several days; during this time the colour became a clearer red but no NaI precipitate appeared.

The solvent was removed and the product isolated as a pale yellow solid by sublimation at 40 °C (0.1 mmHg). The NMR spectrum (Me = CH_3) indicated the presence of traces of impurity (δ 1.2–1.3). These were removed and the colourless pure product obtained by a careful repeat sublimation. The initial sublimation products for Me = CD_3 and Me = CHD_2 (which were prepared on a very small scale) were quite strongly coloured and the IR spectra contained carbonyl impurity bands. These were again satisfactorily purified by repeat sublimations, yield *ca.* 25–30%.

Infrared Spectra.—The infrared spectra were recorded for CCl_4 solutions using a Nicolet 7199 FTIR spectrophotometer at 1 cm^{-1} resolution. The samples began to show evidence of decomposition (IR and NMR) after about 30 min in solution: all spectra were recorded using freshly prepared solutions.

Results

Cyclopentadienyl and Carbonyl Vibrations.—Absorptions arising from vibrations of the cyclopentadienyl[20] and carbonyl ligands are listed in Tables 1 (4000–800 cm^{-1}) and 2 (650–450 cm^{-1}, δMCO modes). The wavenumbers in Table 1 are quoted for the CH_3 isotopomers only; deuteriation of the methyl group affects certain bands in the δMCO region in the iron compound (see further below) which in turn cause the wavenumbers of combination bands near 2600 cm^{-1} in [Fe(CH_3)(cp)$(CO)_2$] to differ from those in [Fe(CD_3)(cp)$(CO)_2$]. Apart from this, the cyclopentadienyl and carbonyl bands in the CH_3, CD_3 and CHD_2 species are identical. In general, the cyclopentadienyl bands in the ruthenium compound are found a few wavenumbers lower than the corresponding transitions in the iron compound. The a_2 δ_{ip}CH mode is obscured by traces of impurity in some samples but is seen very weakly at 1262 cm^{-1} in the very pure iron compound, and is inferred at 1258 cm^{-1} from the combinations at 2269 (1258 + 1011) cm^{-1}, and 2258 (1258 + 998) cm^{-1} in the ruthenium compound. The e_1 νCC and δ_{ip}CH levels are split into two well-defined components, separated by 10–15 cm^{-1}, in both compounds. Similar but smaller splittings are observed in [MMe(cp)$(CO)_3$] (M = Cr, Mo or W), but not in [TiMe(cp)Cl_2] or [TiMe_2(cp)$_2$].[2] The e_1 δ_{op}CH mode is not split, nor are any of the e_2 modes.

The region 650–450 cm^{-1} contains the strong bands arising from the δMCO modes (Table 2). The assignments in the Table follow those of Manning[21] and use the same designations,

Table 1 Cyclopentadienyl and carbonyl bands in the region 4050–650 cm^{-1} for [M(CH_3)(cp)$(CO)_2$] (M = Fe or Ru)

ν_{obs} (M = Fe)	Assignment	Group	ν_{obs}* (M = Ru)
4010w	2 × 2011	CO	4029w
3943mw	2011 + 1955 3121 + 830	CO cp	3953mw
3897w	2 × 1955	CO	3904w
3121w 3107 (sh)	νCH a_1, e_1	cp cp	3121w 3103 (sh)
2647vw	2011 + 637	CO	2620w
2580vw	2011 + 570	CO	2544w
2524vw	1995 + 570	CO	2482w
2463vw	1955 + 510	CO	2467w
2420vw	1360 + 1060	cp	2408vw
2359vw	2011 + 350	CO	2368w
2340vw	1955 + 383	CO	
2277vvw	1261 + 1016	cp	2269vw
2263vvw	1261 + 1001	cp	2258vw
2011.2vs	$\nu_{asym}CO_2$ a″	CO	2019vs
1954.8vs	$\nu_{sym}CO_2$ a′	CO	1958vs
1924.7s	^{13}CO	CO	1929.7s
1844w	2 × 922	cp	1820w
1761w	922 + 844	cp	1736w
1670w	844 + 830 2 × 844	cp	1631w
1431.8 1419.3	νCC e_1	cp	≈1431ms 1417.5 (sh)
1360w	νCC e_2	cp	1352.2
1262vw	δ_{ip}CH a_2	cp	(1258)
1115.5mw	νCC a_1	cp	1108.1m
1108 (sh)	^{13}C	cp	1101.2 (sh)
1060vw	δ_{op}CH e_2	cp	1057.5w
1015.5 1001.2 ms	δ_{ip}CH e_1	cp	1010.8ms 998.2ms
921.5w	δ_{ip}CC e_2	cp	912.2w
844 (sh)	δ_{op}CH e_1	cp	≈827 (sh)
≈830vs	δ_{op}CH a_1	cp	≈816vs

* Assignments analogous to those for [Fe(CH_3)(cp)$(CO)_2$]. Values obtained from combination bands in parentheses. Additional bands and assignments for [Ru(CH_3)(cp)$(CO)_2$]: 2527w = 2019 + 507 or 1958 + 573; 2506w, 2444w, 2421vw cm^{-1}.

Table 2 Infrared bands in the region 650–450 cm^{-1} [a]

Compound	Δ_4 (b_1)	Δ_2 (a_2)	Δ_3 (b_2)	Δ_1 (a_1)	S_1 [b]
[Fe(CH_3)(cp)$(CO)_2$]	637.1vs	603.6(sh)	592.1vs	569.6s	≈515w
[Fe(CHD_2)(cp)$(CO)_2$]	637.3vs	597vs	br [c]	558.2s 543.4s	≈510vw
[Fe(CD_3)(cp)$(CO)_2$]	642.3vs	604.7s	594vs	541.7s	≈510vw
[Ru(CH_3)(cp)$(CO)_2$]	612.0s	599.5s	573vs	525vs	507vs
[Ru(CD_3)(cp)$(CO)_2$]	614.5s	595.3s	572.3vs	524.4vs	≈500s

[a] Notation from ref. 21. [b] Assigned to M–C stretching motion. [c] Asymmetric.

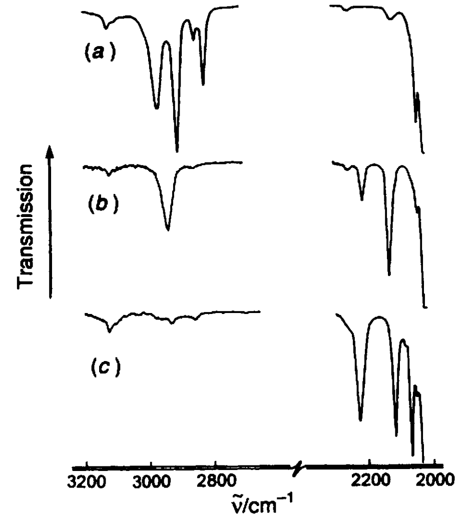

Fig. 1 Spectra of (*a*) [Fe(CH_3)(cp)$(CO)_2$], (*b*) [Fe(CHD_2)(cp)$(CO)_2$], (*c*) [Fe(CD_3)(cp)$(CO)_2$] in CH and CD stretching regions (CCl_4 solutions, maximum feasible concentrations, various pathlengths)

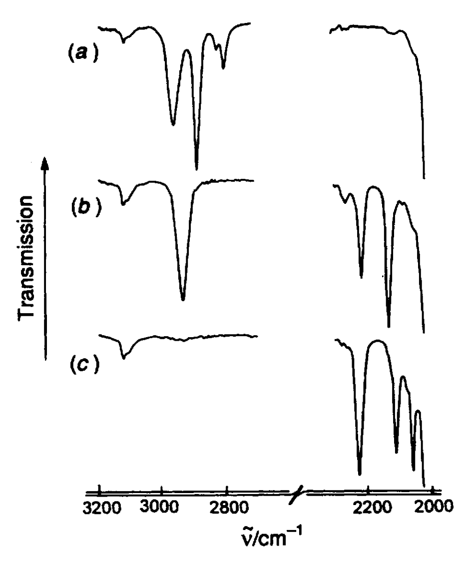

Fig. 2 Spectra of (*a*) [Ru(CH_3)(cp)$(CO)_2$], (*b*) [Ru(CHD_2)(cp)$(CO)_2$], (*c*) [Ru(CD_3)(cp)$(CO)_2$] in CH and CD stretching regions (CCl_4 solutions, maximum feasible concentrations, various pathlengths

Table 3 Infrared bands (cm^{-1}) assigned to the methyl group *

	[MMe(cp)$(CO)_2$]		
	M = Fe	Ru	Assignment
CH_3	2968.4ms	2964.2ms	$\nu_{asym}CH_3$ e
	2894.6s	2904.6s	$\nu_{sym}CH_3$ a_1
	2833.9w	2845.9w	$2\delta_{asym}CH_3$ E
	2810.6w	2820.9m	$2\delta_{asym}CH_3$ A_1
	≈1420	1424 (sh)	$\delta_{asym}CH_3$ e
	1172.9s	1194.6s	$\delta_{sym}CH_3$ a_1
CD_3	2224.3s	2225.5s	$\nu_{asym}CD_3$ e
	2110.5s	2117.3s	$\nu_{sym}CD_3$ a_1
	2077 (sh)	2087 (sh)	$2\delta_{asym}CD_3$ E
	2058.1s	2065.1s	$2\delta_{asym}CD_3$ A_1
		2050 (sh)	
	1038.1w	1044.9w	$\delta_{asym}CD_3$ e
	893.9s	909.4m	$\delta_{sym}CD_3$ a_1
CHD_2	2935.4	2939.8s	$\nu^{is}CH$
	2217.1ms	2219.6ms	$\nu_{asym}CD_2$
	2133.1s	2138.4s	$\nu_{sym}CD_2$
	2091vw		
	2056 (sh)		
	1294.5w		δCH
	1125.0	1139.3m	δCH
	974.5s	988.1s	δCD_2
	676ms	692w	δCD_2

* CCl_4 solution.

adding the supposed local C_{2v} symmetry labels. A weak cyclopentadienyl mode (δCCC, e_2) should also occur in the region 600–620 cm^{-1}, but is not observed and is unlikely to contribute significantly to the strong δMCO bands. There are several interesting differences between the iron and ruthenium compounds. The Δ_2 (a_2) band is observed as a shoulder on the intense Δ_3 (b_2) band in the iron compound, but appears as a separate strong band with intensity comparable to Δ_4 in the ruthenium compound. The Δ_1, Δ_3 and Δ_4 bands shift markedly downwards from iron to ruthenium, whereas Δ_2 moves very little. Deuteriation of the methyl group in [FeMe(cp)$(CO)_2$] produces a small upwards shift in Δ_4 and a marked downwards shift in Δ_1, suggesting the arrival of a′ and a″ ρCD_3 modes in this region. There is no sign of a corresponding effect in [RuMe(cp)$(CO)_2$]

Methyl Group Vibrations.—The spectra of the two compounds in the methyl CH and CD stretching regions are illustrated in Figs. 1 and 2, and frequency data for the CH_3, CD_3 and CHD_2 isotopomers are collected in Table 3. With the exception of $\nu_{asym}CH_3$, discussed further below, the frequencies in the ruthenium compound are consistently slightly higher than those in the iron compound, but apart from this the spectra of the analogous iron and ruthenium isotopomers are very similar.

In the CH_3 species we observe a single broad band due to $\nu_{asym}CH_3$, a narrower $\nu_{sym}CH_3$ band, and two weaker bands arising from the A_1 and E components of the bending overtone, $2\delta_{asym}CH_3$, at slightly lower frequencies. In the CD_3 species we observe a corresponding single $\nu_{asym}CD_3$ band, with $\nu_{sym}CD_3$ about 100 cm^{-1} lower, and in the CHD_2 species the $\nu^{is}CH$ band appears as a single, broad, symmetrical absorption with no evidence of resolution into components deriving from the isolated stretching motions of inequivalent in-plane and out-of-plane CH bonds.

These experimental observations are not consistent with a simple model which assumes the methyl group to be subject to a significant barrier to internal rotation and the lengths and stretching force constants of the methyl CH bonds to vary markedly with orientation. The simplest explanation is that $\nu^{is}CH$ is invariant, and that the broadening of the $\nu_{asym}CH_3$ and $\nu^{is}CH$ bands arises from relatively free internal rotation. In such a case, the methyl groups would resemble those in [MnMe$(CO)_5$] and [ReMe$(CO)_5$], in which the barrier to internal rotation must be very small indeed.[5] However, comparisons of the halfwidth data for the CH stretching vibrations in the manganese and rhenium compounds with those in [Fe(CH_3)(cp)$(CO)_2$] and [Ru(CH_3)(cp)$(CO)_2$] reveal certain differences (Table 4). The $\nu^{is}CH$ bands in the manganese and rhenium compounds are markedly narrower than those in the iron and ruthenium compounds, while the $\nu_{asym}CH_3$ bands are somewhat broader {the $\nu_{asym}CH_3$ band in [Re(CH_3)$(CO)_5$] is decidedly asymmetric and direct comparisons here may not be reliable}. It seems likely that in the iron and ruthenium compounds there is a larger variation of CH stretching force constant than is the case in [Mn(CH_3)$(CO)_5$] or [Re(CH_3)$(CO)_5$]. Nevertheless, whether there is free rotation or not, the variation in $\nu^{is}CH$ must still be very small: even if there is an effective barrier, the change in $\nu^{is}CH$ with orientation must be too small to be detected in those torsional levels which are occupied at room temperature. Overall, it is hard to escape the conclusion that in these molecules the methyl groups experience significantly lower barriers than are typically

Table 4 Bandwidths ($\nu_{\frac{1}{2}}$/cm^{-1}) of ν^{is}CH and νCH$_3$ bands in [MMe(cp)(CO)$_2$] (M = Fe or Ru) and [MMe(CO)$_5$] (M = Mn or Re)*

	[FeMe(cp)(CO)$_2$]	[RuMe(cp)(CO)$_2$]	[MnMe(CO)$_5$]	[ReMe(CO)$_5$]
ν^{is}CH	32	36	20	24
ν_{sym}CH$_3$	16	16	12	13
ν_{asym}CH$_3$	40	40	52	56

* In CCl$_4$ solution at *ca.* 20 °C.

found for methyl groups in aliphatic compounds ($\approx$12 kJ mol^{-1}).[22]

At lower frequencies, the bands due to δ_{asym}CH$_3$ cannot be located accurately, as they are partially obscured by a cyclopentadienyl band near 1430 cm^{-1}. The δ_{sym}CH$_3$ bands are obvious, at 1172.9 cm^{-1} (Fe) and 1194.6 cm^{-1} (Ru). In the CD$_3$ spectra the ν_{asym}CD$_3$ and 2δ_{asym}CD$_3$ (A$_1$) bands have equal intensities, indicating a very strong Fermi resonance. The δ_{asym}CD$_3$ and δ_{sym}CD$_3$ bands are easily recognised.

Fermi-resonance Corrections.—The superimposed spectra of the two [M(CH$_3$)(cp)(CO)$_2$] compounds in the CH stretching region are shown in Fig. 3. Two anomalies are immediately apparent: ν_{asym}CH$_3$ is lower in the ruthenium compound than in the iron compound, although every other methyl frequency is higher for ruthenium than for iron, and the intensity of the bending overtone 2δ_{asym}CH$_3$ (A$_1$) is much greater in the ruthenium compound.

The only acceptable explanation for the reversal in the expected order of the ν_{asym}CH$_3$ frequencies is that these bands are unequally affected by Fermi resonances, either raising ν_{asym}CH$_3$ (Fe) or lowering ν_{asym}CH$_3$ (Ru). As there are no bands above the CH stretching region which could interact appreciably with ν_{asym}CH$_3$, and hence depress it, we conclude that the observed effect must arise from differing interactions between the ν_{asym}CH$_3$ modes and lower-frequency modes, the interaction being the greater in the iron compound. The differing intensities of the two 2δ_{asym}CH$_3$ (A$_1$) overtones indicate that resonances involving this overtone must be stronger in [Ru(CH$_3$)(cp)(CO)$_2$] than in [Fe(CH$_3$)(cp)(CO)$_2$].

An initial estimate of the extent of Fermi resonance in the two molecules can be obtained from the frequency sum rule[1,9] [equation (3)].

$$\sum_3 (\nu^{is}\mathrm{CH} - 2) = \sum_2 \nu\mathrm{CH}_3 \qquad (3)$$

Here we use (ν^{is}CH − 2) rather than ν^{is}CH, to allow for a small coupling, which is present in the harmonic local-mode treatment, of about 2 cm^{-1} between CH and CD stretching in the CHD$_2$ group. For a symmetrical methyl group $\sum_2 \nu$CH$_3$ = 2ν_{asym}CH$_3$ + ν_{sym}CH$_3$.

If the νCH$_3$ frequencies are properly corrected for Fermi resonance, the difference $\Delta = \sum_2 \nu$CH$_3$ − $\sum_3(\nu^{is}$CH − 2) should be less than $\approx$10 cm^{-1}.

Using the observed experimental frequencies, we find that Δ = 31 cm^{-1} and 20 cm^{-1} for the iron and ruthenium compounds respectively (Table 5). Fermi resonances in symmetrical methyl groups arise potentially from three sources: primarily, from the ν_{sym}CH$_3$ (a$_1$)/2δ_{asym}CH$_3$ (A$_1$) resonance, with additional smaller contributions from ν_{sym}CH$_3$ (a$_1$)/2δ_{sym}CH$_3$ (A$_1$) and ν_{asym}CH$_3$ (e)/2δ_{asym}CH$_3$ (E). Estimates of the possible effects of the latter two resonances can be obtained by standard techniques[23,24] using the Fermi-resonance parameters W_{122} = 40 cm^{-1} and W_{455} = 20 cm^{-1} transferred from methyl halides.* These yield possible upward shifts of 2.9 cm^{-1} (Fe) or 3.2 cm^{-1} (Ru) in ν_{sym}CH$_3$, and 3.0 cm^{-1} (Fe) or 3.5 cm^{-1} (Ru) in ν_{asym}CH$_3$.

Table 5 Effects of Fermi-resonance corrections on frequency sum rule and estimates of HCH angles for [MMe(cp)(CO)$_2$] (M = Fe or Ru)[a]

	M = Fe	Ru
ν^{is}CH	2935.4	2939.8
$\sum_3$ (ν^{is}CH − 2)	8800.2	8813.4
$\sum_3$ (νCH$_3$)	8831.4	8833.0
Δ[b]	31.2	19.6
(ν_{asym}CH$_3$/ν_{asym}CD$_3$)$_{obs}$	1.33453	1.33195
HCH predicted/°	106.95	110.95
ν_{asym}CH$_3$ corr. (1)[c]	2965.4	2960.7
ν_{sym}CH$_3$ corr. (1)[d]	2865.4	2872.9
$\sum_2$ (νCH$_3$) corr. (1)[c,d]	8796.2	8794.3
Δcorr. (1)[b]	−4.0	−19.1
(ν_{asym}CH$_3$/ν°_{asym}CD$_3$)corr. (1)	1.33402	1.33125
HCH predicted/°	107.8	111.95
ν°_{asym}CH$_3$ corr. (2)	2965.4[c]	2964.2[e]
ν°_{sym}CH$_3$ corr. (2)	2870.4[c,f]	2876.4[e]
$\sum_3$ (νCH$_3$) corr. (2)	8801.2	8804.8
Δcorr. (2)	1.0	−8.6
ν°_{asym}CD$_3$ corr. (1)[c]	2222.9	2224.0
ν°_{sym}CD$_3$ corr. (1)[d,g]	2087.6	2091.1
W_{155} CH$_3$ corr. (2)	35.7	37.3
W_{155} CD$_3$ corr. (1)	24.5	24.7

[a] All data in cm^{-1}, except angles (°). [b] $\Delta = \sum_3(\nu$CH$_3) - \sum_3(\nu^{is}$CH − 2). [c] After Fermi-resonance corrections with W_{455} = 20 cm^{-1} (CH$_3$), 14.28 cm^{-1} (CD$_3$), corr.(1). [d] Includes resonances ν_{sym}/2δ_{asym}Me(A$_1$), ν_{sym}/2δ_{sym}Me. [e] Excludes resonance ν_{asym}CH$_3$/2δ_{asym}CH$_3$ (E). [f] Includes $g_{5,5}$ = +1.25 cm^{-1}. [g] Assuming $W_{122} = 40 \times 2^{-\frac{1}{2}}$, $g_{5,5}$ = 0.

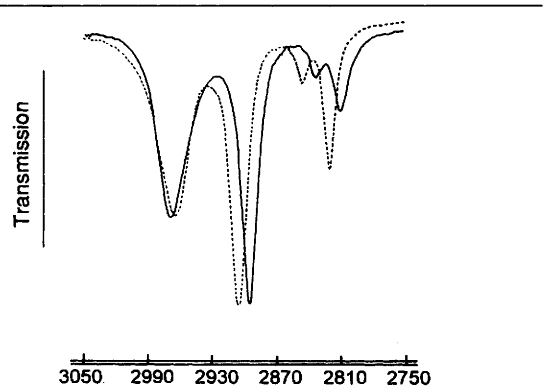

Fig. 3 Methyl CH stretching fundamentals and bending overtones in [M(CH$_3$)(cp)(CO)$_2$]; M = Fe (——) and Ru (– – – –) (CCl$_4$ solutions, arbitrarily scaled to same peak heights for stretching fundamentals)

The major Fermi resonance, between ν_{sym}CH$_3$ and 2δ_{asym}CH$_3$ (A$_1$) is more difficult to calculate directly, in these compounds, because the δ_{asym}CH$_3$ frequency is not exactly known. We therefore turn to the separation 2δ_{asym}CH$_3$ (E) − 2δ_{asym}CH$_3$ (A$_1$) to provide us with an estimate of this effect. The bending overtones are defined by equations (4) and (5),

$$2\delta_{asym}\mathrm{CH_3(E)} = 2 \times \delta_{asym}\mathrm{CH_3} + 2(x_{5,5} + g_{5,5}) \qquad (4)$$

$$2\delta_{asym}\mathrm{CH_3(A_1)} = 2 \times \delta_{asym}\mathrm{CH_3} + 2(x_{5,5} - g_{5,5}) \qquad (5)$$

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* Methyl halide nomenclature; W_{122} refers to the ν_{sym}/2δ_{sym}(ν_1/2ν_2) (A$_1$) resonance, and W_{455} to the ν_{asym}/2δ_{asym}(ν_4/2ν_5) (E) resonance.

where x and g are anharmonicity constants, the subscripts being derived from methyl halide nomenclature (where $\delta_{asym}CH_3 = \nu_5$). The separation $2\delta_{asym}CH_3$ (E) − $2\delta_{asym}CH_3$ (A_1) is therefore defined initially by the value of $g_{5,5}$, and modified by Fermi resonances which perturb the frequencies of the two bands. The effect of Fermi resonance is usually much greater than that due to $g_{5,5}$, and if $g_{5,5}$ is zero the separation will arise entirely from Fermi resonance.

If we assume initially that $g_{5,5} = 0$, the shift in $2\delta_{asym}CH_3$ (E) from its resonance with $\nu_{asym}CH_3$ means that $2\delta_{asym}CH_3$ (E) should be observed 3.0 cm^{-1} *below* $2\delta_{asym}CH_3$ (A_1) in the ruthenium compound.

In fact, the E level is found above the A_1 level in both compounds, the separations being 23.3 cm^{-1} (Fe) or 25.0 cm^{-1} (Ru). We conclude that the A_1 level must be depressed by 26.3 cm^{-1} (Fe) or 28.5 cm^{-1} (Ru) from its unperturbed position as a result of its resonance with $\nu_{sym}CH_3$, the latter being of course raised by the same amount. Adding the small shift in $\nu_{sym}CH_3$ deriving from its resonance with $2\delta_{sym}CH_3$, we obtain a total shift of 29.2 cm^{-1} (Fe) or 31.7 cm^{-1} (Ru). The estimated unperturbed frequencies $\nu^{\circ}_{sym}CH_3$ are then 2865.4 cm^{-1} (Fe) or 2872.7 cm^{-1} (Ru). Using these frequencies, the sum rule deficit Δ for the iron compound changes to an acceptable value of −4.0 cm^{-1}, but is still unacceptable for the ruthenium compound, at −19.1 cm^{-1} (Table 5). If we remove the $\nu_{sym}CH_3$ resonance in the ruthenium compound, the value of Δ (Ru) becomes −8.6 cm^{-1} and the frequencies $\nu^{\circ}_{asym}CH_3$ (Fe) and $\nu^{\circ}_{asym}CH_3$ (Ru) become almost equal, accounting at least to some extent for the anomalous observation of $\nu_{asym}CH_3$ (Fe) above $\nu_{asym}CH_3$ (Ru) in the experimental spectra.

In making this analysis, we have assumed that the anharmonicity constant $g_{5,5}$ can be ignored in both compounds. The calculated Fermi-resonance shift on $2\delta_{asym}CH_3$ (A_1) in [Fe(CH_3)(cp)$(CO)_2$] is 26.3 cm^{-1} and implies a strong interaction. If so, we would expect the intensity of the overtone to be considerably enhanced. In fact, as already noted, this band is relatively weak in the experimental spectra, and the calculated shift is perhaps unrealistically high. If we assume a reasonable small value of $g_{5,5} = +1.25$ cm^{-1}, the shift in $2\delta_{asym}CH_3(A_1)$ is reduced by 5 cm^{-1} to a more acceptable value, $\nu^{\circ}_{sym}CH_3$ becomes 2870.4 cm^{-1}, and $\Delta = 1.0$ cm^{-1}. In the ruthenium compound, the evidence for a substantial transfer of intensity to $2\delta_{asym}CH_3$ (A_1) is strong, and so no correction for a $g_{5,5}$ factor is introduced. The difference between the resonance shifts on $2\delta_{asym}CH_3$ (A_1) in the iron and ruthenium compounds, of 21.3 and 28.5 cm^{-1} respectively, is then consistent with the marked differences between the intensities of these bands in the experimental spectra.

In the νCD_3 region of the CD_3 isotopomers, $\nu_{asym}CD_3$ (Fe) is slightly lower than $\nu_{asym}CD_3$ (Ru), as expected, lending further support to the assumption that the reversal of the order of the corresponding bands in the CH_3 isotopomer must arise from significant differences in the resonance shifts. The distribution of intensity between the $\nu_{sym}CD_3$ and $2\delta_{asym}CD_3$ bands is almost equal, suggesting that the unperturbed levels must be almost coincident. The $\delta_{asym}CD_3$ band, unlike $\delta_{asym}CH_3$, is not obscured and the band centre is clearly measurable.

Calculating the Fermi-resonance shifts on $\nu_{asym}CD_3$ and $\nu_{sym}CD_3$ in the same way as those for the corresponding νCH_3 bands, with W_{455} and W_{122} reduced by a factor of $2^{-\frac{1}{2}}$ to allow for the effect of deuteriation, we obtain $\nu^{\circ}_{sym}CD_3 = 2087.6$ cm^{-1} (Fe) or 2091.1 cm^{-1} (Ru). The calculated values for $\nu^{\circ}_{sym}CD_3$ are close to those obtained assuming an exact coincidence between $\nu^{\circ}_{sym}CD_3$ and $2\delta^{\circ}_{asym}CD_3$ [2083 cm^{-1} (Fe) or 2089.8 cm^{-1} (Ru) after deducting the $\nu_{sym}CD_3/2\delta_{sym}CD_3$ shift]. The calculated values of W_{155} and the change in $\nu^{\circ}_{sym}CD_3$ from iron to ruthenium are acceptable. The anharmonicity constant $g_{5,5}$ is assumed to be negligible throughout.

In the CHD_2 species, the $\nu_{asym}CD_2$ band is 6–7 cm^{-1} lower than its counterpart in the CD_3 spectrum ($\nu_{asym}CD_3$); we attribute this to small resonances with ($\delta CH + \delta CD_2$), or $2\delta CH$. A small upwards shift in $\nu_{sym}CD_2$, resulting from a resonance with a $2\delta CD_2$ level, is also to be expected.

HCH *Angles and Force-field Calculations.*—Estimates of HCH angles can be obtained from the $\nu_{asym}CH_3/\nu_{asym}CD_3$ ratio, as described previously.[1] The values obtained are shown in Table 5. Using the experimentally observed $\nu_{asym}CH_3$ and $\nu_{asym}CD_3$ frequencies, the predicted angles are 107.0° (Fe) or 111.0° (Ru). With the corrected frequencies, the angles increase to 107.8° (Fe) or 112.0° (Ru). The values for the iron compound seem reasonable, but those for the ruthenium compound are unusually high for a methyl–metal compound.

These predictions can be further tested by a harmonic local-mode force-field calculation,[1] treating the CH and CD stretching motions only. Table 6 shows the results obtained for several choices of HCH angle. The weighting of the corrected experimental frequencies was chosen to reflect individual uncertainties in the Fermi-resonance corrections. For the iron compound, the two HCH angles chosen were those indicated by the uncorrected and corrected $\nu_{asym}CH_3/\nu_{asym}CD_3$ ratios. Both give a fit which may be considered satisfactory. The sum of the weighted squares of errors (Σw.s.e.) is slightly greater for the lower HCH angle, but the errors on $\nu_{sym}CD_3$ and $\nu_{sym}CD_2$ are lower for HCH 107°, and this angle is marginally to be preferred. A realistic estimate would be 107 ± 1°. In the case of the ruthenium compound, we quote results for angles of 107 and 110.95°, the latter corresponding to the prediction from the uncorrected $\nu_{asym}CH_3/\nu_{asym}CD_3$ ratio. There is little change in Σw.s.e., but with the larger angle we find much larger errors in the $\nu_{sym}CH_3$, $\nu_{sym}CD_3$ and $\nu_{sym}CD_2$ frequencies, together with a much larger value for the interaction constant f' than is usual in methyl–metal compounds. We conclude that an angle near 107° is more likely than one of about 111°. For this type of methyl group, the $\nu_{asym}CH_3/\nu_{asym}CD_3$ ratio is apparently not a very helpful indicator of the HCH angle. Whether this is due to the breadth of the ν_{asym}bands, with a possible link to internal rotation, or to incomplete Fermi-resonance corrections, is not yet clear.

Discussion

The predicted methyl C–H bond lengths, r_0CH, in [FeMe(cp)$(CO)_2$] and [RuMe(cp)$(CO)_2$] derived from the usual equation $r_0CH(\text{Å}) = 1.3982 - 0.000\,102\,3\ \nu^{is}CH\ (cm^{-1})$[10] are listed in Table 7 together with those for other methyl transition-metal compounds. As the r_0CH − ν^{is}CH correlation is based on gas-phase data, the observed solution frequencies are increased by 10 cm^{-1} to allow for the usual solution–gas frequency shift, before calculation of r_0CH.

The spectra of the iron and ruthenium compounds are strikingly different from those of the tricarbonyl chromium group compounds [MMe(cp)$(CO)_3$] (M = Cr, Mo or W), or of [TiMe(cp)Cl_2] or [$TiMe_2Cl_2$]. If we assume a significant barrier to internal rotation in [FeMe(cp)$(CO)_2$], then we must also accept that the methyl CH bonds in the iron and ruthenium compounds are not affected by their orientation relative to the cyclopentadienyl and carbonyl ligands, despite the very different natures of these ligands (the one being essentially electron donating, the others electron withdrawing) and the clear evidence of strong orientational effects in the other methyl–metal compounds. Given that we would expect to be able to detect differences in ν^{is}CH of as little as 2 cm^{-1}, this approach seems inherently improbable. Overall, we feel that the most reasonable interpretation of the experimental data must be in terms of an almost freely rotating methyl group with a possible small periodic fluctuation in CH bond strength and stretching force constant. The resulting variation in ν^{is}CH cannot, however, be comparable with the differences observed between the $\nu^{is}CH^{a}$ and $\nu^{is}CH^{s}$ bonds in the chromium group or titanium compounds.

This conclusion implies that the internal rotation barrier of

Table 6 Harmonic local-mode treatments for [MMe(cp)(CO)$_2$] (M = Fe or Ru)

		M = Fe				Ru			
		ν_{obs}	σ_ν[a]	ε_ν[b] (1)	ε_ν[b] (2)	ν_{obs}	σ_ν[a]	ε_ν[b] (1)	ε_ν[b] (2)
CH_3	ν_{asym}	2965.4[c]	3	1.1	1.0	2964.2	3	−2.1	−0.1
	ν_{sym}	2870[c]	5	1.1	1.7	2876[c]	10	−1.5	−5.7
CD_3[d]	ν_{asym}	2222.9[c]	3	1.7	0.8	2224.0[c]	3	1.3	−1.6
	ν_{sym}	2088[c]	5	2.0	4.6	2091[c]	5	−1.3	6.1
CHD_2[d]	$\nu^{is}CH$	2935.4	1	−0.4	−0.3	2939.8	1	0.2	0.2
	$\nu_{asym}CD_2$	2217.1	1000	−4.1	−5.0	2219.6	1000	−3.1	−6.0
	$\nu_{sym}CD_2$	2133.1	1000	5.1	6.6	2138.4	1000	5.4	9.3
HCH/°				107.0	107.8			107.0	110.95
f/mdyn Å^{-1}				4.7123	4.7118			4.7259	4.7277
f′/mdyn Å^{-1}				0.0053	0.0095			0.0126	0.0440
Σw.s.e.[e]				0.78	0.37			0.033	0.040

[a] Uncertainty in ν_{obs} used in calculation. [b] $\nu_{obs} - \nu_{calc}$. [c] Corrected for Fermi resonance. [d] All νCD values are divided by 1.011 before input to the refinement to offset incompatibility with νCH values arising from anharmonicity. [e] Σw.s.e. = sum of weighted squares of errors.

Table 7 Isolated CH stretching frequencies, CH bond lengths and HCH angles in methyl–metal compounds

	$\nu^{is}CH$[a]/cm^{-1}		$r^{\circ}CH$/Å[b]	HCH/°
[FeMe(cp)(CO)$_2$]		2935	1.096_9	≈107
[RuMe(cp)(CO)$_2$]		2940	1.096_4	≈107
[MnMe(CO)$_5$]		2951	1.095_9[c]	
[ReMe(CO)$_5$]		2929	1.098_0[c]	
[CrMe(cp)(CO)$_3$][d]	2966 2953 × 2	(2957)	1.093_8 1.095_1	≈108[e]
[MoMe(cp)(CO)$_3$][d]	2964 2946 × 2	(2952)	1.094_0 1.095_8	≈108[e]
[WMe(cp)(CO)$_3$][d]	2956 2933 × 2	(2941)	1.094_8 1.097_1	≈108[e]
[TiMe(cp)Cl$_2$][f]	2948 × 2 2908	(2935)	1.095_6 1.100_0	108.9[g] 107.5[h]
[TiMe$_2$(cp)$_2$][i]	2922 × 2 2905	(2916)	1.098_3 1.100_3	106.7[e]
[ZrMe$_2$(cp)$_2$][i]		2894	1.101_1	105.6
[HfMe$_2$(cp)$_2$][i]		2890	1.101_5	105.4

[a] CCl$_4$-solution wavenumbers, $\nu^{is}CH$(av.) in parentheses. [b] From $r_0 = 1.3982 - 0.000\,1023\,(\nu^{is}CH + 10)$. [c] From ref. 5, directly measured gas-phase frequencies. [d] Ref. 4. [e] Average values. [f] Ref. 1. [g] H^aCH^a. [h] H^aCH^s. [i] Ref. 2.

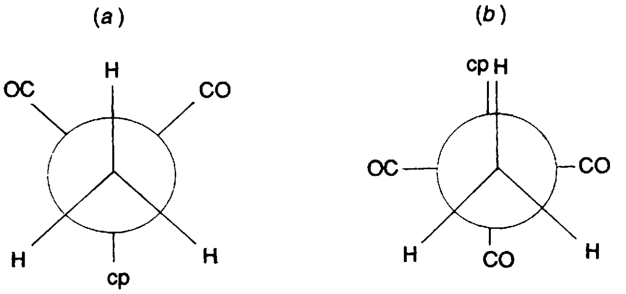

Fig. 4 Conformations in (*a*) [MMe(cp)(CO)$_2$] (M = Fe or Ru) staggered, (*b*) [MMe(cp)(CO)$_3$] (M = Cr, Mo or W), H and cp eclipsed

ca. 5 kJ mol^{-1} derived from the molecular-mechanics treatment[14] is more likely to be correct than the earlier higher estimates.[12,13] The molecular-mechanics calculation shows that the barrier in [FeMe(cp)(CO)$_2$] arises from the energy difference between the staggered conformation [Fig. 4(*a*)] and one in which a C–H bond eclipses the Fe–cp bond (taken as being to the centre of the C_5H_5 ring). At this point the other two C–H bonds almost eclipse the Fe–CO bonds. The barrier is thus essentially the same in nature, if not in magnitude, as those in ethane and substituted ethanes.

The tricarbonyl complexes [MMe(cp)(CO)$_3$] (M = Cr, Mo or W) present a different picture. Here the methyl group rotates against a four-fold M(cp)(CO)$_3$ group [Fig. 4(*b*)] and in the conformation in which one C–H bond eclipses the M–cp bond, the other two will be very close to the minimum-energy staggered orientations. The periodic energy variations for the three C–H bonds should therefore tend to cancel each other, and the overall barrier should be very small, as it is in [MnMe(CO)$_5$].[5] The experimental data clearly show that this is not the case, and we can only conclude that in the [MMe(cp)(CO)$_3$] compounds the barrier has an additional steric component which is not present in the less crowded dicarbonyl [MMe(cp)(CO)$_2$] compounds.

These observations in turn help to clarify the nature of the barrier in [TiMe(cp)Cl$_2$].[1] The evidence for hindered rotation here is very clear. If there is no significant steric interference with methyl group rotation in [FeMe(cp)(CO)$_2$], then there certainly should be none in [TiMe(cp)Cl$_2$], and the barrier must be electronic in origin. The obvious difference between the iron and titanium compounds is of course that whereas the former is a 'conventional' 18-electron molecule, the titanium atom in the latter has a formal electron count of 12. The most likely source of the barrier, therefore, is an interaction between one or more CH bonding pairs and an unoccupied titanium orbital or orbitals. Given that the $\nu^{is}CH^a$ frequency is relatively normal, whereas $\nu^{is}CH^s$ is much lower, it seems that any such effect is most likely to involve the CH^s bond.[1] Whether or not this should be described as 'agostic'[25,26] is debatable: a weak interaction with a titanium orbital would be sufficient to create a significant barrier to internal rotation (≈5–10 kJ mol) which would be clearly detectable in the spectrum, but a much more major effect would be required to produce a recognisable agostic bond.

In the 16-electron molecule [TiMe$_2$(cp)$_2$][2] the barrier is more likely to have a substantial steric component and there is no need to propose an interaction analogous to that in [TiMe(cp)Cl$_2$]. The eight-electron molecule [TiMeCl$_3$] presents more of a problem and has been the subject of considerable controversy.[27] We can only observe here that while there appears to be no evidence of an α-agostic interaction, the molecule has C_{3v} symmetry and the presence of a barrier to internal rotation would not be indicated, in this situation, by a splitting of the $\nu^{is}CH$ level.

A further point of interest in the iron and ruthenium compounds arises from the relative values of the $\nu^{is}CH$ frequencies. Our results for neighbouring groups, and for p-block elements, demonstrate a qualitative general relationship between $\nu^{is}CH$ and the mean M–CH_3 bond dissociation energy, in the sense that $\nu^{is}CH$ decreases as $\bar{D}_{M-C}$ increases.[3,5]

Within those groups for which accurate bond energy data are available,[3] the relationship is nearly linear and a change of a few wavenumbers in ν^{is}CH can reflect a significant change in $\bar{D}_{M-C}$. In the titanium, chromium and manganese groups the M–CH_3 bond energies consistently increase down each group, whereas in the zinc group and in the carbon group, the bond energies decrease. The ν^{is}CH frequency in $[Ru(CHD_2)(cp)(CO)_2]$ is 4.5 cm^{-1} higher than that in $[Fe(CHD_2)(cp)(CO)_2]$, sufficient to indicate that $\bar{D}_{Ru-C}$ must be somewhat smaller than $\bar{D}_{Fe-C}$, a reversal of the order found in the earlier groups. Bearing in mind that in the d^{10} group the M–CH_3 bond energy falls by about 50% from $ZnMe_2$ to $HgMe_2$,[3] the iron and ruthenium compounds appear to occupy an intermediate position, further reinforcing the idea that predictions based on observations made in the earlier d-block groups may not be readily transferable to the later groups.

Finally, our results demonstrate the importance of accurate corrections for Fermi resonance in any complete vibrational study. Our primary conclusions are derived from ν^{is}CH frequency data, which are not affected by Fermi resonance, and the reliability of the relationship between ν^{is}CH and r_0CH is now very well established. However, the calculation of HCH angles, whether from the $\nu_{asym}CH_3$: $\nu_{asym}CD_3$ ratio or from trial force-field calculations requires reliable values for the unperturbed CH_3 and CD_3 stretching frequencies and thus depends critically upon the proper assessment of Fermi-resonance effects. It is fair to say that although great progress has been made in this direction, there are still problems to be solved, at least in these relatively complicated organometallic systems.

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