Analysis of Substituted Ferrocenes by Infrared Spectroscopy

Leonidas Phillips,* Anthony R. Lacey,* and Mervyn K. Cooper
Departments of Inorganic and Physical Chemistry, University of Sydney, N.S.W. 2006, Australia

The i.r. spectra of substituted ferrocenes were investigated to determine and analyse the appropriate ring–metal stretching force constants. Assignment of the ring-mode vibrations is attempted.

The nature of the charge distribution in delocalized organometallic systems, typified by ferrocene, $[Fe(\eta\text{-}C_5H_5)_2]$, has been the goal of many theoretical and experimental investigations and is by no means quantitatively finalised.[1] To further our studies of the electric and magnetic properties of these molecules[2] the synthesis of substituted ferrocene compounds was necessary, including persubstitution by electron-withdrawing and donating groups. To aid in the interpretation of these data the homoannularly pentasubstituted molecules were also synthesised. The development of a new and more effective preparation of the 1,2,3,4,5-pentamethylferrocene molecule, $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$, is reported together with relevant structural data. This molecule has previously been formed only as a component in mixtures, both conventionally[3] and by electrochemical alkylation.[4] We have developed more effective synthetic routes to improve the purity and quantity of material prepared. These involved decarbonylation of the dicarbonyl(pentamethylcyclopentadienyl)iron halides (**1**; X = Cl or Br), the reaction being promoted either chemically[5] with Me_3NO[6] or by ultraviolet irradiation. Photolytic cleavage proved to be the cleanest and most efficient method, whilst the choice of (**1**; X = Br) produced higher yields of this halide (70—79%) in its preparation. It is interesting that the previously unreported (**1**; X = Cl) was prepared from the dicarbonyl dimer by reaction with freshly distilled thionyl chloride in yields of *ca.* 29% {*cf.* preparation[7] of $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$}.

The i.r. spectrum may help to elucidate the nature of specific bonds within a molecule, most pertinently the bond between the metal and the cyclopentadienyl rings. Attention is focused upon the frequencies of the ring–metal vibrations which are assigned and analysed in terms of a simple three-body oscillator model. Incidental to this is the assignment of the ring-mode vibrations for these molecules, essentially by comparison with similar molecules.

An integral part of the vibrational analysis involves an accurate knowledge of the structure of these metallocenes. Attempts to determine[8] the *X*-ray structure of decachloroferrocene $[Fe(\eta\text{-}C_5Cl_5)_2]$ resulted in decomposition of the crystal. Gas-phase electron diffraction[9] was equally fruitless although, provided thermal stability[10] is adequate, current development of a high-temperature inlet[9] may overcome the low vapour pressure. Although stability presented no problem for 1,2,3,4,5-pentachloroferrocene, $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5Cl_5)]$, both initial[8] and later[11] attempts at *X*-ray structure determination, using differently grown crystals, failed to solve the diffraction pattern. Presumably this is due to severe rotational disorder, a problem encountered with ferrocene itself.[12–14] The structures of decamethylferrocene, $[Fe(\eta\text{-}C_5Me_5)_2]$,[15–17] and ferrocene[15,18,19] were available from the literature, while the data relevant to pentamethylferrocene are reported in this study.

Results and Discussion

The structure of $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ indicates pentahapto bonding of both rings to the iron atom and, due to the general similarity between its i.r. spectrum and that of $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5Cl_5)]$, the perchloro ring in the latter is assumed to be pentahapto. This assumption is reinforced by the absence of any band near 1 560 cm^{-1} which would be indicative of monohapto[20] bonding of the perchloro ring. A similar situation pertains to the spectrum of $[Fe(\eta\text{-}C_5Cl_5)_2]$.

Table 1 lists a summary comparison of bond distances for $[Fe(\eta\text{-}C_5Me_5)_2]$, $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$, and ferrocene from both the available *X*-ray and electron-diffraction studies. The structure[8] of $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ is shown in Figure 1. The molecule is monomeric, and the two five-membered rings adopt an *eclipsed* configuration in the solid state, as shown in Figure 2, with an average dihedral angle of 4.28° between the two different ring carbons.

As in $[Fe(\eta\text{-}C_5Me_5)_2]$, the methyl groups of $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ lie above the C_5 ring plane away from the Fe atom. The H atoms of the cyclopentadienyl ring are displaced slightly towards the Fe atom, as observed in ferrocene. In the present case the perpendicular distance from the Fe atom to the C_5H_5 ring of 1.663 Å is significantly longer than that of 1.641 Å to the C_5Me_5 ring. The Fe–C_5H_5 ring distance is very similar to that of 1.661 Å observed for ferrocene from electron diffraction. However the Fe–C_5Me_5 ring distance is shorter than the mean distance of 1.662 Å in $[Fe(\eta\text{-}C_5Me_5)_2]$. It seems probable that

Table 1. Structural data on ferrocene and methylated derivatives

	$[Fe(\eta\text{-}C_5Me_5)_2]$		$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$	$[Fe(\eta\text{-}C_5H_5)_2]$	
	a, ref. 15	*b*, ref. 16	*b*, *c*, ref. 8	*b*, ref. 12	*a*, refs. 15, 18
$r_{C_5H_5}$ [d]			2.045(3)	2.033	2.064
$Z_{C_5H_5}$ [e]			1.663(8)	1.654	1.661
C–C(C_5H_5)			1.399(6)	1.389	1.440
$r_{C_5Me_5}$	2.064	2.050	2.031(6)		
$Z_{C_5Me_5}$	1.662	1.657	1.641(9)		
C–C(C_5Me_5)	1.439	1.419	1.408(6)		

[a] Electron diffraction data. [b] *X*-Ray diffraction data. [c] Estimated standard deviations in parentheses. [d] r_X is the radial distance from Fe to ring carbon of group X. [e] Z_X is the perpendicular distance from Fe to the plane of group X (*i.e.* along the C_5 axis of the molecule).

Table 2. Ring modes assignments for the ferrocene derivatives studied

C_5H_5 and C_5Me_5 Assignments[a]	Decamethyl-ferrocene		Pentamethyl-ferrocene		Dimethyl-ferrocene[21]		Ferrocene			Chloro-ferrocene		Dichloro-ferrocene		Pentachloro-ferrocene			Decachloro-ferrocene		C_5H_5 and C_5Cl_5 Assignments
	b	*c*	*b*	*c*	Vib. no.		*b*	Vib.[20] no.	*c*	*b*	*c*	*b*	*c*	*b*	*d*	*c*	*b*	*c*	
ν(C–H): C_5H_5			3 098	3 096	9b	3 087	3 094	17, 29	3 094	3 104	3 100	3 102	3 102		3 110				ν(C–H): C_5H_5
ν(C–H): CH_3	2 964		2 964			2 966													
	2 943		2 945			2 950													
	2 893		2 902			2 922													
	2 853		2 857																
	2 712																		
											1 648								
										1 635	1 633	1 636	1 638						
ν(C–C)					12a	1 609													
ν(C–C)					12b	1 558													
Symmetric bending CH_3	1 471		1 474			1 478													
	1 445		1 446			1 464													
ν(C–C)	1 423		1 422		8a	1 440													
Asymmetric stretch ν(C–C): C_5H_5			1 410				1 406	20		1 412	1 413	1 415	1 415	1 412		1 411			Asymmetric stretch ν(C–C): C_5H_5
Asymmetric bending CH_3	1 370	1 373	1 376	1 374		1 384													
In-plane skeletal vibration: ν(C–C)	1 353	1 354	1 361		8b	1 373				1 381	1 377	1 385	1 384						
										1 357	1 358	1 366	1 365						
														1 351		1 348	1 352	1 351	Ring mode ν(C–C)
										1 344	1 345	1 349	1 349						
														1 313		1 312	1 312	1 310	Ring mode/C_5Cl_5
ν(C–CH_3)					9a	1 229													
δ(C–H)					4	1 207						1 208	1 208						
δ(C–H)					6b	1 115													
Asymmetric ring breathing			1 102	1 102			1 103	10	1 103	1 103	1 103			1 107		1 106			Asymmetric ring breathing: C_5H_5
(C–H)					10a	1 106													
												1 179	1 178						
										1 165	1 165	1 166	1 166						‘q’ mode, *X*-sensitive vibration
ν(C–CH_3)	1 067	1 068	1 068	1 068								1 061	1 061						
δ(C–H)						1 053				1 050	1 049								
δ(C–H)	1 026	1 026	1 031	1 030		1 037													
Ring breathing					3	1 025				1 018	1 017	1 023	1 022						
Out-of-plane bend δ(C–H) parallel			997	997	11a	1 002	999	18	999	999	999			1 003		1 003			δ(C–H)
π(C–H)					11b	975													
δ(C–H)					6a	919													
δ(C–C)					13b	892													
												891	891						‘r’ mode, *X*-sensitive vibration
										881	881								
δ(C–C)					13a	851						873	873						
												846	845						
												836	836						
										823	820			826		825			δ(C–H)

Out-of-plane bend			804	804	2	811	815	9	814	812	809	807	805					
π(C–H) perpendicular							788		788									
														692	692	708	707	ν(C–Cl)
δ(C–C)					14b	632												
Ring deformation																		
δ(C–C)	592	590	588	588	14a	597												
																		Metal–ring fundamentals
				434						452	452			416	416			
	382	382								391	391		380	382	382	381	380	
δ(C–CH$_3$)				335							348		343		352	370	370	Ring breathing (symmetric)[e]
					10b	328					319		316					
											277		280		272			In-plane bend
		256											254					
Out-of-plane CH$_3$											226		226		220			Out-of-plane bend δ(C–Cl)
oscillations					7	217							205		208			
δ(C–CH$_3$)		200		192														

[a] ν, stretch; δ, bend; π, deformation. [b] KBr disc. [c] Nujol mull. [d] Halogenocarbon mull. [e] See text.

Table 3. Metal–ring modes (cm^{-1}), assignments, and stretching force constants (N m^{-1})

	[Fe(η-C$_5$Me$_5$)$_2$][a]		[Fe(η-C$_5$H$_5$)(η-C$_5$Me$_5$)]		[Fe(η-C$_5$H$_4$Me)$_2$][a,b]	[Fe(η-C$_5$H$_5$)$_2$]		[Fe(η-C$_5$H$_5$)(η-C$_5$H$_4$Cl)]		[Fe(η-C$_5$H$_4$Cl)$_2$]		[Fe(η-C$_5$H$_5$)(η-C$_5$Cl$_5$)]		[Fe(η-C$_5$Cl$_5$)$_2$]	
	c	*d*	*c*	*d*		*c*	*d*	*c*	*d*	*c*	*d*	*c*	*d*	*c*	*d*
ν_{asym}(M–R)	511	511m	504	503s	496	477	478vs	504	502vs	510	506vs	524	523m	512	511w
ν_{sym}(M–R)	169[e]			236m	311	306[f]			226m	344[g]			208w		
δ_{asym}	454	454vs		485vs	482	491	492vs	483	482s	471	470s	466	465m-s	415	415m
k_1	356		331		299			370		329		391		384	
k_2[h]	—		284		—	263		198		—		258		—	
k(ferrocene) + k(substituted)	619									592				647	
$k_1 + k_2$			615					568				649			

[a] The asymmetric ring tilt (δ) and stretch (ν) frequencies are reversed in a previous assignment for 1,1′-dimethyl-[21] and decamethyl-ferrocene.[46] [b] Frequencies taken from ref. 21. [c] KBr disc. [d] Nujol mull; v = very, s = strong, m = medium, and w = weak. [e] Ref. 46, Raman active. [f] Ref. 38, Raman active. [g] Ref. 23, Raman active. [h] k_2 is the Fe–C$_5$H$_5$ force constant.

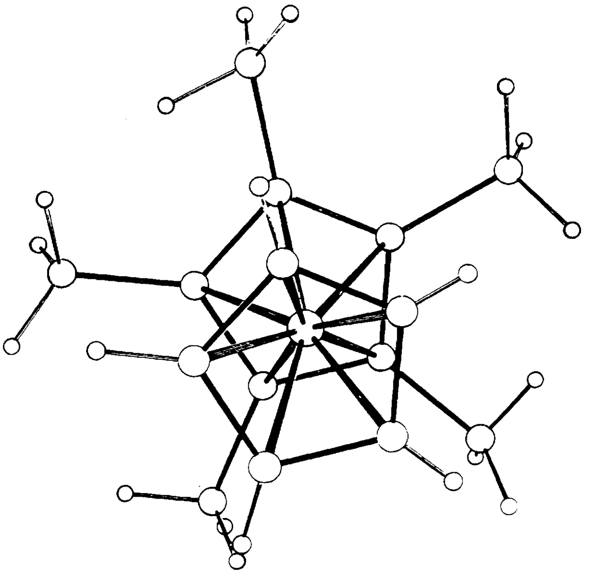

Figure 1. ORTEP diagram of pentamethylferrocene

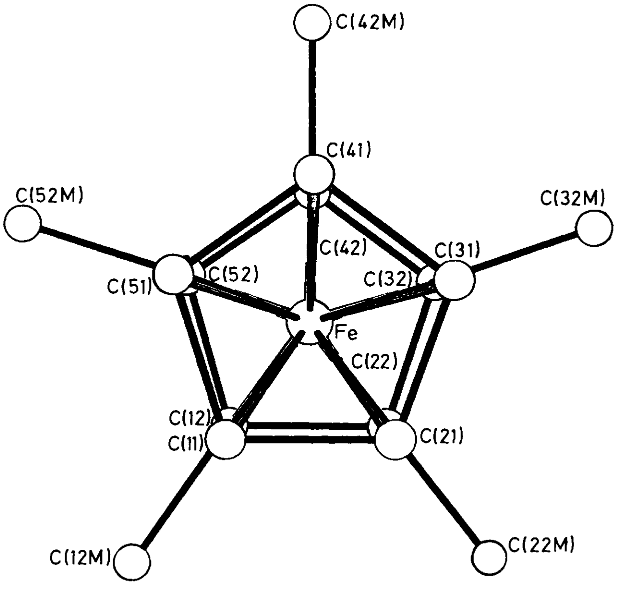

Figure 2. Carbon skeleton of pentamethylferrocene

steric factors in the latter would prevent closer approach, and therefore may contribute to the longer Fe to ring distances observed.

Details of the vibrational spectra of substituted ferrocenes are contained in Tables 2 and 3. The first table lists vibrations arising from the aromatic rings and the assignment of these ring modes, the second the analogous information for the ring–metal vibrations or skeletal modes.

The assignments proposed for the ring modes of pentamethyl-, chloro-, and pentachloroferrocene are based on a comparison with similar modes for 1,1′-dimethyl-,[21] ferrocene,[22] 1,1′-dichloroferrocene[23] and hexasubstituted benzenes, *e.g.* hexamethylbenzene,[24–26] charge-transfer complexes of C_6Me_6,[27,28] and hexachlorobenzene.[29–34] Literature assignments of the ring modes of decamethyl-[35] and decachloroferrocene[36] are verified by this comparative procedure. To assign the skeletal vibrations of the substituted ferrocenes, recourse was made to a simplified model, wherein the rings are treated as 'atoms' with the solution of the equations, relating to the vibrational frequencies and their corresponding force constants, being carried out for two linear model compounds: (*i*) XYX and (*ii*) XYZ. In this system Y is the iron atom and X or Z are the pentahapto rings, with model (*i*) applying to the homoannularly substituted compounds decamethyl-, 1,1′-dimethyl-, 1,1′-dichloro-, decachloro-ferrocene, and ferrocene whereas model (*ii*) applies to the heteroannularly substituted compounds pentamethyl-, chloro-, and pentachloro-ferrocene.

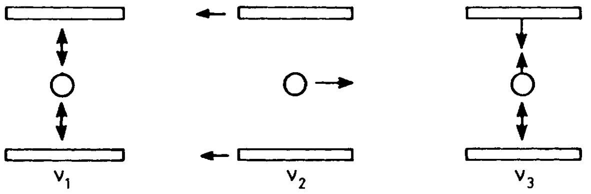

Figure 3. Diagrammatic representation of the skeletal vibrations of the two ring systems with respect to the central metal atom

In these models a point mass is ascribed to the rings and the system is treated as a three-body harmonic oscillator.[37] For the approach adopted here, the two stretching-frequency vibrations correspond to the symmetric and antisymmetric stretch, ν_1 and ν_3 respectively, and the bend to the ring tilt, ν_2. Each of the molecules with similarly substituted rings is represented by a linear XYX model[38,39] for which the appropriate equations are (1)—(3)[37] where l is the separation between the metal and ring

$$40 \times \pi^2 c^2 \nu_1{}^2 = k_1 \cdot \frac{N_A}{M_X} \tag{1}$$

$$40 \times \pi^2 c^2 \nu_2{}^2 = \frac{10^{-20} k_\delta}{l^2} \cdot \frac{2N_A}{M_X}\left(1 + \frac{2M_X}{M_Y}\right) \tag{2}$$

$$40 \times \pi^2 c^2 \nu_3{}^2 = k_1 \cdot \frac{N_A}{M_X}\left(1 + \frac{2M_X}{M_Y}\right) \tag{3}$$

in metres, N_A is Avagadro's number, k_1 is the primary stretching force constant in N m^{-1}, k_δ is the bending force constant in N m^{-1}, ν_1, ν_2, and ν_3 are given in wavenumbers (cm^{-1}), with M_X and M_Y in atomic mass units. A schematic representation of these vibrations is given in Figure 3.

The stretching force constant, k_1, can be determined from either equation (1) or (2), but since (1) describes the symmetric stretch, then for molecules with like rings (*i.e.* XYX) there will be no overall change in the dipole moment on vibration and so the symmetric stretch will be i.r. inactive. Equation (3) is thus employed to determine k_1 from ν_3 and (2) to determine k_δ from ν_2, or the reverse procedure, *i.e.* estimation of ν_3 from an assumed k_1 and ν_2 from an assumed k_δ. In the i.r. spectral range observed, 4 000—180 cm^{-1}, only two, ν_2 and ν_3, of the nine possible[38] skeletal modes are expected to occur.

Included in this study are three molecules with dissimilar rings for which an XYZ model was adopted. Due to the lower symmetry of this class of compound, seven normal ring–metal modes should be i.r. active,[38] four of which are expected in the range observed. The equations appropriate to the XYZ system are (4)—(6)[37] where l_1 and l_2 are the Y–X and Y–Z distances,

$$[(40 \times \pi^2 c^2)/N_A](\nu_1{}^2 + \nu_3{}^2) = k_1\left(\frac{1}{M_X} + \frac{1}{M_Y}\right) + k_2\left(\frac{1}{M_Y} + \frac{1}{M_Z}\right) \tag{4}$$

$$1600 \times \pi^4 c^4 \nu_1{}^2 \nu_3{}^2 = k_1 k_2 N_A{}^2 \cdot \frac{M_X + M_Y + M_Z}{M_X M_Y M_Z} \quad (5)$$

$$40 \times \pi^2 c^2 \nu_2{}^2 = \frac{10^{-20} N_A}{l_1{}^2 l_2{}^2} \cdot k_\delta \left[\frac{l_1{}^2}{M_Z} + \frac{l_2{}^2}{M_X} + \frac{(l_1 + l_2)^2}{M_Y} \right] \quad (6)$$

respectively, in metres. Unlike the XYX system, the symmetric stretch and tilt vibrations will now be i.r. allowed. The frequencies ν_1 and ν_3 and the two stretching force constants k_1 and k_2, defined for each metal–ligand bond, are not independent of each other for the heteroannular molecules. In order to use equations (4) and (5) to solve for k_1 in terms of k_2 a simultaneous choice of ν_1 and ν_3 must be made from the observed absorptions in a suitable region, *i.e.* below 600 cm^{-1}. The force constant appears as a squared term whose root is in terms of the particular choice of ν_1 and ν_3. Since the determinant of this quadratic must be positive in order to yield real solutions, many of the trial combinations of observed bands are precluded from being candidates for ν_1 and ν_3.

The following assumptions are made: the absorption is sufficiently intense to be observed, and the higher and lower metal–ring frequencies are assigned to the asymmetric and symmetric stretch modes, respectively.[21–23] The calculated force constant for a specific ring–metal bond in the XYZ system can then be compared to the corresponding force constant determined from an XYX type model. Since the XY interactions in the molecules XYZ and XYX are expected to have a similar bond order, as for example[37] in the molecules OCS, CO_2, and CS_2, a further reduction of available solutions is possible.

For the ferrocene molecules mentioned above, the extraction of each unique solution was eventually achieved by making use of the ring-tilt equations for both the XYX and XYZ systems to predict possible values of ν_2. The assumption was made that the bending force constant, k_δ, is essentially unchanged from that for the ferrocene value, the tilt frequency of which has been previously assigned.[40] Justification of this procedure is found in the small variation[37] of k_δ for the compounds ClCN, BrCN, ICN, and SCN^- where k_δ = 40, 37, 30, and 36 N m^{-1}, respectively. A larger variation is found for CO_2 and CS_2, k_δ being 77 and 57 N m^{-1}, respectively. For the metallocenes investigated, the ring orbitals would not be expected to vary significantly[41,42] and so only small variations in k_δ would be expected.

To derive ν_2 rigorously from an assumed k_δ, the metal–ligand bond lengths must be known. These distances are known for $[Fe(\eta\text{-}C_5Me_5)_2]$ and $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ but are unknown for the remaining substituted ferrocenes. Accordingly for the XYX systems the ferrocene distance was used, while for the XYZ type molecules the values for $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ were used. Support for this choice for $[Fe(\eta\text{-}C_5Cl_5)_2]$ arises when the metal–ligand distance in decachlororuthenocene[43] (1.80 Å) is compared to the analogous distance in decamethylruthenocene[44] (1.81 Å) and ruthenocene[19,45] (1.82 Å). Furthermore the metal–ligand distances[15] in ferrocene and $[Fe(\eta\text{-}C_5Me_5)_2]$ are equal at 1.66 Å.

Using these distances and setting k_δ equal to the value in ferrocene, the differences are found between the predicted value and an experimental band head, *i.e.* $|\nu_{pred.} - \nu_{expt.}|$ (Table 4).

Table 4. Differences between predicted and experimental frequencies when assigning[a] the ring-tilt vibration

	$\nu_{expt.}$/cm^{-1}	$\lvert\nu_{pred.-expt.}\rvert$/cm^{-1}
$[Fe(\eta\text{-}C_5Me_5)_2]$	454	0
$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$	485	8
$[Fe(\eta\text{-}C_5H_4Me)_2]$[b]	482	1
$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Cl)]$	482	2
$[Fe(\eta\text{-}C_5H_4Cl)_2]$	470	2
$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5Cl_5)]$	465	4
$[Fe(\eta\text{-}C_5Cl_5)_2]$	415	22

[a] Prediction calculated by setting k_δ equal to the value for ferrocene. [b] The experimental frequency is taken from ref. 21.

Table 5. Frequencies calculated from primary and interaction force constants

	Decamethylferrocene		
	a	*b*	Ferrocene
ν/cm^{-1}	$\nu_1 = 169, \nu_3 = 511$	$\nu_1 = 169, \nu_3 = 451$	$\nu_1 = 306, \nu_3 = 478$
k_1/N m^{-1}	292	253	311
k_{12}/N m^{-1}	−65	−25	48

[a] This work. [b] From ref. 46.

Previously, Duggan and Hendrickson[46] assigned the band of $[Fe(\eta\text{-}C_5Me_5)_2]$ at 451 cm^{-1} (454 cm^{-1} in this work) to the asymmetric stretch mode and the band at 515 cm^{-1} to the asymmetric tilt mode (*i.e.* the reverse of our assignments). In fact both bands are described as strongly i.r.-active absorptions, with these authors[46] choosing between them on the basis of Herzberg's[37] equations involving the primary (k_1) and interaction (k_{12}) force constants, together with the symmetric, ν_1, and asymmetric, ν_3, stretching vibrations. However upon calculating these constants using the value of 511 cm^{-1}, from this work, for the asymmetric stretch, better agreement is obtained between the calculated force constants and the values for ferrocene. The results are given in Table 5.

Due to the closer agreement of k_1 for $[Fe(\eta\text{-}C_5Me_5)_2]$ and ferrocene using our assignment of the asymmetric stretch and because of the exact prediction of the asymmetric tilt at an observed band head, we prefer to assign the absorptions at 511 and 454 cm^{-1} to the asymmetric tilt and stretch respectively. A similar situation prevails in the band assignments for 1,1′-dimethylferrocene. The previous[21] assignment of the absorption at 482 cm^{-1} was to the asymmetric ring–metal stretch, the authors choosing the band at 496 cm^{-1} as the asymmetric ring tilt. The basis of this choice was by comparison with the band positions of ferrocene, since both absorptions are of similar intensity, and in 1,1′-dimethylferrocene are separated by only 14 cm^{-1}. In view of this small energy difference, the previous assignment cannot be regarded as unequivocal. The absorptions at 482 and 496 cm^{-1} are therefore assigned to the asymmetric ring–metal tilt and stretch respectively.

Examining the chlorinated ferrocenes, the overall trend which emerges from Table 4 is a decrease in the frequency of ν_2 as the mass of the rings increases, lending support to the reassignment of the values for decamethyl- and 1,1′-dimethyl-ferrocene. The discrepancy of 22 cm^{-1} with respect to the band at 415 cm^{-1} for $[Fe(\eta\text{-}C_5Cl_5)_2]$ could arise from the unknown metal–ligand distance, but a more relevant factor may be the occurrence of iron–chlorine interactions, postulated to explain n.q.r. results[47] for this molecule. Any such factor would have a profound effect on the bending force constant and thereby invalidate the inherent assumption that this quantity is to a first approximation invariant. The absence of an absorption of $[Fe(\eta\text{-}C_5Cl_5)_2]$ that might be assigned to either a C–Cl in-plane or out-of-plane bend (approximately 250 or 225 cm^{-1} respectively[23,48]) could be interpreted as supportive evidence for some form of metal–halide interaction in this molecule.

The predicted values of the tilt frequency discussed above leave only one solution that produced internally consistent values for the remaining choice of symmetric and asymmetric stretching vibrations (ν_1 and ν_3 for the XYZ systems and ν_3 for the XYX systems). The assignments are given in Table 3.

Table 6. Skeletal modes of $[Cr(C_6H_6)_2]$ and $[Cr(C_6H_6)(C_6F_6)]$

	Ring tilt/cm^{-1}		Metal–ring stretch/cm^{-1}	
	Symmetric	Asymmetric	Symmetric	Asymmetric
$[Cr(C_6H_6)_2]$	335	459	277	490
$[Cr(C_6H_6)(C_6F_6)]$	466	497	340	589

The molecule that provides the most valid comparison for the homoannularly pentasubstituted members is the hexafluorobenzene analogue of dibenzenechromium $[Cr(C_6H_6)(C_6F_6)]$.[49] It is interesting that the skeletal vibrations of dibenzenechromium[50] and the corresponding frequencies of the hexafluoro-substituted compound, as shown in Table 6, display features in common with the present assignments, *e.g.* the asymmetric stretch is at higher energy than both the symmetric stretch and the asymmetric tilt modes. Also the asymmetric stretch is at a much higher frequency for the fluorinated member than for the unsubstituted compound, a result most prominently displayed in the pentachloroferrocene molecule.

From a comparative viewpoint, our assignments based on the three-body oscillator appear quite reasonable, the asymmetric metal–ring stretches and tilts being, with only one exception, within the range observed for some forty-nine substituted ferrocenes.[51] The exception is the metal–ring stretch of pentachloroferrocene which lies 11 cm^{-1} higher than the upper limit given in this reference.

The homoannular molecules *e.g.* ferrocene, $[Fe(\eta\text{-}C_5Me_5)_2]$, *etc.*, have only one primary force constant since the rings are identical. The heteroannular molecules *e.g.* pentamethyl-, chloro-ferrocene, *etc.*, have two force constants, one for each iron–ring bond. These force constants are given in Table 3 where k_2 is assigned to the force constant of the iron–cyclopentadienyl bond and k_1 to that of the iron–substituted ring bond. An inference for the XYZ chlorinated species is that as substitution of chlorine atoms for protons increases, and electron density is withdrawn from the Fe–C_5H_5 moiety, the force constant for this segment reduces relative to the value for ferrocene while that for the chlorinated segment increases. The opposite is true for the methylated series, reflecting the opposite electronegativities of the substituents. The hyperconjugative effect of the methyl group is expected to increase the electron density in the Fe–C_5H_5 moiety by transferring the donated charge of the methylated ring, *via* the iron atom, to the protonated ring.

A similar conclusion has been reached by Slocum and Ernst.[52] Based on the rate of ligand exchange of monosubstituted ferrocenes, they find that electron-donating rings facilitate ligand exchange, while electron-withdrawing groups impede such exchange. If, as a first approximation, the stretching force constants are regarded as representing the ring–metal bond strength, then k_1(pentachloro) > k_1(pentamethyl) for the substituted ring–metal force constants and k_2(pentachloro) < k_2(pentamethyl) for the protonated ring–metal force constants fully supports the suggestion by these authors. Overall it appears that electron-withdrawing groups strengthen the substituted ring–metal bond more than the unsubstituted ring–metal bond, with the reverse holding true for electron-donating groups.

Another interesting point is that for the XYZ type molecules the sum of the stretching force constants for each bond, *i.e.* $k_1 + k_2$, is effectively equivalent to the summation of the force constant for ferrocene and the appropriate di- or decasubstituted ferrocene, k(ferrocene) + k(decasubstituted) [*e.g.* k(ferrocene) + k(decachloro) = k_1(pentachloro) + k_2(pentachloro)]. This same sort of additivity is true for the molecule OCS relative to the force constants of CO_2 and CS_2.[37] Since the determination of k_1 for the XYX system depends on a choice of ν_1 independently of the choice of ν_1 and ν_3 for the XYZ system, in order to generate k_1 and k_2 this apparent 'additivity' of force constants is not a result of the mathematical modelling.

It is fortunate, regarding the above analysis, that there is little vibrational interaction between the rings in ferrocene-type molecules. This has also been noted for 1,1′-dimethyl-[21] and 1,1′-dichloro-ferrocene.[23] A vivid manifestation of the independent nature of each cyclopentadienyl ring, for the pentasubstituted series, is the excellent simulation in the composite spectra for pentamethyl- and pentachloro-ferrocene, shown in Figure 4. These composite spectra reproduce the main spectral features of the real molecules and were generated by superimposing the spectra of the decasubstituted molecules *i.e.* $[Fe(\eta\text{-}C_5Me_5)_2]$ or $[Fe(\eta\text{-}C_5Cl_5)_2]$ on to that of ferrocene. Intensities were rescaled for the various compounds.

The symmetric ring-breathing modes are worthy of mention. In hexachlorobenzene this Raman-active scattering occurs[34] at 372 cm^{-1}, while for hexamethylbenzene the symmetric ring-breathing mode occurs[25,26,28] at 559—561 cm^{-1}. For the ferrocenes, it appears that complexation of the pentamethyl- and pentachloro-rings has made these modes weakly i.r. active, which may allow the assignment of the absorptions at 370 or 380 cm^{-1} $[Fe(\eta\text{-}C_5Cl_5)_2]$, 352 or 382 cm^{-1} in $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5Cl_5)]$, 588 cm^{-1} in $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$, and 590 cm^{-1} in $[Fe(\eta\text{-}C_5Me_5)_2]$ to the symmetric ring-breathing mode. A possible mechanism is suggested based on the structure of $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ and that of another pentasubstituted metallocene, pentakis(methoxycarbonyl)ruthenocene.[53] Both these molecules have slightly different metal–carbon distances for the substituted and unsubstituted rings, and this is also associated with different ring sizes, the substituted ring being the larger. If one postulates that the ring breathing of the complexed ring is coupled to the ring–metal stretching vibration then a mechanism exists for making the ring breathing i.r. active, since the breathing ring will now also involve movement towards and away from the metal atom, thereby producing an oscillating dipole moment.

Experimental

The preparation and reaction of the complexes described were carried out under an atmosphere of dry nitrogen; solvents were dried and purified by standard methods. Infrared spectra were measured on a Perkin-Elmer 580B spectrometer coupled to a model 3500 data station, from 180 to 4 000 cm^{-1} using Nujol mulls and KBr discs. Compounds were characterised where possible by mass spectrometry, ^1H and ^{13}C n.m.r. spectroscopy, m.p., and i.r. spectroscopy. The sample of ferrocene used for measurements (Merck AR grade) was recrystallised from several solvents and vacuum sublimed [0.05 Torr (Torr $\approx$ 133 Pa), 25—50 °C], at least three times.

Decamethylferrocene.—Pentamethylcyclopentadiene[54] (C_5Me_5H) (10.0 g, 73.4 mmol) and dry 1,2-dimethoxyethane (dme) (500 cm^3) were added to an oven-dried round-bottom flask. The solution was cooled to −78 °C and n-butyl-lithium in hexane solution was added slowly (53 cm^3 of 1.5 mol dm^{-3}, 80 mmol). The solution was then allowed to warm to room temperature, after which a mixture of $FeCl_2$[55] and reduced iron powder (6.1 g—3.0 g, 38 mmol—54 mmol) was added against a counterstream of nitrogen. The resultant mixture was refluxed overnight, then the solvent was removed and the crude product extracted with hot cyclohexane. After filtration and evaporation, clean yellow crystals of $[Fe(\eta\text{-}C_5Me_5)_2]$ were obtained (11.03 g, 33.8 mmol), yield 92%. This material was further purified by recrystallisation from cyclohexane or diethyl ether

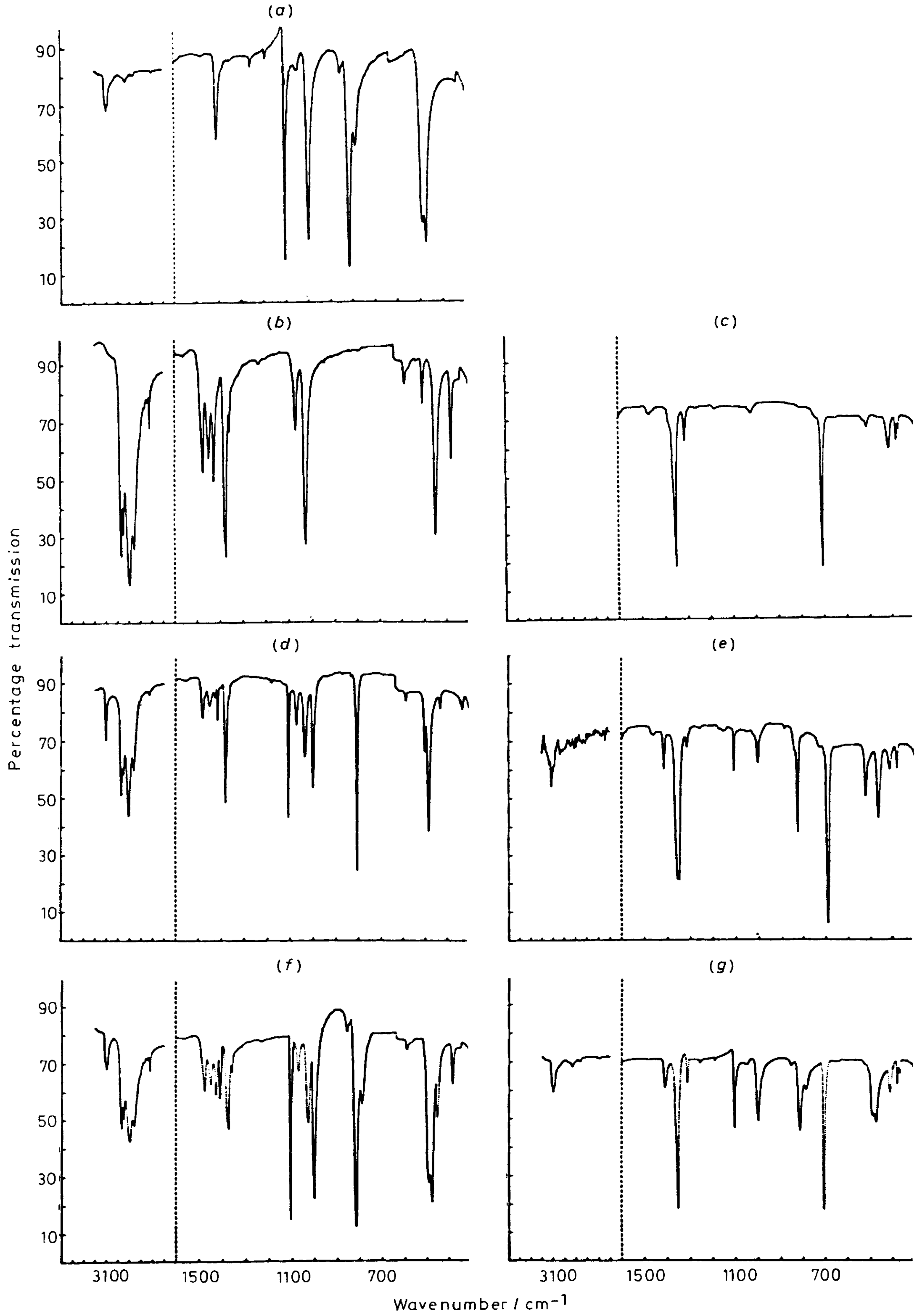

Figure 4. Infrared spectra of substituted ferrocenes: (a) ferrocene, (b) decamethyl-, (c) decachloro-, (d) pentamethyl-, (e) pentachloro-ferrocene, (f) composite of ferrocene and [Fe(η-C_5Me_5)$_2$], and (g) composite of ferrocene and [Fe(η-C_5Cl_5)$_2$]

followed by several vacuum sublimations (0.06 Torr, 110 °C), m.p. 294 °C. Crude yields ranged from 83 to 99%.

1,2,3,4,5-*Pentamethylferrocene*.—Solid, colourless, Na(C_5H_5) (2.7 g, 33 mmol) was placed in an oven-dried water-jacketed u.v. apparatus, fitted with a mercury vapour lamp (National HF 125X-S). Dry tetrahydrofuran (thf) (500 cm^3) was added and the solution stirred as a stream of nitrogen was bubbled through it. Attached to the entry port of the apparatus was a dropping funnel charged with a thf solution of [Fe(η-C_5Me_5)(CO)$_2$Br][56]

(2.00 g, 6.12 mmol). Sublimation of this complex should be avoided when purifying as [Fe(η-C_5Me_5)$_2$] is formed as a contaminant. The mercury-vapour discharge lamp was turned on. The addition of the solution of the complex should extend over not less than 4 h, to enable maximum reaction with the Na(C_5H_5) solution and to avoid a build up in the concentration of the iron reagent which would lead to a higher probability of formation of the dicarbonyl dimer. The colour change of the solution from the deep red of the iron reagent to the distinctive golden-brown of [Fe(η-C_5H_5)(η-C_5Me_5)] provided a convenient means of monitoring the progress of the reaction. The thf in the reaction vessel was replenished as required and the reaction was usually allowed to proceed overnight. The solution was evaporated to dryness, the product extracted with hot cyclohexane, and the filtered solution reduced in volume before being chromatographed on silica gel using cyclohexane as eluant. Crude yields were 70—90%. The product was dissolved in ethanol and filtered, evaporated to dryness, and similarly treated with hexane. Recrystallisation was effected, first from MeCN then from MeOH. Subsequently, three vacuum sublimations (0.05 Torr) at oil-bath temperatures of 60, 35, and 25 °C respectively were performed using an ice-cooled probe, m.p. 96—97 °C.

Chloroferrocene.—To a stirred solution of ferrocene (20.2 g, 0.109 mol) in dry ether (500 cm^3) was added a $LiBu^n$–hexane solution (220 cm^3 of 0.49 mol dm^{-3}, 0.108 mol) and stirred for 6 h.[57] The flask was then cooled to -78 °C and distilled tosyl (toluene-*p*-sulphonyl) chloride (23.1 g, 0.12 mol) was added, the solution being stirred a further 3 h at -78 °C, then left overnight. Water (3 cm^3) was added, after which the solution was filtered through Celite and rapidly chromatographed (activity II alumina) with light petroleum (b.p. 40—60 °C). The clear solution was evaporated and the product recrystallised three times to remove the bulk of the unreacted ferrocene. Separation of the remaining $\sim$30% of ferrocene was by nitrogen-forced high-speed preparative chromatography[58] [column (15 cm × 80 cm), silica gel (Merck, Kieselgel 60, 230—400 mesh ASTM), eluant hexane]. The resultant eluant was collected in fractions, and impure fractions of similar concentration were combined and recycled to improve separation. The high concentration batches were chromatographed on activity II alumina to allow oils to elute before the product. Final purification was achieved by chromatography on the silica column resulting in clear separation of chloroferrocene from any remaining traces of ferrocene. Yield 3.3 g, 15 mmol (14%), m.p. 55—55.5 °C. The refractive indices, permittivities, and densities of the product were in agreement with those for a sample prepared *via* the ferrocenylboronic acid intermediate [Fe(η-C_5H_5){η-$C_5H_4B(OH)_2$}].[59]

1,1′-Dichloroferrocene.—To a stirred solution of ferrocene (25.1 g, 0.135 mol) in distilled hexane (1 l) was rapidly added a complex[60] formed by mixing $Me_2NCH_2CH_2NMe_2$ (distilled from Na, 34.9 g, 0.30 mol) with $LiBu^n$ (200 cm^3 of 1.5 mol dm^{-3}, 0.30 mol) and allowing it to stand for 10 min. After stirring the reaction mixture for 5 h at 25 °C, the temperature was cooled to -74 °C and tosyl chloride (distilled and recrystallised from hexane, 57.2 g, 0.30 mol) was then added. The solution was allowed to warm to 25 °C and stirred overnight before being filtered and chromatographed on activity II alumina, using light petroleum as eluant. The mixture was then twice recrystallised, first from light petroleum and then from methanol. The remaining (*ca.* 30%) ferrocene was then oxidised by stirring it with a methanol solution of $AgNO_3$ (10% excess above stoicheiometric amount). Addition of water to the solution was followed by extraction with cyclohexane in a separating funnel. The characteristic blue ferrocenium ion remained in the aqueous methanol phase, leaving the 1,1′-dichloroferrocene in a high state of purity. The sample was then chromatographed on alumina using hexane as eluant and evaporated to dryness. Yield 7.78 g, 30.5 mmol (23%), m.p. 81 °C. These results compare favourably with literature values.[23]

1,2,3,4,5-Pentachloroferrocene, m.p. 154—155 °C, and decachloroferrocene, m.p. 230—235 °C (decomp.), were prepared according to the literature method.[61]

Conclusions

The proposed assignments of the metal–ring vibrations and the resultant force constants appear self consistent, when based on a simple three-body oscillator model. A reasonable assignment of the ring modes is given along with a tenable rationalisation of some of the low-frequency vibrations. A new preparation of pentamethylferrocene is presented.

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