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The charge distribution on metal-bonded cyclopentadienyl rings from infrared intensities

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Dedicated to Professor Fausto Calderazzo.

Abstract

The IR intensities of the C–H vibrational modes of a hydrocarbon fragment bonded to a metal atom are a useful probe to evaluate the charge distribution on the fragment. The values of *R*, the ratio of the overall C–H bending and C–H stretching IR intensities of the cyclopentadienyl ligand, are reported for several organometallic complexes containing the η^5-C_5H_5–M unit. The parameter *R* is related to several properties of the complexes, such as the ionic charge, the nature of the metal and of the ancillary ligands, the C–H bending force constant and to the solid-state structure. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Cyclopentadienyl; Metallocene; Infrared intensity; Raman spectra

1. Introduction

The IR intensities of vibrational modes are an important source of information regarding electronegativity, bond lengths, stretching force constants and binding energies [1]. In organometallic complexes they may be used to describe the character of the metal–ligand interaction [2], because they can be both related to the charge distribution and also be a marker, more sensitive than the frequencies, to the effect of the environment on a chemical group [3]. Unfortunately, the correct application of the intensity properties to complex molecules like organometallic compounds requires a prohibitive effort. Moreover, the problem is very often largely undetermined and even the experimental measurement of the absolute intensity of a vibrational mode is not an easy task. This accounts for intensity data being largely neglected in the IR spectroscopy of organometallics, where usually only frequency data are considered.

Nevertheless, an approximate approach has been suggested for the CH modes of hydrocarbon molecules [4]. The average intensity contribution per CH bond of a particular set of vibrations $\Sigma_i I_i(v_i)/n_{\mathrm{CH}}$ depends on the equilibrium charge of the hydrogen atom q°_{H} and on the charge flux $\mathrm{CF}(v_i)$ during the vibration (Eq. (1)). As the charge fluxes have a roughly constant value for CH stretching modes and are zero for the CH bending [3], the ratio, *R*, of the integrated intensities of the CH bending and of the CH stretching modes (Eq. (2)) is a simple function of the equilibrium charge on the H atoms and, consequently, on the C atoms also:

$$\Sigma_i I_i(v_i)/n_{\mathrm{CH}} \propto [q^{\circ}_{\mathrm{H}} + \mathrm{CF}(v_i)]^2 \qquad (1)$$

$$R = \frac{\Sigma_i I_i(\delta_{\mathrm{CH}})/n_{\mathrm{CH}}}{\Sigma_i I_i(v_{\mathrm{CH}})/n_{\mathrm{CH}}} \qquad (2)$$

Note that the $\Sigma_i I_i$ values in Eqs. (1) and (2) are the total intensity of a particular set of vibrational modes. In other words, for the calculation of *R* neither mode assignment nor a measurement of absolute intensities is required, but simply the evaluation of the relative intensities of groups of bands in selected spectral regions.

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In a recent paper we reported a complete assignment of the vibrational modes of the η^5-C_5H_5–M unit in several organometallic complexes [5]. The vibrational pattern (IR and Raman) of the intra-ring modes is basically the same, despite the different metal–ring interactions, and can be assumed to be a vibrational 'finger print' of the cyclopentadienyl group bonded to metal atoms. In this light, the IR intensities of the CH modes should be susceptible to analysis by Eqs. (1) and (2): this study is the object of the present paper. To extend the range of the metal–Cp interactions, selected examples where the cyclopentadienyl group is bonded to 4f and 5f elements and to transition metal clusters are included. Finally, because of the importance of decamethylated ferrocene ($Fe[C_5(CH_3)_5]_2$ or $FeCp_2^*$) in the field of charge–transfer systems, [6] we also report a comparative vibrational analysis of $FeCp_2^*$ and $[FeCp_2^*]^+$ complexes.

2. Experimental

The synthesis of most of the complexes, the purification of the solvents and the reactants and the spectroscopic measurements have been described previously (see Ref. [5] and references cited therein). The complexes $LaCp_3$ [7], CpNiNO [8], $Cp_2Ru_2(\mu CO)_2(CO)_2$ [9], Cp_4U [10], $CpFe(CO)(\mu CO)_2Co(CO)_3$ [11], $Cp_2Ni_2(\mu CO)_2Fe(CO)_3$ [12], and $CpNiRu_3(\mu H)_3(CO)_9$ [13], were prepared by literature methods. Commercial $FeCp_2^*$ (Aldrich) was purified by crystallisation from cyclohexane and used to obtain $[FeCp_2^*]^+[PF_6]^-$ [14].

IR spectra were recorded as CsI or KBr discs on a Bruker FTIR spectrophotometer mod. Equinox 55. Raman spectra were measured with a Bruker RFS 100, with Nd^{3+}/YAG laser and Ge-diode detector (laser powers 20–100 mw, res. 4 cm^{-1}).

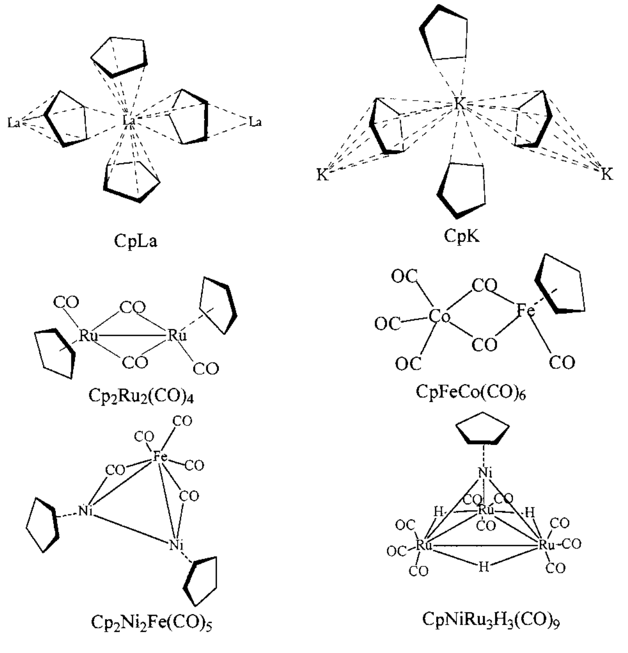
3. Results

3.1. Spectra and assignment

$LaCp_3$ forms nonlinear polymeric chains, with well-defined $(\eta^5Cp)_2La(\mu$-η^2:$\eta^5Cp)$ units [15] (see Scheme 1). Nevertheless, the spectral IR and Raman patterns are very close to those of a single Cp–M unit with C_{5v} local symmetry, showing, as usual, no coupling between the intra-ring modes (Table 1). Additional medium-weak features in the ν(CH) region indicate the presence of the bridging Cp group. On the other hand, the inter-ring M–Cp modes are usually strongly coupled and, on the basis of an idealised C_{3v} symmetry of the $LaCp_3$ unit, a total of ten bands ($3A_1 + 2A_2 + 5E$) is expected. At least five can be distinguished in the strong and broad Raman pattern between 300 and 180 cm^{-1}. A complete assignment is clearly impossible, but we may confidentially attribute, on intensity and frequency grounds, the strong Raman band at 243 cm^{-1} to the symmetric stretching of the three La–Cp bonds and the medium-broad IR absorption (without Raman counterpart), centred at 350 cm^{-1}, to the corresponding asymmetric stretching (E mode).

The IR and Raman spectra of the metal carbonyl compounds are dominated by the strong bands belonging to the ν(CO) modes; moreover, significant features corresponding to ν(M–M) (Raman) and to δ(M–C–O) and ν(M–CO) (mainly IR) are evident. Among them, it is possible to distinguish medium-weak bands associated with the MCp unit and assign them on the basis of the well-known spectral pattern [5].

The ν(CO) vibrations of $Cp_2Ru_2(CO)_4$ has been well studied [16]. Detailed data are not available for the vibrations of the CpRu unit and so they are collected in Table 1. The complex in the solid state has the *trans* structure (Scheme 1) [17] and the IR and Raman spectra are very close to those of the *trans* isomer of $Cp_2Fe_2(CO)_4$ [5]. An exception is the ν(CH) pattern, where the number of the IR and Raman bands and the relevant intensities do not agree with the simple model of two uncoupled M–Cp groups, a characteristic also found for $Cp_2Fe_2(CO)_4$ (*cis* isomer) and for other $Cp_2M_2(CO)_n$ complexes [5]. The assignment of the ν(Ru–Ru) mode is not straightforward: a possible candidate is a medium-weak Raman band at 215 cm^{-1}. Its intensity, much lower than expected, is presumably a consequence of large coupling and intensity sharing with the proximate ν(Cp–Ru) mode.



Scheme 1.

Table 1
Frequency values (cm^{-1}) of the main cyclopentadienyl modes of some M-(η^5-C_5H_5) complexes

Species [a]	Description	Cp_3La		$Cp_2Ru_2(CO)_4$		$CpFe(CO)_2Co(CO)_4$		$CpNiRu_3(H)_2(CO)_9$		$Cp_2Ni_2(CO)_2Fe(CO)_3$	
		Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR
A_1	CH stretching	3104 s	ca. 3102 w,sh	3110 m,sh	3116 w	3130 s	3130 w		ca. 3105vw	3114 vw	
				3104 s							
	CH bending (oop)	ca. 777 mw	770 vs,br	815 vw	810 s	845 w	844 s		817 s		798 s
	Ring breathing	1126 vs		1098 vs	1108 vw	1112 s		1112 s		1108 s	
	M-ring stretch	243 s,br	ca. 350 m,br	333 vs		368 s		188 s		ca. 250 s	
A_2	CH bending (ip)										
	Torsion										
E_1	CH stretching	ca. 3080 m,sh	3079 m	3084 m		3120 m, sh	ca. 3120 w, br		ca. 3105vw		3100 vw
	CH bending (ip)		1011 ms		1012 m		999 w	1000 w	1003 m		1014 m
				994 vw	994 m		1005 w				
	CH bending (oop)	798 w		839 w			885 w		843 m, sh	802 m	805 s
				831 w	834 m					810 m	
	CC stretching	1437 w	1440 w		1429 w	1430 m	1429 m	ca. 1420 w	1422 m		1413 m
				1409 m	1413 m		1414 m				1384 m
	Ring tilt			375 w		385 w					
	M-ring bending			215 m?							
E_2	CH stretching	3094 s			3094 vw	3120 m, sh	ca. 3120 w, br		ca. 3105vw		3100 vw
	CH bending (ip)	1065 m, br		1063 m	1055 m	1062 m		1053 w	1053 m	1047 m	1052 m, br
	CH bending (oop)	840 w					924 m		ca. 910 m	837 m	836 m
	CC stretching	1356 m		1359w	1355 m			1342 w	1342 w	1335 w	1335 m
					1346 m						
	Ring deform. (ip)										
	Ring deform. (oop)			399 m							

[a] On the basis of a local C_{5v} symmetry of the MCp unit.

Fig. 1. IR (KBr disk, upper curves) and Raman (crystals, lower curves) of the FeCp_2^* (a) and $[\mathrm{FeCp}_2^*]^+[\mathrm{PF}_6]^-$ (b) complexes. The arrows show the most significant differences between the spectra of the complexes (see text).

In the spectra of the clusters, the ν(M–Cp) modes are often mixed and/or overlapping with the strong ν(M–CO) and ν(M–M) features. In particular, the case of the $\mathrm{CpNiRu_3(H)_3(CO)_9}$ complex is unusual. A strong Raman band in the 300–350 cm^{-1} region, to which the symmetric mode is commonly assigned, is completely absent. Either there is an unexpected very low Raman intensity of this mode or it has to be assigned to a band in a different spectral region. A possible candidate is the medium-strong feature at 188 cm^{-1}, among the very strong bands associated with the ν(M–M) modes. In an M_4 cluster with approximate tetrahedral symmetry these modes give rise to three bands, with relative frequencies in the ratio 1:0.72:0.5 [18]. The set of bands spans frequencies at 206, 157 and ca. 110 cm^{-1}, for which the ratios (1:0.76:0.53) are close to those predicted. This assignment implies rather unexpected low values of the frequency of the symmetric ν(Ni–Cp) and of therefore of the (approximate) Ni–Cp stretching force constant (64 N m^{-1}). These values are close to those of complexes (CpLi, CpTl) [5], for which a significant ionic character of the Cp–M bond has been suggested. A low value (250 cm^{-1}) of the frequency of the symmetric ν(M–Cp) mode is also shown by the cluster $\mathrm{Cp_2Ni_2(\mu CO)_2Fe(CO)_3}$, but not by the complex $\mathrm{CpFe(CO)(\mu CO)_2Co(CO)_3}$, indicating that this is a characteristic of the Ni–Cp bond.

Fig. 1 illustrates the IR and Raman spectra of the FeCp_2^* and $[\mathrm{FeCp}_2^*]^+[\mathrm{PF}_6]^-$ complexes and Table 2 reports the frequency values and approximate assignments of the most prominent bands. The pattern between 2900 and 3000 cm^{-1} corresponds to $\nu(\mathrm{CH_3})$ modes, the high frequency side being the asymmetric stretching. The symmetric stretching in both complexes gives rise to the most intense Raman band; this band is significantly shifted (ca. 30 cm^{-1}) towards high energy in the ferrocinium salt. The features in the 1300–1500 cm^{-1} range have been assigned, as usual [19], to $\mathrm{CH_3}$ deformations and C=C stretching modes; some C–$\mathrm{CH_3}$ stretches and $\mathrm{CH_3}$ rocks appear as medium/weak bands

Table 2
Frequency values (cm^{-1}) and assignments of the vibrational modes of the FeCp_2^* and $[\mathrm{FeCp}_2^*]^+[\mathrm{PF}_6]^-$ complexes

Assignment	FeCp_2^*		$[\mathrm{FeCp}_2^*]^+[\mathrm{PF}_6]^-$	
	IR	Raman	IR	Raman
$\nu_{\mathrm{as(CH_3)}}$	2965 m	2967 w	2990 w	
$\nu_{\mathrm{as(CH_3)}}$	2945 w	2944 m	2965 w	2965 w
$\nu_{\mathrm{s(CH_3)}}$	2896 m, br	2894 s	2924 m	2926 s
$\nu_{\mathrm{s(CH_3)}}$			2900 w, sh	ca. 2905 m, sh
2δ	2854 w	ca. 2855 w, sh	2856 w	ca. 2855 w, sh
2δ	2713 w	2710 vw		
$\delta_{\mathrm{as(CH_3)}}$	1473 m	1476 m	1474 m	ca. 1475 m, br
$\delta_{\mathrm{as(CH_3)}}$		1465 m	ca.1460 w, sh	ca. 1460 m, br
$\delta_{\mathrm{as(CH_3)}}$	1449 m	1445 m		
$\delta_{\mathrm{as(CH_3)}}$/ $\nu_{\mathrm{C=C}}$	1426 m	1423 s	1423 w	1420 s
$\delta_{\mathrm{s(CH_3)}}$	1377 s		1390 m	
$\delta_{\mathrm{s(CH_3)}}$	1373 s	1369 w	1380 m	1381 m
$\delta_{\mathrm{s(CH_3)}}$		1363 m		
$\nu_{\mathrm{C=C}}$	1356 w			1405 m
$\nu_{\mathrm{C–CH_3}}$				1164 w
$\nu_{\mathrm{C–CH_3}}$	1070 w	ca. 1064 w	1072 w	1072 w
$\rho_{\mathrm{CH_3}}$	1029 m	1033 w	1025 m	1027 m
$[\mathrm{PF_6}]^-$			837 vs, br	
$[\mathrm{PF_6}]^-$				742 m, br
		616 w		625 m
‘breathing’	587 mw	587 s		591 s
				569 w
$[\mathrm{PF_6}]^-$			559 s	
		ca. 550 m		
$\mathrm{tilt_{as(CpFeCp)}}$	ca. 515 mw	511 m	543 w	546 m
				470 w
$\nu_{\mathrm{as(Fe–Cp)}}$	453 s	453 m	452 w	
$\mathrm{tilt_{s(CpFeCp)}}$	381 mw	376 m		370 s
			346 w	
		282 mw		
$\delta_{\mathrm{C–CH_3}}$	256 mw			
$\delta_{\mathrm{C–CH_3}}$	200 mw			ca. 218 m, br
$\nu_{\mathrm{s(Fe–Cp)}}$		178 s, 172 s		173 s
		162 s		ca. 160 m, sh

around 1100 cm^{-1}. All these assignments have been previously reported for FeCp_2^* [20,21]; the assignment for $[\mathrm{FeCp}_2^*]^+$ is similar and does not require any further comment. More interesting and more debatable are the spectra in the low-frequency region (less than 600 cm^{-1}), where skeletal ring modes appear together with modes involving the iron atom. The strong band at ca. 590 cm^{-1}, which corresponds to a medium/weak absorption in the IR, dominates the Raman spectra. On the basis of the IR spectrum alone this band was assigned to a π ring deformation mode [20]. We believe it to be more reliably assigned to the totally symmetric ring 'breathing' mode on the basis of its Raman intensity — this mode gives rise to the strongest Raman band for metallocenes [5] — and of its similarity to the same mode of hexamethylbenzene [22]. The symmetric Fe-ring stretch is the very strong Raman feature at ca. 170 cm^{-1} (both complexes) and the corresponding antisymmetric mode, the medium IR absorption at 453 cm^{-1} (FeCp_2^*). It is noteworthy that this last mode has almost zero intensity for the $[\mathrm{FeCp}_2^*]^+$ complex. The (ring)–Fe–(ring) tilting modes appear at ca. 510–540 cm^{-1} (antisymmetric) and at ca. 310–380 cm^{-1} (symmetric). We prefer this assignment, in accordance with Ref. [21] rather than the alternative assignment to bending modes [20] which is clearly unacceptable, as the same modes in the metallocenes have frequencies lower than 200 cm^{-1}.

3.2. Intensity

For all the complexes discussed above or reported in a previous paper [5] the IR bands corresponding to the C–H stretchings, and to the C–H in-plane and out-of-plane bendings, lie in well delimited frequency regions, without significant coupling with other modes or accidental overlap with other absorptions. Therefore, the integrated IR intensities of the absorptions in the appropriate regions enable reliable calculations of the *R* parameter, as defined by Eq. (2), to be made. The values are listed in Table 3. The same is true for Fe Cp_2^* and $[\mathrm{FeCp}_2^*]^+$ (of course, the stretching and the bending modes here refer to the CH_3 groups). Really, the bending region also includes some C=C stretching modes, but their IR intensities are so low that the overall intensity of the CH_3 bending modes is not significantly affected.

Table 3
Values of the IR intensity ratio between the C–H stretching and bending modes

Complex	*R*
Cp_2Mg	37
Cp_2Ca	16
Cp_2V	9.3
Cp_2Cr	8.6
Cp_2Mn	17
Cp_2Fe	8.8
$[Cp_2Fe]^+$	2.2
Cp_2Ru	11
Cp_2Co	11
$[Cp_2Co]^+$	1.5
Cp_2Ni	23
CpLi	38
CpNa	11
CpK	17
CpTl	22
Cp_3La	8.0
Cp_4U	12
$CpMn(CO)_3$	7.1
$CpRe(CO)_3$	5.0
$CpFe(CO)_2Cl$	1.5
$CpFe(CO)_2Br$	1.7
$CpFe(CO)_2I$	2.3
$CpCo(CO)_2$	9.0
CpNiNO	18
$Cp_2Mo_2(CO)_6$	4.8
$Cp_2W_2(CO)_6$	3.4
$Cp_2Fe_2(CO)_4$ (*cis* form)	6.8
$Cp_2Fe_2(CO)_4$ (*trans* form)	3.7
$Cp_2Ru_2(CO)_4$	6.4
$Cp_2Ni_2(CO)_2$	21
$CpFe(CO)(\mu CO)_2Co(CO)_3$	12
$Cp_2Ni_2(\mu CO)_2Fe(CO)_3$	40
$CpNiRu_3(\mu H)_3CO)_9$	53
FeCp_2^*	0.3
$[\mathrm{FeCp}_2^*]^+$	1.2

4. Discussion

The most obvious feature of the data collected in Table 3 is the range of *R* values, which are generally greater, or much greater, than the values for typical hydrocarbon molecules. For example, *R* lies in the range 0.1–0.3 the alkanes, is ca. 2.4 for ethylene and 1.8 for benzene [4]. Large *R* values reflect a low integrated intensities value for the C–H stretching absorptions, a common behaviour of the Cp group bonded to metal atoms. As the IR intensities of the free C_5H_5 radical are not known, we use benzene as a reference model, recognising the aromaticity of the M-bonded cyclopentadienyl ring. The dramatic change due to coordination is remarkable. The same trend was observed for alkynes, [23] ethylene [24] and other C_xH_y fragments [25].

A low C–H stretching intensity suggests (Eq. (1)) either that both q_H° and $CF(\nu_{CH})$ have near-to-zero values or, alternatively, that they have significant values and opposite signs. The former assessment can be reasonably discarded because the high C–H bending intensity requires that q_H° be far from zero. It follows that $CF(\nu_{CH})$ must be large and negative, assuming that q_H° is positive as in all hydrocarbon molecules [1b,26]. The meaning of $CF(\nu_{CH})$ being negative is clear: during the stretching of the C–H bond q_H° tends to decrease, becoming zero at the dissociation limit. In other words, the positive charge on the H atom is reflected in a corresponding negative charge on the C atom. This an important point for the character of the M–Cp bond because, if the trend of the *R* values roughly reflects the trend of the negative charge on the C_5 ring, it is likely to indicate the extent of σ–π interaction between metal and ligand.

Consider some examples. The two pairs MCp_2/$[MCp_2]^+$ (M = Fe, Co) show significantly lower *R* values for the ions than for the neutral molecules: this clearly reflects a lower π-back-donation from metal to ring when the metal has a greater positive charge. Similarly, low back-donation is indicated by the low values for the $FeCp(CO)_2X$ complexes (X = Cl, Br, I): the reason here may be ascribed to the electron-attracting power of the halide ligands (the trend is in the expected order Cl > Br > I). The well-known electron-attracting power of the CO ligand is also evident: comparing complexes with the same metal atom, the presence of CO groups usually reduces the *R* values of the Cp rings.

Evidently, the *R* factor for the neutral metallocenes of the first transition series cannot be related to any electronic parameter (ionisation energy, electronegativity etc.) of the metal: three (V, Cr, Fe) are very close, one (Co) is a little greater and the other two (Mn and Ni) clearly greater. This behaviour can be rationalised in terms of the electronic structures of the complexes. The e_{1g}^* MO is doubly occupied in both $MnCp_2$ and $NiCp_2$, is singly occupied in $CoCp_2$ and is empty in the others [27]. This orbital has a π-back-donation (from M to Cp) character: as its electron content increases, both the extent of the π-back-donation and the value of *R* increase.

Few data are available for complexes with metals of the second or third transition rows; however, no significant difference compared with the first row elements is evident.

The metal clusters show great *R* values, clearly ascribed to the very low intensity of the C–H stretching modes. This effect has previously been noted in $M_3(\mu_3CH)$ systems [25] and underlines the behaviour of clusters as electron sinks, which allows a large electron flux from cluster to ligand.

Previous examples, with Cp bonded to a transition metal, demonstrate the effect of the π component of the bond on the charge delocalisation into the ring. When the ring interacts with a non-transition, electropositive, metal atom, the effect must primarily be based on a σ donation from ligand to metal. Traditionally, [28] Cp complexes of alkali and alkaline-earth metals are considered purely 'ionic', but we have recently shown [5] that this model is a simplification, as the spectra suggest a non-zero ligand–metal covalent interaction. Only the IR and Raman patterns of the sodium complex strictly conform obeys to the D_{5h} symmetry of the C_5H_5 unit and can be considered as typical spectra of the cyclopentadienide anion; the *R* value, ca. 11, its characteristic value. This is not very large, compared with other Cp complexes, but reflects the fact that the positive charge on the H atoms is partially reduced by the anionic charge distributed thorough the whole fragment. The other complexes, with M = Li, Mg, Tl, have greater values of the *R* factor. A reasonable explanation is that there is some M–Cp interaction, as evidenced by the presence of the ν(M–Cp) Raman bands [5]. This is probably via σ-donation from ligand to metal, which increases q_H°. The *R* value of the Cp_4U complex is not much different: a significant donation here occurs from the Cp π orbitals into the 6d and 5f U orbitals [29]. CpK is an interesting case. It is expected to be at least as ionic as CpNa, but the 'anomalous' pattern of the C–H stretching bands points to a structural oddity [5]. A very recent determination of the CpK solid-state structure has shown a distorted tetrahedral co-ordination of two η^5-Cp and two η^2-Cp around the K atom [30]: as a consequence a greater *R* factor for CpK may well result. A similar geometry for calciocene [31] gives rise to a similar *R* value.

Among the intra-ring vibrational modes of the M–Cp complexes, the out-of-plane C–H bending vibrations are the most interesting. One of them in particular, the A-type mode, which is the strongest IR band of the spectrum, shows the largest frequency change. Several arguments have been invoked to explain this effect [28], but the most convincing relates the frequency shift to the difficulty of moving the hydrogen towards the C_5 ring [32]. We have suggested, considering the electrostatic interaction between the charge on the H atoms and that on the ring, that the bending force constant f_γ is smaller when the difference between the two charges is larger [5]. In this light, the value of the *R* factor can be a guideline: a high *R* value should correspond to a greater ease of bending and a lower f_γ value. The plot of f_γ versus *R* (Fig. 2) is indicative of the expected trend, at least in the homogeneous series of metallocene compounds.

Finally, a comment about the two complexes bearing pentamethylated cyclopentadienyl groups. The effect of the ionic charge on the CH_3 unit is not expected to be great because the H atoms are not directly bonded to the ring. However, the relevant *R* values are sufficiently different (1.1 vs. 0.25) for them to be used as spectroscopic probes of the charge of the complexes. Other significant probes are the values of the $\nu(CH_3)$ symmetric mode, the difference in the IR intensities of the antisymmetric Fe-ring stretching (medium-strong in $FeCp_2^*$, very weak in $[FeCp_2^*]^+$) and in the Raman intensities of the symmetric Fe-ring tilting (medium in $FeCp_2^*$, strong in $[FeCp_2^*]^+$). All these probes can be confidentially and easily used to test the charge distri-

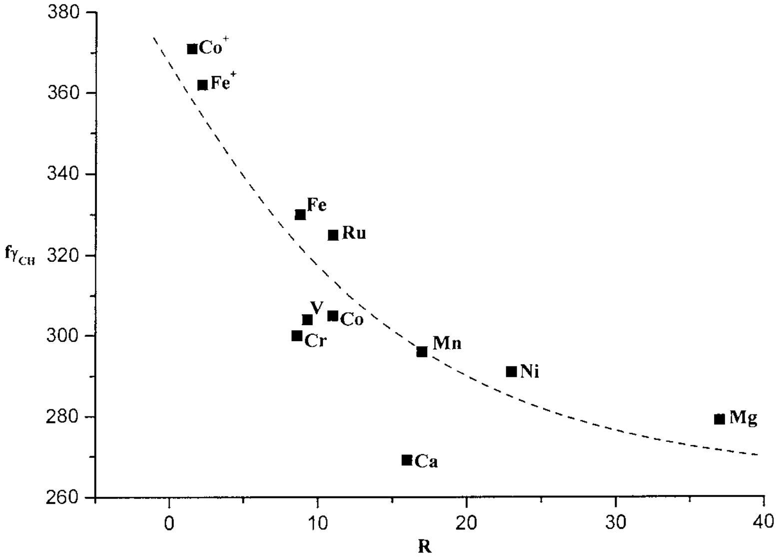


Fig. 2. Plot of the out-of-plane C–H bending force constant vs. the *R* factor for MCp_2 complexes. The values of f_γ ($N\ m^{-1}$) have been calculated as reported previously [5].

bution on charge–transfer complexes, where $FeCp_2^*$ is the donor.

5. Conclusions

Previous papers and the preceding discussion point to the *R* factor as a suitable parameter to give approximate but reliable value for the relative charges on H atoms in any C_xH_y fragment bonded to metal in different species of organometallic complexes. Other parameters can offer such information, for instance the ^1H NMR chemical shift: lowfield values are, in principle, indicative of an increase in positive charge on H atoms. Some attempts have been made to correlate such NMR data with the electronic density on the M-bonded Cp group [33]. They have shown some success only with a series of very similar compounds, when most parameters influencing the chemical shift are reasonably constant. More recently [34], by comparing the free arenes and the $Cr(CO)_3$-bonded arenes, the weaknesses in simplified interpretations of the variation of the chemical shifts of arene protons have been pointed out.

MO calculations on complex molecules cannot afford, at the moment, simple and reliable evaluation of the Mulliken charges. Simpler examples, like $[Cp]^-$, CpLi and Cp_2Fe, calculated by density functional methods, may give reliable results [32]: in this case the calculated charges on the H atoms of the Cp groups are in line with our *R* values. Further, the calculation of the charge based on the absolute IR band intensities requires gross approximations. Moreover, it is significantly undetermined: 16 equally reliable sets of atomic charges have been calculated for the Cp_2M systems [35]. In conclusion, we believe that at the moment the evaluation of *R* offers an easy way to compare different charge distribution on organometallic complexes and to give insights into the nature of the metal–ligand bond.

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