Journal of Organometallic Chemistry, 441 (1992) 285–294
Elsevier Sequoia S.A., Lausanne
JOM 22963

Substituted cyclopentadienyl complexes

X *. An absolute integrated infrared intensity study of $[(\eta^5\text{-}C_5H_4R)Fe(CO)(L)I]$

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(Received April 15, 1992)

Abstract

The absolute integrated intensities, A, of the ν(CO) stretching band for a range of $(\eta^5\text{-}C_5H_4R)Fe(CO)(L)I$ complexes ($L = PPh_3$, $R = H$, Me, ${}^tBu$, $SiMe_3$, I, COOMe; $R = Me$, $L = P(CH_2C_6H_5)_3$, PPh_3, $P(OMe)_3$, $P(O^iPr)_3$, $P(OPh)_3$, $P(O\text{-}o\text{-}Tol)_3$ have been measured. The values of A vary between 286 and 377 km mol^{-1}, and the largest values are observed when (i) R is an electron donating group and (ii) L is small and electron donating. The steric effect can be rationalized in terms of the influence of L and R on the overlap of orbitals between Fe and CO.

Introduction

Electronic and steric parameters associated with Group 15 donor ligands have provided fertile ground for rationalizing the chemical and physical properties of transition metal complexes containing these ligands [1,2]. Numerous attempts have also been made to separate the contributions of these steric and electronic (σ and π) parameters [3,4]. Much of the impetus for these studies arises from the important role played by Group 15 donor ligands in homogeneous catalysis [5,6].

Another important class of organometallic complexes are those containing the cyclopentadienyl ligand. Although the impact of this class of ligand on the field of homogeneous catalysis has been less dramatic [7], the ligand has played an important historical role in the development of both low [8] and, more recently, high oxidation state chemistry [9]. However, much less quantitative information is available on the influence of the substituted cyclopentadienyl ligand on the chemical and physical properties of complexes containing this ligand type [10].

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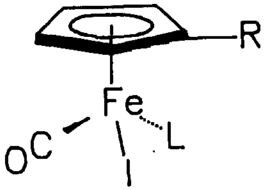

Fig. 1. Structure of (η^5-C_5H_4R)Fe(CO)(L)I.

Indeed, it was only recently that the first cone angle measurements were reported for a series of substituted cyclopentadienyl ligands [11].

To obtain information on the electronic parameter associated with the cyclopentadienyl ring substituent, we have carried out a study involving the measurement of the intensity of the ν(CO) band of a range of (η^5-C_5H_4R)Fe(CO)(PPh_3)I complexes (Fig. 1, L = PPh_3), *i.e.* on complexes in which only the ring substituent has been varied. To our knowledge, there has been only one report of a related study on ν(CO) intensity measurements; in that study, the combined intensities of the two ν(CO) bands observed for a series of substituted cyclopentadienyl tricarbonyl manganese and rhenium complexes were measured [12].

To complete our study we also measured the intensity of the ν(CO) band of a range of (η^5-C_5H_4Me)Fe(CO)(L)I complexes. Part of our interest in this study was to establish whether the measurement of integrated intensities could provide further information on electronic effects to complement the usual data available from band position measurements. For instance, Giering and co-workers [3] recently reported on the electronic and steric properties of a series of (η^5-C_5H_4Me)Fe(CO)(L)(COMe) complexes obtained from electrochemical and spectroscopic procedures. For L = $P(O^iPr)_3$ three, and for L = $P(CH_2C_6H_5)_3$(PBz_3) two ν(CO) bands were observed, and there was thus difficulty in quantifying an electronic parameter for those ligands. Intensity measurements should overcome this problem.

Experimental

The complexes (η^5-C_5H_4R)Fe(CO)(L)I (R = Me, [13] L = PPh_3, PBz_3, $P(OMe)_3$, $P(O^iPr)_3$, $P(OPh)_3$, P(O-*o*-Tol)$_3$; R = H, [14] ^{t}Bu, [15] $SiMe_3$, [11] I, [16] L = PPh_3) were prepared by previously reported methods. $Fe(CO)_4I_2$ was prepared from $Fe(CO)_5$ and I_2 [17]. All reactions were carried out under nitrogen or argon. All solvents were dried and distilled prior to use by standard procedures. Column chromatography was carried out on Merck silica gel (0.063—0.200 mm particle size).

Preparation of Tl($C_5H_4CO_2Me$)

This salt was prepared by a modification of the published procedures [18,19]. Sodium cyclopentadienide was formed as a violet solution in THF from the reaction between sodium sand (4.5 mmol) and freshly cracked cyclopentadiene (131 mmol) at 0°C [20]. Dimethylcarbonate (143 mmol) was added to this solution at room temperature. The mixture was then heated under reflux for 2 h, to give a yellow-brown coloured solution. A yellow-brown residue was left behind after the solvent and newly formed methanol were removed under high vacuum. This residue was redissolved in *ca.* 20 cm^3 THF and transferred *via* a cannula into a solution of thallium chloride (45 mmol) and potassium hydroxide (450 mmol) in *ca.* 200 cm^3 of water under argon. The solution was then stirred for 3 h during which a white precipitate was formed. The product, $Tl(C_5H_4CO_2CH_3)$, a white powder, was filtered off, washed with water, diethyl ether, and ethanol, and dried *in vacuo* (yield 79%). Spectroscopic data are in agreement with previous reports [19].

Preparation of $(\eta^5\text{-}C_5H_4CO_2CH_3)Fe(CO)_2I$

A slurry of $Tl(C_5H_4CO_2CH_3)$ (4 mmol) in dry THF (120 cm^3) was stirred rapidly under an inert atmosphere. A solution of $Fe(CO)_4I_2$ (4.4 mmol in dry THF (60 cm^3) was added slowly from a dropping funnel. The mixture was then stirred at room temperature, in the dark for 21 h, during which the reaction went to completion, as indicated by IR spectroscopy. The reaction mixture was then filtered through Celite (with benzene as solvent) and the solvent removed by rotary evaporation. Column chromatography (silica gel, hexane/dichloromethane eluants) yielded the product, $(\eta^5\text{-}C_5H_4CO_2CH_3)Fe(CO)_2I$, as a dark brown crystalline solid (10% yield) whose identity was confirmed by infrared spectroscopy [11]. This complex was treated with PPh_3 by standard procedures to yield $(\eta^5\text{-}C_5H_4CO_2CH_3)Fe(CO)(PPh_3)I$ [11].

Infrared measurements

A Bruker IFS 85 infrared spectrometer was used to measure the absorbances, and to integrate the areas under the absorption bands. A Beckman XL-C variable pathlength infrared cell was used, and the pathlengths, in the region 0.05–1.00 mm, were calibrated by the interference fringe method.

The samples of $(\eta^5\text{-}C_5H_4R)Fe(CO)(L)I$ were made up as solutions in chloroform (chloroform purified and dried by filtration through neutral alumina). For each compound, two to four solutions of different concentrations, within the range $(0.5\text{–}2.5) \times 10^{-5}$ mol cm^{-3}, were employed. The spectrum of each solution was recorded at six to twelve different pathlengths. The spectra of $(\eta^5\text{-}C_5H_4I)Fe(CO)(PPh_3)I$, recorded at various pathlengths (same concentration) are shown as examples in Fig. 2. Care was taken to choose only the concentration–pathlength combinations which resulted in absorbance readings in the range 0.3–0.6 (corresponding to 30–70% transmittance). The reference employed for each infrared measurement consisted of a previously measured spectrum of the solvent at the same pathlength. The absorption bands were broad, and the integration limits, which were chosen manually, extended over approximately 200 cm^{-1}.

The area under an infrared absorption band is given by

$$\int_{\bar{\nu}_1}^{\bar{\nu}_2} A' \, d\bar{\nu} = \int_{\bar{\nu}_1}^{\bar{\nu}_2} \ln(I_0/I) \, d\bar{\nu} = Bcl$$

where I_0 and I are the percentage transmittances at wavenumber $\bar{\nu}$, of the baseline and sample spectrum, respectively, A' is the absorbance at wavenumber $\bar{\nu}$, $\bar{\nu}_1$ and $\bar{\nu}_2$ are the integration limits, c is the concentration in mol cm^{-3}, l is the cell pathlength in cm, and B is the apparent integrated band intensity. The true integrated band intensity, A, is the limiting value of B as $cl \to 0$, or the slope at $cl = 0$ of a plot of the integrated band area *versus* cl [21,22].

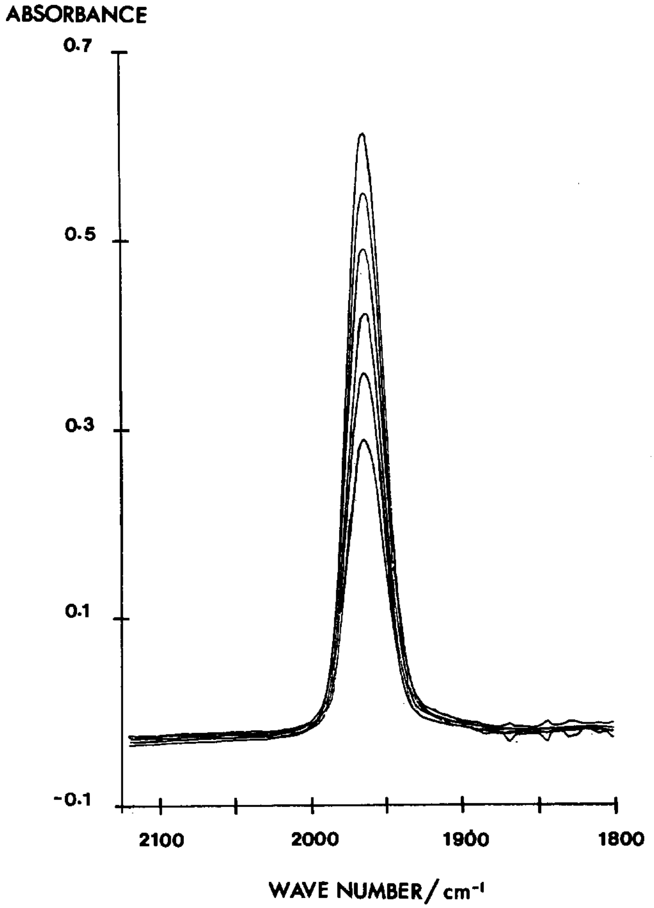

Fig. 2. The infrared spectra obtained for (η^5-C_5H_4I)Fe(CO)(PPh_3)I at different pathlengths (l = 0.0242–0.0489 cm), for the same concentration ($c = 1.366 \times 10^{-5}$ mol cm^{-3}).

The intensity was obtained as the slope of a linear regression plot of the integrated absorbance area ($\int A'$ cm^{-1}) against the product of the concentration and pathlength ($c \times l$ mol cm^{-2}). A is most conveniently expressed in km mol^{-1} (1 km $mol^{-1} = 10^5$ cm mol^{-1}) [23]. The computer package STATGRAPHICS [24] was used for the linear regression analysis. The data always gave good correlation coefficients (> 0.99) (for example, see Fig. 3) and the intensity values obtained in this way are given, together with the possible errors within a 95% confidence interval, in Tables 1 and 2.

Results and discussion

It has long been recognized that the chemical and physical properties associated with a metal centre can be influenced by surrounding bound ligands. These effects can be broken down into electronic and steric effects, and a general property, P, can be expressed as [25]

$$P = aS + bE + c$$

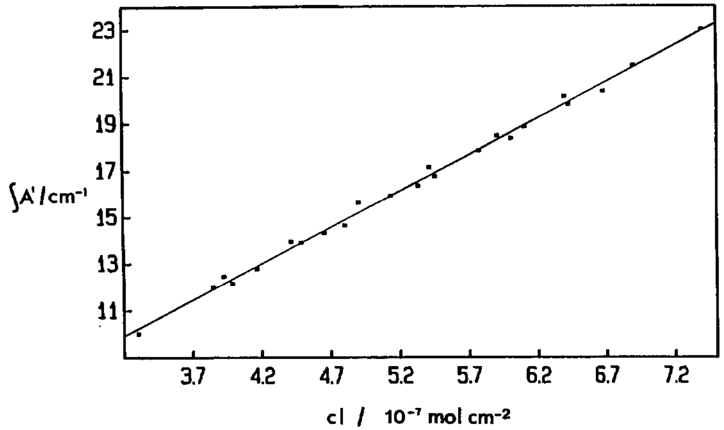

Fig. 3. Intensity determination for $(\eta^5\text{-}C_5H_4I)Fe(CO)(PPh_3)I$. The integrated absorbance areas are plotted against the products of the concentration and pathlength combinations.

where S is the steric effect, usually described by the Tolman cone angle, θ [1], E is the electronic effect associated with the ligand, *e.g.*, a Hammett function [26], pK_a [27], or IR stretching wave number $\bar{\nu}$(CO) [1], and a, b and c are constants.

For some time now, we [10b] and others [7,10a,28], have been interested in the steric and electronic properties associated with a metal bonded to a substituted cyclopentadienyl ligand in complexes of the type $(\eta^5\text{-}C_5H_4R)ML_x$. For instance, NMR parameters can be used to probe both steric and electronic [11] parameters associated with R. Infrared spectroscopy can also be used to examine electronic effects associated with R by using the ν(CO) position if the metal is bonded to a CO ligand. However, only one report has appeared on the correlation of the integrated intensity measurements of ν(CO) with the electronic property associated with a substituted cyclopentadienyl ligand in substituted cyclopentadienyl metal carbonyl complexes [12]. In that study, the combined ν(CO) intensities for the two CO bands of a series of substituted cyclopentadienyl tricarbonyl man-

Table 1

Infrared data (carbonyl stretching wave numbers and absolute intensities), electronic and steric parameters for $(\eta^5\text{-}C_5H_4R)Fe(CO)(PPh_3)I$

R	$\bar{\nu}$ [a] (cm^{-1})	A [a] (km mol^{-1})	σ_m [b]	σ_p [b]	F [b]	R^1 [b]	θ_1 [c] (degrees)	θ_2 [c] (degrees)
$SiMe_3$	1951	339(7)	−0.04	−0.07	0.01	−0.08	158	138
Me	1951	347(7)	−0.07	−0.17	0.01	−0.18	141	64
^{t}Bu	1951	349(6)	−0.10	−0.20	−0.02	−0.18	154	128
H	1958	354(5)	0	0	0	0	128	55
I	1964	310(2)	0.35	0.18	0.42	−0.24	131	62
CO_2Me	1971	286(2)	0.37	0.45	0.34	0.11	132	47

[a] Stretching wave numbers, $\bar{\nu}$, and absolute integrated intensities, A, of the terminal CO group of $(\eta^5\text{-}C_5H_4R)Fe(CO)(PPh_3)I$, recorded in $CHCl_3$. [b] The electronic parameters for the R group, σ_m, σ_p, F and R^1, are Hammett and modified Swain–Lupton constants, obtained from ref. [26]. [c] The cone angles, θ_1 and θ_2, were obtained from ref. [11], and refer to the angle where the apex is defined as the metal and the cyclopentadienyl ring centroid, respectively.

Table 2

Infrared data (carbonyl stretching wave numbers and absolute intensities), electronic and steric parameters for (η^5-C_5H_4Me)Fe(CO)(L)I

L	$\bar{\nu}$ [a] (cm^{-1})	A [a] (km mol^{-1})	θ [b] (degrees)	pK_a [b]	χ [b]	$\bar{\nu}_A$ [c] (cm^{-1})	$\bar{\nu}_B$ [c] (cm^{-1})
PBz_3	1951	344(9)	165	6.00 [d]	10.35	1919.2 [e]	1915.5 [e]
PPh_3	1951	347(7)	145	2.73	13.25	1922.0	1918.0
$P(OiPr)_3$	1958	369(7)	130	4.08	19.50	1930.0 [f]	1927.0 [f]
$P(OMe)_3$	1966	377(6)	107	2.6	24.10	1939.5	1934.0
$P(OPh)_3$	1979	325(5)	128	−2.00	30.20	1951.0	1947.0
P(O-*o*-Tol)$_3$	1979	327(6)	141	−1.83	27.7	1952.0	1947.0

[a] Stretching wave numbers, $\bar{\nu}$, and absolute integrated intensities, A, of the terminal CO group of (η^5-C_5H_4Me)Fe(CO)(L)I, recorded in $CHCl_3$. [b] The cone angles, θ, and the pK_a and χ of the ligands, L, were obtained from ref. [3c]. [c] $\bar{\nu}_A$ and $\bar{\nu}_B$ are the stretching wave numbers, reported in ref. [3c], of the terminal carbonyl of (η^5-C_5H_5)Fe(CO)(L)(COMe) and (η^5-C_5H_4Me)Fe(CO)(L)(COMe), respectively. Spectra were recorded in cyclohexane. [d] This value was taken from ref. [3b]. [e] The value given is the average for the two peaks observed. [f] The value given is the average for the three peaks observed.

ganese and rhenium complexes were found to decrease as the electron withdrawing property associated with the cyclopentadienyl substituents increased.

To obtain further information on the possible use of absolute integrated intensity data for assessing electronic properties, we carried out a study on a series of (η^5-C_5H_4R)Fe(CO)(L)I complexes, for which only one ν(CO) band is expected. However, as mentioned in the introduciton, more than one ν(CO) vibration is sometimes observed in non-polar solvents [3].

The infrared data obtained for our complexes are shown in Tables 1 and 2, and the correlations of these data with various electronic and steric parameters are shown in Tables 3 and 4. Note that the error limit on a particular intensity

Table 3

Correlation of infrared data with various electronic and steric parameters for (η^5-C_5H_4R)Fe(CO)(PPh_3)I [a]

Variables			R^2
x	y	z	
$\bar{\nu}$	A	–	0.7906
σ_m	A	–	0.8714 [b]
σ_p	A	–	0.8657 [c]
F	A	–	0.8139
θ_1	A	–	0.1600
σ_m	$\bar{\nu}$	–	0.8947 [d]
σ_p	$\bar{\nu}$	–	0.9542 [e]
$\bar{\nu}$	θ_1	A	0.8675 [f]
σ_m	θ_1	A	0.8841 [g]
σ_p	θ_1	A	0.8532 [h]

[a] There are six data points for each plot. Results are given for the equations $y = a + bx$, or $z = a + bx + cy$. [b] $a = 341$, $b = -117$; $F = 27.1$, $P = 0.0065$. [c] $a = 334$, $b = -102$; $F = 25.8$, $P = 0.0071$. [d] $a = 1955$, $b = 36.8$; $F = 34.0$, $P = 0.0043$. [e] $a = 1957$, $b = 33.3$; $F = 83.3$, $P = 0.0008$. [f] $a = 8500$, $b = -4.09$, $c = -1.12$; $F = 17.4$, $P = 0.0224$. [g] $a = 436$, $b = -141$, $c = -0.665$; $F = 20.1$, $P = 0.0183$. [h] $a = 416$, $b = -120$, $c = -0.578$; $F = 15.5$, $P = 0.0261$.

Table 4

Correlation of infrared data with various electronic and steric parameters for $(\eta^5\text{-}C_5H_4Me)Fe(CO)(L)I$ [a]

Variables			R^2
x	y	z	
$\bar{\nu}$	A	–	0.2340
pK_a	A	–	0.3997
χ	A	–	0.0830
θ	A	–	0.2396
pK_a	θ	A	0.9280 [b]

[a] There are six data points for each plot. Results are given for the equations $y = a + bx$, or $z = a + bx + cy$. [b] $a = 455$, $b = 5.95$, $c = -0.869$; $F = 33.2$, $P = 0.0090$.

measurement is 1–3%. We had hoped that this value would have been smaller (±1%), especially since wave number data can be measured to ± 0.5 cm^{-1}.

The influence of the variation of R and L on A is discussed below.

Variation of R

Reasonable correlations are obtained when A is plotted against the electronic parameters $\bar{\nu}$(CO), σ_m, σ_p or F as reflected by the correlation data shown in Table 3. The intensity of the ν(CO) band decreases with the increasing electron withdrawing ability of R, which confirms the results reported for substituted cyclopentadienyl complexes of manganese and rhenium [12]. There is no correlation between the intensities in this series of compounds and the steric size [11] of the cyclopentadienyl ligand. Combining the steric size, θ, (Fig. 4) with the electronic parameters has only a minor effect on the observed correlation in most instances, although a larger improvement is noted when the electronic parameter is $\bar{\nu}$(CO).

Variation of L

The most surprising result emerged from attempts to correlate the electronic properties of L ($\bar{\nu}$(CO), pK_a, χ) with the intensity. No correlation was found between A and $\bar{\nu}$(CO), pK_a or χ (see Table 3). Both the highest and the lowest intensity values of this series are associated with electron withdrawing ligands ($P(OPh)_3$, $A = 325$ km mol^{-1} and P(OMe), $A = 377$ km mol^{-1}). There is also no direct correlation between the steric size of L and A. However, when the two

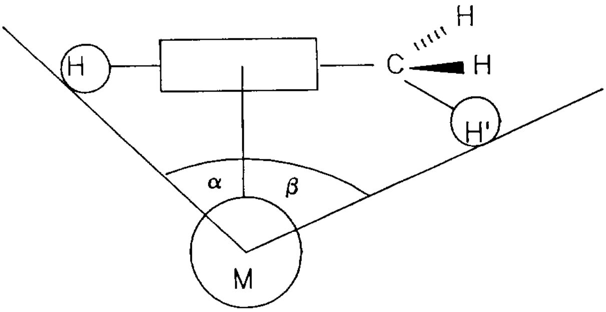

Fig. 4. Steric measurement of a ring substituted cyclopentadienyl ligand. See [11] for further details.

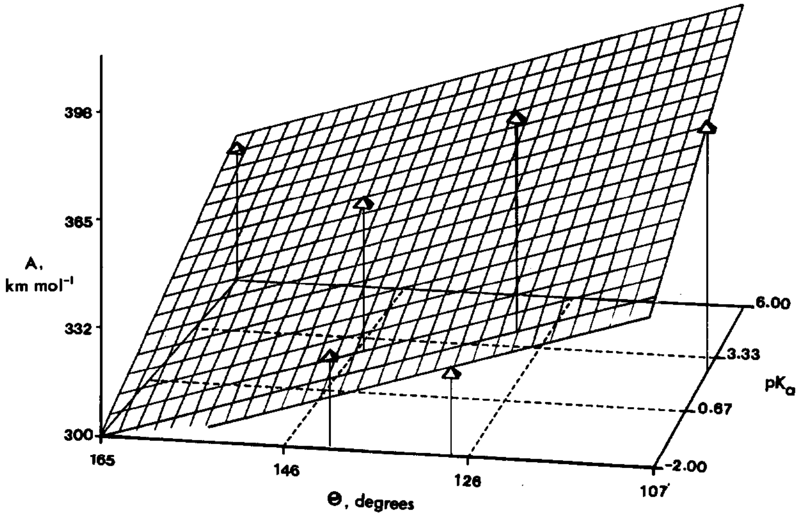

Fig. 5. A three-dimensional plot of A against θ (steric size) and pK_a (electronic parameter) associated with the L group for the complexes (η^5-C_5H_4Me)Fe(CO)(L)I.

effects (pK_a as electronic parameter, and the cone angle, θ, as the steric parameter) are combined, a very good correlation ($R^2 = 0.93$) is found (Fig. 5).

The observed steric effect can be rationalized as follows. If R is large, interaction between R and the rest of the molecule can be relieved by distortions of R away from the ring plane (Fig. 6a) [11], lengthening of the Fe-ring bond, or a distortion of the whole ring (Fig. 6b) [29]. In all the above mechanisms, the effect on the Fe–CO bonding interaction should be small. On the other hand, variations of the size of L will result in steric interaction with CO, and in particular could decrease the Fe–CO orbital interaction.

The intensity measurements reflect the ability of the iron atom to transfer electron density on to the carbon atom of the CO ligand, via the π bond, during a vibration [30]. Since the transfer of electron density is from L via Fe to CO, this effect will be enhanced by the electron donating ability of L. Steric effects associated with L could also be important. A measure of this steric effect can be obtained from L–Fe–CO bond angle measurements. These data are available for a series of (η^5-C_5H_4R)Fe(CO)(L)I complexes and are given in Table 5. As can be

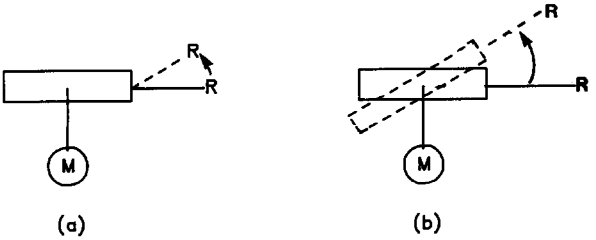

Fig. 6. Distortions of the substituted cyclopentadienyl ring in (η^5-C_5H_4R)Fe(CO)(L)I to relieve steric stress.

Table 5

Bond angle measurements for a series of (η^5-C_5H_4R)Fe(CO)(L)I complexes

R	L	θ [a] (degrees)	L–Fe–CO angle (degrees)	Ref.
Me	2,6-$Me_2C_6H_3NC$	88	91.8(4)	31
Me	$P(OMe)_3$	107	92.4(5)	31
Me	$P(C_6H_{11})_3$	170	95.4(2)	31
$CHPh_2$	PPh_3		91.0(1)	16
I	PPh_3		89.2(6)	16
$CH(CH_3)_2$	PPh_3		91.4(2)	16

[a] Tolman cone angle, ref. 1.

seen, variation of the R group has little influence on the PPh_3–Fe–CO angle, while an increase in the size of L increases the L–Fe–CO bond angle significantly.

Notwithstanding the rationalization above it is apparent that ν(CO) position and intensity data do not correlate for the complexes investigated. This is not surprising, since the value of the CO stretching wave number is determined by the bond stretching force constant, and its intensity is governed by the dipole moment function. While these two properties are themselves dependent on the electronic nature of the CO bond, the relative importance of the quantities σ_m, σ_p, F, R^1 θ, pK_a and χ, quoted in Tables 1 and 2, will be different for the force constant and for the dipole moment function. Thus the relationship between the wave number and the intensity is a complex one, and one property is certainly not a simple monotonic function of the other. The CO stretching wave number and integrated intensity therefore provide two separate and distinct probes for obtaining information on metal–ligand interactions.

Conclusion

The measurement of A, the absolute integrated absorption intensity, is a good indication of electronic effects associated with a ligand, provided steric effects are not significant. In particular, variation of A with the cyclopentadienyl ring substituent, R, provides a useful means of estimating the electron donating or withdrawing ability of the R group.

Acknowledgements

We wish to thank the FRD and the University of the Witwatersrand for financial assistance and Ms P. Möhring for the synthesis of Tl[$C_5H_4CO_2Me$].

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