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MÖSSBAUER, ^{13}C NMR AND INFRARED SPECTROSCOPIC STUDIES OF ARYLIRON DERIVATIVES [$Fe(Ar)(CO)L(\eta^5\text{-}C_5H_5)$]

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Summary

^{57}Fe Mössbauer, $^{13}C\{^1H\}$ NMR and IR spectroscopic investigations have been carried out on the aryliron derivatives [$Fe(Ar)(CO)L(\eta^5\text{-}C_5H_5)$] (L = CO, Ar = C_6H_5, C_6F_5, 2-FC_6H_4, 2-ClC_6H_4, 2-IC_6H_4, 2-$CH_3C_6H_4$, 2-($C_6H_5CH_2$)C_6H_4 and C_6H_5CO; L = PPh_3, Ar = C_6H_5, 2-FC_6H_4). Mössbauer isomer shifts and quadrupole splittings, ^{13}C NMR chemical shifts and IR ν(CO) stretching force constants are presented. These data are discussed in relation to variation of the aryl ligand, Ar, and the Fe–C bonds. Evidence is presented for some *ortho* interactions between the iron and the 2-phenyl substituent and is discussed.

Introduction

The technique of Mössbauer spectroscopy has been widely employed to probe the bonding and structures of organo-iron compounds [1]. These studies have encompassed a number of derivatives of the type [$FeX(CO)L(\eta^5\text{-}C_5H_5)$] where L = CO or PR_3 and X = unidentate ligand (including alkyl, acyl, silyl, stannyl, halogen or pseudohalogen) [1–6]. However, with the exception of a brief report of complexes with X = C_6F_5, 2,4,6-$C_6F_3H_2$ and 4-$CF_3C_6F_4$ [3], no Mössbauer effect investigations of aryl derivatives, X = Ar, have been carried out.

Transition metal aryl compounds often possess more kinetic stability than related alkyl derivatives but decomposition does occur and may involve intra- or intermolecular elimination of *ortho*-hydrogen to form an intermediate arylene complex [7]. Such intermediates are generally unstable [7,8] but under suitable coordination conditions a stable mononuclear η^2-benzyne complex may result [9]. Other *ortho*-arylene ligands may be trapped in bridging environments in bi- or poly-nuclear complexes [10]. We have an interest in the properties of *ortho*-substituted aryl-metal complexes which have potential for further reaction to form coordinated aryne and related ligands [11]. In the course of these studies with various transition metals [11,12] we have produced a series of iron complexes $[FeAr(CO)L(\eta^5\text{-}C_5H_5)]$; in this paper we report physical studies by ^{57}Fe Mössbauer, $^{13}C\{^1H\}$ NMR and IR spectroscopy on these iron complexes to monitor the effects of varying *ortho*-phenyl substitution.

Experimental

Organometallic complexes were prepared and manipulated under dry, oxygen-free nitrogen or in vacuo and experimental techniques have been previously described [11]. The following compounds were prepared as described in the literature and purified by chromatography on neutral alumina and crystallisation from hexane/ether: $[Fe(Ar)(CO)_2(\eta^5\text{-}C_5H_5)]$, (Ar = C_6H_5 [13], C_6H_5CO [13], 2-FC_6H_4 [11], 2-ClC_6H_4 [11], 2-BrC_6H_4 [11], 2-IC_6H_4 [11], 2-$CH_3C_6H_4$ [11], 2-$(C_6H_5CH_2)C_6H_4$ [11], C_6F_5 [11,12]); $[Fe(Ar)(CO)(PPh_3)(\eta^5\text{-}C_5H_5)]$ (Ar = C_5H_5 [14], 2-FC_6H_4 [11]). IR spectra were recorded at ambient temperature (ca. 20°C) in CCl_4 solution using a Perkin–Elmer 580 spectrometer. $^{13}C\{^1H\}$ NMR spectra were recorded at 28 ± 3°C in $CDCl_3$ solutions using a Bruker WP200SY instrument operating at 50.32 MHz; chemical shifts are given relative to internal $SiMe_4$. Mössbauer spectra were recorded at 78 K at Birkbeck College. University of London, using a Cryophysics MS-102 Microprocess Mössbauer spectrometer in the constant acceleration mode. Spectra were fitted using standard non-linear least squares techniques.

Results

Mössbauer spectra

All of the compounds studied in this work gave a well-resolved quadrupole doublet spectrum as shown in Fig. 1. In all cases an asymmetry in the areas of the two quadrupole lines was observed. This effect was also observed by Long [5] for the series $[FeX(CO)_2(\eta^5\text{-}C_5H_5)]$, where X was a halogen or pseudohalogen, and is the result of preferential crystal orientation.

The observed ^{57}Fe Mössbauer parameters, in Table 1, are in good agreement with other low spin Fe^{II} cyclopentadienyl compounds [1,15]. All are characterised by small positive isomer shifts and quadrupole splittings of ca. 2 mm s^{-1}. There is a systematic increase in the isomer shift for the 2-halophenyl complexes $[Fe(Ar)(CO)_2(\eta^5\text{-}C_5H_5)]$ in the order Ar = C_6H_5 < 2-IC_6H_4 < 2-BrC_6H_4 < 2-ClC_6H_4 < 2-FC_6H_4 < C_6F_5. $\Delta R/R$ is negative for ^{57}Fe and so an increase in isomer shift represents a decrease in *s*-electron density. This decrease may be due to σ and/or π effects. Increased σ donation by the iron would lead to a decreased *s*-electron density at the metal and hence an increased isomer shift. π Effects may be of two types: π donation from the aryl group onto the metal and donation of π electrons from the iron into the π^* orbitals of the aryl group. The former would lead to a decreased *s*-electron density at the iron but the latter would result in a decrease in chemical shift. The compounds are low spin Fe^{II} and so it is unlikely that donation from the aryl group would be important (vide infra). Halo-aryl groups are good acceptors, the acceptor properties increasing with increasing electronegativity, and so the observed trend may be explained by increased donation by the metal as the electronegativity of the halogen increases.

The alkyl-substituted aryl groups, Ar = 2-$CH_3C_6H_4$, 2-($C_6H_5CH_2$)C_6H_4, should be better σ donors than the halogenated compounds and so increase the electron density at the iron. Hence both compounds should have smaller isomer shifts. The value for Ar = 2-$CH_3C_6H_4$ is, however, larger than for any of the monohalogenated aryl complexes and the isomer shift for Ar = 2-($C_6H_5CH_2$)C_6H_4 is the same as that for Ar = 2-BrC_6H_4. Since π-bonding effects will be small in these complexes we suggest a direct interaction between the alkyl groups and the iron as the mechanism for the anomalously low *s*-electron density on the metal (vide infra).

The value of the isomer shift for Ar = C_6H_5CO may be rationalised as a balance between two opposing effects. The benzoyl group is a good σ acceptor resulting in an increased value of the isomer shift as *s*-electron density is lost from the iron. It is, however, also a π acceptor, leading to a reduction of the isomer shift. The observed value of 0.032 mm s^{-1} is thus the resultant of these two competing effects.

Replacement of one of the carbonyl groups by a PPh_3 group reduces the amount of π donation by the metal and thus increased values of the isomer shift should be expected. This is observed in our data where phosphination leads to an increase of ca. 0.1 mm s^{-1}. This agrees well with Long [5] who observed an increase of 0.08–0.09 mm s^{-1} on phosphination of [$FeX(CO)_2(\eta^5\text{-}C_5H_5)$], where X = halogen or pseudohalogen, and the very large change in isomer shift between [$FeMe(CO)_2(\eta^5\text{-}C_5H_5)$] ($\delta$ 0.11 mm s^{-1}) and [$FeMe(dppe)(\eta^5\text{-}C_5H_5)$] ($\delta$ 0.53 mm s^{-1}) observed by Mays [16]. The increase is much greater, however, than is observed for [$FeX(CO)_2(\eta^5\text{-}C_5H_5)$], X = alkyl or acyl, where it is about 0.03 mm s^{-1} [7].

There is an increase in the quadrupole splitting for the complexes in the order Ar = $C_6H_5CO < C_6H_5 <$ 2-$CH_3C_6H_4 <$ 2-$FC_6H_4 <$ 2-($C_6H_5CH_2$)$C_6H_4 < C_6F_5 <$ 2-ClC_6H_4 = 2-$BrC_6H_4 <$ 2-IC_6H_4. There appears to be no obvious correlation be-

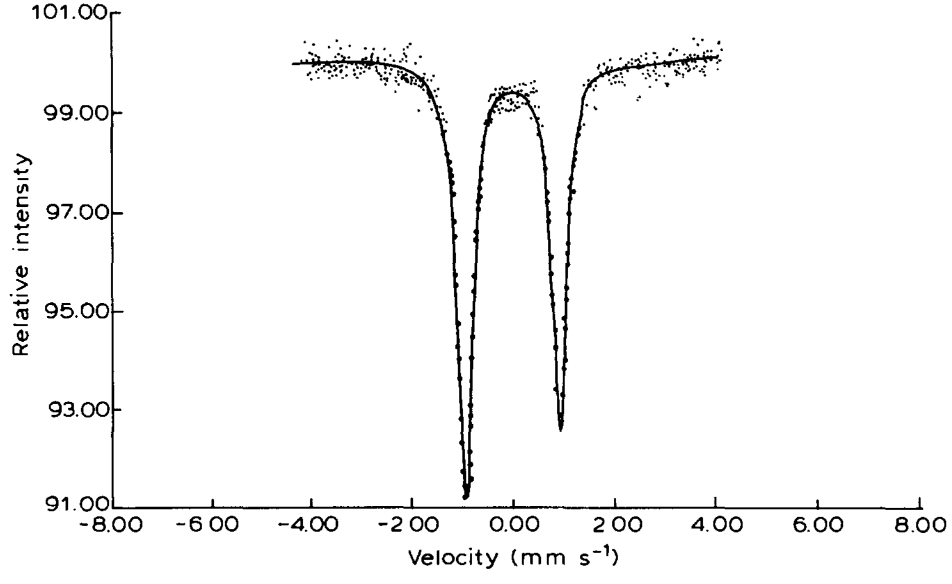

Fig. 1. ^{57}Fe Mössbauer spectrum of [$Fe(C_6H_5)(CO)_2(\eta^5\text{-}C_5H_5)$].

TABLE 1

MÖSSBAUER AND INFRARED SPECTRAL DATA OF TITLE COMPOUNDS

Compound	δ (mm s^{-1})[a]	Δ (mm s^{-1})[b]	$\nu(CO)_{sym}$ (cm^{-1})[c]	$\nu(CO)_{antisym}$ (cm^{-1})[c]	k (mdyn Å^{-1})[d]	k_i (mdyn Å^{-1})[d]
$[Fe(C_6F_5)(CO)_2(\eta^5\text{-}C_5H_5]$	0.083	1.976	2046	1997	16.50	0.400
$[Fe(2\text{-}FC_6H_4)(CO)_2(\eta^5\text{-}C_5H_5)]$	0.039	1.912	2028	1974	16.17	0.436
$[Fe(2\text{-}ClC_6H_4)(CO)_2(\eta^5\text{-}C_5H_5)]$	0.033	2.002	2026	1973	16.15	0.428
$[Fe(2\text{-}BrC_6H_4)(CO)_2(\eta^5\text{-}C_5H_5)]$	0.028	2.000	2026	1973	16.15	0.428
$[Fe(2\text{-}IC_6H_4)(CO)_2(\eta^5\text{-}C_5H_5)]$	0.028	2.013	2024	1972	16.12	0.420
$[Fe(C_6H_5)(CO)_2(\eta^5\text{-}C_5H_5)]$	0.019	1.863	2024	1969	16.10	0.443
$[Fe(2\text{-}CH_3C_6H_4)(CO)_2(\eta^5\text{-}C_5H_5)]$	0.044	1.881	2017	1962	15.99	0.442
$[Fe\{2\text{-}(C_6H_5CH_2)C_6H_4\}(CO)_2(\eta^5\text{-}C_6H_5)]$	0.028	1.944	2016	1962	15.98	0.434
$[Fe(COC_6H_5)(CO)_2(\eta^5\text{-}C_5H_5)]$	0.032	1.844	2029	1969	16.14	0.484
$[Fe(2\text{-}FC_6H_4)(CO)(PPh_3)(\eta^5\text{-}C_5H_5)]$	0.136	1.974	1938		15.17	–
$[Fe(C_6H_5)(CO)(PPh_3)(\eta^5\text{-}C_5H_5)]$	0.119	1.918	1930		15.05	–

[a] Relative to natural α-iron foil, error ±0.001. [b] Error ±0.002. [c] In CCl_4, error ±0.5. [d] C–K [17] stretching force constant (k) and stretch–stretch interaction constant (k_i).

tween the observed quadrupole splitting and the aryl group and this supports a similar observation for [$FeX(CO)_2(\eta^5\text{-}C_5H_5)$] where X = halogen or pseudohalogen.

IR spectra

The band maxima of ν(CO) vibrations are listed in Table 1; compounds of type [$Fe(Ar)(CO)_2(\eta^5\text{-}C_5H_5)$] exhibit strong symmetric and antisymmetric stretching vibrations and compounds [$Fe(Ar)(CO)(PPh_3)(\eta^5\text{-}C_5H_5)$] only a single band. Using the Cotton-Kraihanzel method [17], approximate values for the stretching force constants (k) and the stretch–stretch interaction constant (k_i) have been calculated for these compounds (Table 1). A previous report of ν(CO) bands for compounds [$FeX(CO)_2(\eta^5\text{-}C_5H_5)$] ($X = C_6H_5$, C_6F_5, C_6H_5CO) in CH_2Cl_2 solution [18] indicates that a distinct reduction of these frequencies occurs in the more polar solvent but our ν(CO) values for $X = C_6H_5$ are close to those reported for this compound in cyclohexane [19].

There is a systematic increase in the stretching force constant for the complexes [$Fe(Ar)(CO)_2(\eta^5\text{-}C_5H_5)$] in the order $Ar = 2\text{-}(C_6H_5CH_2)C_6H_4 \sim 2\text{-}CH_3C_6H_4 <$ C_6H_5 $2\text{-}IC_6H_4 < 2\text{-}BrC_6H_4 \sim 2\text{-}ClC_6H_4 < 2\text{-}FC_6H_4 < C_6F_5$. This order follows the increasing electron withdrawing properties of the *ortho*-phenyl substituent, as given by the Hammett-Taft inductive constants (σ_I) [20], but is the inverse of the corresponding resonance constants (σ_R). Since, in the absence of other structural changes, increasing ν(CO) frequencies are generally attributed to reduction in retrodative π-bonding between metal d_π and carbon monoxide π^* orbitals, it appears that the major influence of the aryl group on the carbonyl bonding is by variation in charge distribution via the σ-electron of the Fe–aryl bond rather than through a change in any π interactions between metal and aryl π-orbitals. It is to be noted that there is no anomaly in the effects of CH_3 or $C_6H_5CH_2$ substituents on the ν(CO) frequencies. As is well established, substitution of a CO ligand by PPh_3 results in a decrease of ν(CO) for the remaining carbonyl group but it is significant that for [$Fe(2\text{-}XC_6H_4)(CO)(PPh_3)(\eta^5\text{-}C_5H_5)$] the respective force constants also increase in the order $X = H < F$. The benzoyl compound [$Fe(COC_6H_5)(CO)_2(\eta^5\text{-}C_5H_5)$] shows ν(CO) values consistent with moderate electron withdrawing character of the C_6H_5CO ligand by both σ and π mechanisms.

$^{13}C\{^1H\}$ NMR spectra

The relevant $^{13}C\{^1H\}$ resonances of complexes are listed in Table 2; as noted, some of the aromatic ^{13}C resonances have not been uniquely assigned but generally C(1), C(2), C(6) and C(3) resonances have been unambiguously identified. All signals are singlets except when the aryl group contains fluorine substituents or when PPh_3 is a ligand: in these cases some resonances show coupling to ^{19}F or/and ^{31}P nuclei. The $^{13}C\{^1H\}$ NMR data for [$Fe(C_6H_5)(CO)_2(\eta^5\text{-}C_5H_5)$] have been previously reported [21] and, within experimental error, are identical with our results.

The ^{13}CO chemical shifts in the dicarbonyl compounds [$FeAr(CO)_2(\eta^5\text{-}C_5H_5)$] show a progressive trend to higher frequency in the sequence $Ar = C_6F_5 < 2\text{-}ClC_6H_4$ $\sim 2\text{-}BrC_6H_4 \sim 2\text{-}FC_6H_4 < 2\text{-}IC_6H_4 < 2\text{-}C_6H_5CH_2C_6H_4 \sim 2\text{-}CH_3C_6H_4 < C_6H_5$. The ^{13}CO resonances of the mono-triphenylphosphine compounds occur at the highest chemical shifts whereas the benzoyl compound, [$Fe(COC_6H_5)(CO)_2(\eta^5\text{-}C_5H_5)$], has the lowest shift of the series of compounds studied.

TABLE 2

$^{13}C\{^1H\}$ NMR SPECTRA OF TITLE COMPOUNDS (δ in ppm, (J in Hz))^{a}

Compound	C(1)^{b}	C(2)^{b}	C(6)^{b}
$[Fe(C_6H_5)(CO)_2(\eta^5\text{-}C_5H_5)]$	145.5	145.0	145.0
$[Fe(2\text{-}FC_6H_4)(CO)_2(\eta^5\text{-}C_5H_5)]$	127.9(39.5)^{c}	169.5(229.6)^{c}	146.5(13.1)^{c}
$[Fe(2\text{-}ClC_6H_4)(CO)_2(\eta^5\text{-}C_5H_5)]$	145.9	148.2	147.4
$[Fe(2\text{-}BrC_6H_4)(CO)_2(\eta^5\text{-}C_5H_5)]$	149.3	141.5	147.7
$[Fe(2\text{-}IC_6H_4)(CO)_2(\eta^5\text{-}C_5H_5)]$	156.3	121.6	147.4
$[Fe(2\text{-}CH_3C_6H_4)(CO)_2(\eta^5\text{-}C_5H_5)]$	144.1^{d}	148.9^{d}	146.8
$[Fe\{2\text{-}(C_6H_5CH_2)C_6H_4\}(CO)_2(\eta^5\text{-}C_5H_5)]$	144.8^{f}	151.4^{f}	147.3
$[Fe(C_6F_5)(CO)_2(\eta^5\text{-}C_5H_5)]$	110.3^{h}	150.9^{h}	150.9^{h}
$[Fe(C_6H_5)(CO)(PPh_3)(\eta^5\text{-}C_5H_5)]$	156.6(25.7)^{i}	146.6(1.5)^{j}	146.6(1.5)^{j}
$[Fe(2\text{-}FC_6H_4)(CO)(PPh_3)(\eta^5\text{-}C_5H_5)]$	138.9(24.5^{i},42.6^{c})	171.3(228.0)^{c}	147.9(3.0^{i},15.2^{c})
$[Fe(COC_6H_5)(CO)_2(\eta^5\text{-}C_5H_5)]$	150.9	←	127.9/

^{a} δ ppm in $CDCl_3$ to high frequency of $SiMe_4$; J = coupling constant. ^{b} Aromatic ^{13}C resonances of metal bound aryl group. ^{c} Coupling to ^{19}F. ^{d} Tentative assignments: could be reversed. ^{e} $^{13}CH_3$ resonance. ^{f} Tentative assignment: could be reversed. ^{g} $Ph^{13}CH_2$ resonance. ^{h} Complex multiplet; ^{19}F decoupling

Variations in ^{13}C chemical shifts of $\eta^5\text{-}C_5H_5$ groups are small; they show an increase on halogenation of the aryl ligand in the order $Ar = C_6F_5 < 2\text{-}FC_6H_4 < 2\text{-}ClC_6H_4 < 2\text{-}BrC_6H_4 < 2\text{-}IC_6H_4$ which reflects the changes in $\delta(^{13}CO)$ values but other substituent effects on the two different ^{13}C resonances are not related. It may be noted that $\delta(^{13}C)$ values for both CO and C_5H_5 groups are identical for compounds with $Ar = 2\text{-}CH_3C_6H_4$ and $2\text{-}(C_6H_5CH_2)C_6H_4$.

The ^{13}C resonances of the different coordinated aryl ligands show major variations in the chemical shifts of substituted C(1) and C(2) carbons, whereas C(4), C(5) and C(6) are largely unchanged. Replacement of a coordinated carbonyl group by triphenylphosphine increases the chemical shift of aryl C(1) carbon but has little effect on C(2) or C(6). Literature $^{13}C\{^1H\}$ data [21] for $[Fe(C_6H_5)(CO)\{P(OPh)_3\}(\eta^5\text{-}C_5H_5)]$ in $CDCl_3$ show that the $P(OPh)_3$ ligand also deshields the C(1) carbon (δ 150.0 ppm), but less than PPh_3, and causes little change in the other aryl ^{13}C resonances.

Attempts to obtain values for $^{57}Fe\text{-}^{13}C(1)$ coupling constants by prolonged accumulation of spectra of compounds containing natural abundance ^{57}Fe ($I = \frac{1}{2}$, 2.19%) were inconclusive.

Discussion

Compounds of the type $[FeX(CO)L(\eta^5\text{-}C_5H_5)]$ have been the subject of many chemical studies [22]. The frontier orbitals of the d^6 unit $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]^+$ have been calculated by the extended Hückel method [23]: the filled valence orbitals (principally d_{yz}, $d_{x^2-y^2}$ and d_{xz}) are $1a'$, $2a'$ and a''; the LUMO (mainly d_{z^2}) is $3a'$

C(3)[b]	C(5)[b]	C(4)[b]	CO	C_5H_5	Other
127.5	127.5	122.8	216.1	85.7	
113.6(30.9)[i]	$\overbrace{125.1(7.8)^{i}/123.7}$		215.3(3.9)[i]	85.4	
128.7	$\overbrace{125.1/124.8}$		215.1	86.2	
132.3	$\overbrace{125.4/125.1}$		215.2	86.5	
139.7	$\overbrace{125.9/125.2}$		215.6	87.0	
129.3	$\overbrace{124.6/123.4}$		215.9	86.1	28.15[e]
130.4	$\overbrace{124.9/123.4}$		215.9	86.1	46.8[g]
136.5[h]	136.5[h]	137.6[h]	213.2	85.0	
125.8	125.8	120.8	221.9(33.0)[i]	84.8	
112.5(33.0)[i]	$\overbrace{123.1(7.8)^{i}/122.0}$		222.3(25.9)[i]	84.1	
125.7 $\longrightarrow$		130.1	213.9	86.2	254.6[k]

carried out. [i] Coupling to ^{31}P. [j] Probably coupling to ^{31}P (but could arise from prochirality of *ortho*-^{13}C atoms). [k] Ph^{13}CO resonance.

and this orbital can form a strong σ interaction with a ligand X^-. The HOMO's of the iron fragment are of suitable symmetry for π-donation to empty π-orbitals on X and, of the two possible conformations at right angles, Hoffmann and coworkers [23] concluded that such retrodative π bonding is stronger when the π-nodal plane lies in the molecular symmetry plane (i.e. utilising the a'' orbital). Substitution of a CO ligand to form $[Fe(CO)L(\eta^5\text{-}C_5H_5)]^+$ destroys the molecular symmetry and changes the character of the filled orbitals so that the nodal planes of any π-interactions are rotated. When X = Ar, thus, a normal σ-bond is formed between $3a'$ and carbon (sp^2) orbital but the presence of any additional π bonding is not so clear. An aryl group is a potential π-donor ($\sigma_R = -0.11$, $Ar = C_6H_5$) [20] using filled π-orbitals, but such an interaction should be destabilising. An aryl group may also be a π-acceptor, using an unfilled π^* orbital, and thus could strengthen the Fe–Ar bond and may lead to conformational preferences for orientation of the aryl ring.

No structural studies have been carried out on simple compounds $[FeAr(CO)L(\eta^5\text{-}C_5H_5)]$ (L = CO) for which, ignoring steric effects, the ring might be expected to be preferentially in the molecular symmetry plane. The solid state structure of the compound with $L = PPh_3$, Ar = Ph has been determined [25]: in this compound the phenyl ring is virtually coplanar with the Fe–CO unit and this orientation is consistent with maximum overlap with the π HOMO of $[Fe(CO)(PPh_3)(\eta^5\text{-}C_5H_5)^+]$ [24] – this supports some π interaction but could also arise, in part, from steric effects. Although barriers to rotation about the Fe–Ar bond have not been determined, these could be influenced by the extent of π-bonding but again steric factors may be important as these have been invoked to explain a barrier of > 6 kcal mol^{-1} for methyl rotation in $[FeMe(CO)_2(\eta^5\text{-}C_5H_5)]$ [26].

Previous spectroscopic studies [27,28] (IR, ^{1}H and ^{19}F NMR) on *meta*- and *para*-substituted aryl complexes have indicated that bound [Fe(CO)L(η^5-C_5H_5)] groups have both σ- and π-donor character. From such investigations it has been concluded that the Fe–Ar bond is prevalently σ in character [27] although another interpretation has supported significant π-acceptance by the aryl ligand [28].

The Mössbauer isomer shifts, (δ) (Table 1) of compounds studied in this work indicate that iron *s*-electron density is reduced as substituents of increasing σ_I and decreasing σ_R values are introduced into the coordinated aryl group, with the notable exception of methyl in the *ortho*-tolyl ligand. Thus, increasing δ values may be attributed in some part to increasing σ-donation and/or decreasing π-donation from the iron atom [1] to the aryl ligand; that the former is more important is indicated by changes in ν(CO) frequencies. Accompanying the increase in δ values there is a general decrease in retrodative π-bonding to CO ligands which itself will contribute to the Mössbauer shift changes and must result from changes in the Fe–Ar σ-bonding (inductive effects of substituents) rather than the π-effects.

An earlier investigation of some compounds [FeX$(CO)_2$(η^5-C_5H_5)] suggested a linear correlation between isomer shifts and carbonyl stretching force constants [5], although a significant number of exceptions to such a relationship exist [5,6]. A graph of δ_{IS} vs. k for [FeAr$(CO)_2$(η^5-C_5H_5)] is given in Fig. 2; there is a good correlation for most compounds but 2-benzyl- and, more especially, 2-methyl-phenyl derivatives show divergences. A possible explanation for this anomaly is that an *ortho*-methyl hydrogen atom is exhibiting some direct interaction with the iron, although ^{1}H NMR shifts of these hydrogens are normal [11] and there are no abnormally low ν(C–H) bands in the IR spectra. Any such interaction would form a five-membered ring and be more sterically favourable for the CH_3 rather than the $PhCH_2$ group. It is noted that cyclometallations at *ortho*-methyl groups in complexes of P(2-$CH_3C_6H_4)_3$ are known [29]. If such an interaction withdraws σ-electron density from the iron atom this would explain the higher isomer shifts. Examples of interactions between ligand hydrogen atoms and electron deficient metal centres have been established [30] but these probably involve σ-electron donation (C–H → M)

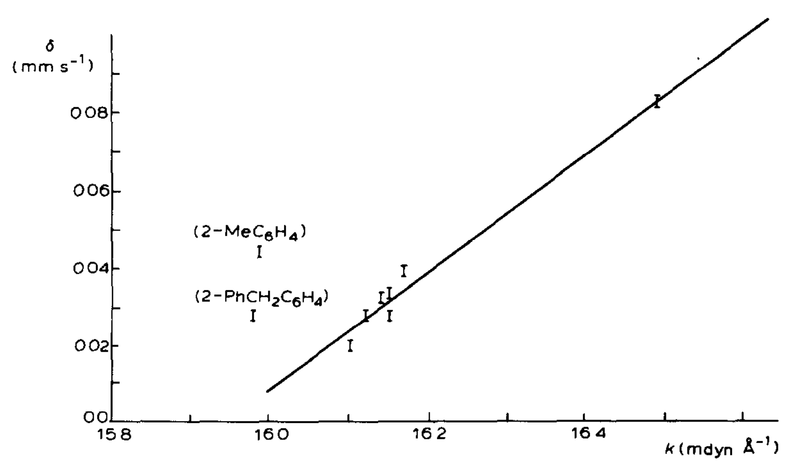

Fig. 2. Plot of Mössbauer isomer shifts vs. carbonyl stretching force constants for complexes [FeAr$(CO)_2$(η^5-C_5H_5)].

to the metal; a CH–Fe interaction in $[Fe_2(\mu\text{-}CH_3)(\mu\text{-}CO)(CO)_2(\eta^5\text{-}C_5H_5)_2]^+$ is of interest [31]. Since no apparent anomalies exist for *ortho*-halogenated aryl derivatives no evidence can be adduced from these Mössbauer studies for any *ortho* interactions between iron and halogen: further comparative studies with *meta* and *para* substituted derivatives might prove instructive.

A correlation between ^{13}CO NMR shifts and $\nu(CO)$ stretching force constants for a series of cyclopentadienyliron carbonyl derivatives has been suggested previously [18]. In the compounds studied here a similar relationship holds approximately.

The ^{13}C chemical shifts for coordinated aryl groups show interesting variations on changing *ortho*-substituents. Generally ^{13}C chemical shifts of substituted benzenes can be predicted by an additive relationship [32] using empirically derived incremental chemical shifts for substituents in appropriate ring positions (C(1), *ortho, meta* or *para*). However, additivity may not hold well when substituents are *ortho* to each other and undergo steric or bonding (e.g. hydrogen bonding) interactions [32]. For compounds $[FeAr(CO)_2(\eta^5\text{-}C_5H_5)]$ (Ar = $2\text{-}FC_6H_4$, $2\text{-}ClC_6H_4$, $2\text{-}BrC_6H_4$, $2\text{-}IC_6H_4$, $2\text{-}CH_3C_6H_4$, $2\text{-}(C_6H_5CH_2)C_6H_4$) the difference in aryl ^{13}C resonances relative to Ar = C_6H_5 may be calculated using tabulated chemical shift increments for the substituents. Using this additive approach there are only small discrepancies between calculated and experimental values for $^{13}C(3)$, $^{13}C(6)$ $^{13}C(4)/^{13}C(5)$ chemical shifts ($\leqslant$ 3 ppm) and also for $^{13}C(1)$ resonances, except when Ar = $2\text{-}FC_6H_4$ or C_6F_5 for which slightly larger shift variations occur. The $^{13}C(2)$ chemical shifts, however, are less predictable and vary more widely (up to 14 ppm) from the additivity principle: this discrepancy of C(2) shift supports some interaction between the iron group and the 2-substituent. Again, comparison of ^{13}C NMR data with *meta* and *para*-substituted aryl compounds would be pertinent.

The effect of $Fe(CO)L(\eta^5\text{-}C_5H_5)$ groups on the chemical shifts of the benzene ring is also of interest. Incremental chemical shifts (ppm) for C(1), C(2)/(6), C(3)/(5), C(4) are: +17.5, +17.0, −0.5, −5.2 (L = CO); +28.6, +18.6, −2.2, −7.2 (L = PPh_3); from the literature [21] respective increments for L = $P(OPh)_3$ are +22.0, +18.5, −1.6, −6.3. These iron substituents show deshielding effects both at C(1), which varies with ligand, L, in the order $PPh_3 > P(OPh)_3 >$ CO, and also at C(2), which is less dependent on the nature of L.

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