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^{13}C CHEMICAL SHIFTS AND CARBONYL STRETCHING FREQUENCIES AS STRUCTURAL PROBES FOR FERROCENYL KETONES

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Summary

^{13}C chemical shifts (δ(CO)) have been measured for a series of aromatic ferrocenyl ketones ($FcCOC_6H_4X$) and some sterically hindered analogues (FcCOR, R = mesityl, anthracyl, t-Bu, adamantyl). The shifts correlated quite well with those of the corresponding benzophenones. From the carbonyl carbon shifts (δ(CO)), estimates were made of the interplanar angle between the carbonyl sp^2 and the phenyl ring planes. Substituent effects of the Cp ring carbons are discussed. The solution (CCl_4) infrared spectra of the derivatives were obtained and the carbonyl stretching frequency (ν(CO)) was found to correlate roughly with δ(CO). Estimates were also made of the interplanar angle between the cyclopentadienyl ring plane and the carbonyl plane, for sterically hindered ketones using δ(ÇO) values.

Introduction

There have been a number of detailed reports on the ^{13}C spectra of carbonyl derivatives. Stothers and Lauterbur [1] examined the carbonyl carbon chemical shifts (δ(C=O)) of a range of ketones, aldehydes, acids and esters, and demonstrated their use as a diagnostic probe of structure. A more detailed and complete ^{13}C analysis of aromatic ketones was undertaken by Dhami and Stothers [2] who obtained evidence for steric hindrance to coplanarity of the acetyl group in several *ortho*-substituted acetophenones. Similar studies have been made of benzophenones [3] and benzaldehydes [4]. More recently, torsional barriers have been investigated in these systems by Jost and co-workers [5,6].

Reversed substituent effects have been reported for δ(C(13)) in *para* substituted benzophenones [7]. ^{17}O NMR studies of acetophenones and benzaldehydes [8] have shown that δ(O(17)) values are very sensitive to substituent effects, particularly in

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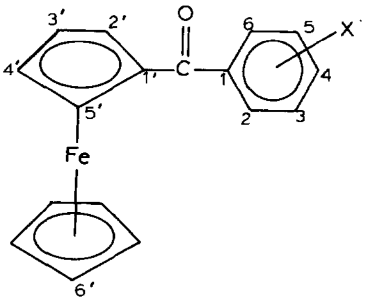
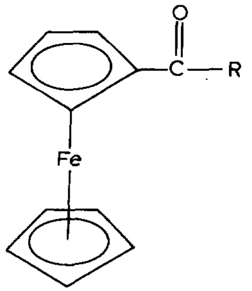
the *ortho* and *para* positions. The results reported here derive from a detailed Mössbauer study of ferrocenyl ketones [9,10], itself a part of a continuing programme of investigation of ferrocene derivatives and complexes.

Results and discussion

^{13}C chemical shifts (δ in ppm from TMS) have been measured for a range of aromatic ferrocenyl ketones and some sterically hindered analogues depicted below.



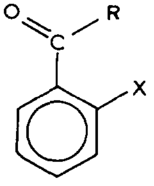


(R = t-Bu, 9-anthracyl,
1-adamantyl, mesityl)

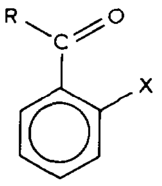
A number of these derivatives are new and have been prepared by conventional methods reported in the experimental section. In addition, we have measured the carbonyl stretching frequencies (ν(CO)) of these derivatives in CCl_4 solution.

Infrared spectra

The carbonyl stretching frequencies for the ferrocenyl ketones appear in Table 1. In every case the resonance appeared as a single peak with relatively minor shoulders. This indicates that all the derivatives have a preferred conformation. For planar *ortho* and *meta* structures, there are two major conformations defined by



S-*trans*



S-*cis*

X being either *cis* or *trans* to the carbonyl group. In the case of acetophenones, the *ortho* methyl derivative adopts the *cis* conformation characterised by a higher ν(CO) [11].

For the ferrocenyl derivatives, severe steric hindrance between X and the ferrocenyl moiety occurs. It is therefore assumed that all the derivatives adopt the S-*cis* conformation, though as will be seen later, the CO group itself will be forced out of the plane of the aromatic ring.

Comparison of the ν(CO) values with those of the corresponding acetophenones

TABLE 1

CARBONYL STRETCHING FREQUENCIES (ν(CO) in cm^{-1}) FOR FERROCENYL KETONES (FcCOR) FOR 0.1 *M* SOLUTIONS IN CCl_4

R	ν(CO) [a]	R	ν(CO)
C_6H_5	1647	H	1647
o-$C_6H_4CH_3$	1650	t-Bu	1661
m-$C_6H_4CH_3$	1646	Ad [b]	1651
p-$C_6H_4CH_3$	1643	An [c]	1647
p-$C_6H_4OCH_3$	1638		
o-C_6H_4Cl	1659		
m-C_6H_4Cl	1645		
p-C_6H_4Cl	1644		
o-C_6H_4Br	1658		
m-C_6H_4Br	1646		
p-C_6H_4CN	1646		
2,4,6-$C_6H_2(CH_3)_3$	1650		

[a] ±0.5 cm^{-1}. [b] 1-Adamantyl. [c] 9-Anthracyl. [d] [3]-Ferrocenophan-6-one (I) gave a value of 1680 cm^{-1}.

reveals that the latter are higher on average by 40–50 cm^{-1}. This signifies a substantial interaction of the carbonyl π orbitals with the ferrocene ring. Such an effect is well documented and has been used to explain the remarkable basicity of ferrocenyl ketones [12]. The carbonyl group and Cp rings in ferrocene carboxaldehyde (FcCHO) are known to be planar [13]. FcCHO has a ν(CO) of 1647 cm^{-1} and may therefore be used as a reference for the other derivatives. FcCOPh has an identical value which strongly suggests that the dominant effect whether conjugative or inductive is via the ferrocene group. Molecular models indicate an interplanar angle of some 45° which would make the phenyl group even less competitive as a conjugating group.

Of considerable importance in this respect is the crystal structure of 1-acetyl-1′-benzoyl ferrocene [14]. The carbonyl of the acetyl group is essentially coplanar with its Cp ring, whereas the benzoyl carbonyl makes a small angle (11.5°) with its Cp nucleus but a large angle of 32° with the plane of the benzene ring. This is strong evidence that the major contribution to resonances involving the carbonyl carbon is via the Cp rings.

The effect of *para* substituents is small but significant for electron releasing substituents. An excellent correlation ($r = 0.999$) is obtained for a plot of ν(CO) vs. σ^+, though admittedly only four points are available. This indicates that a small resonance effect is operating. The geometry of the ferrocenyl ketones will be approximately the same as that of the benzophenones and indeed some correlation appears between the ν(CO) values for the two systems though data is rather scanty [15]. *Ortho* substituents, particularly halogens, significantly increase ν(CO). This supports the *S-cis* structure, since a proximate halogen is known to raise ν(CO) when the dipoles are arranged in the same direction [16]. Steric factors will also play a role as can be seen from the ν(CO) value of 1661 cm^{-1} for FcCO-t-Bu. In this case, the Cp ring twists out of the carbonyl plane. This value can be compared with that of [3]-ferrocenophan-6-one (I) (1680 cm^{-1}) where the twist angle (ϕ) is 42° [17].

ν(CO) should be a function of $\cos^2\phi$ and an empirical expression can be written in the same way as for ^{13}C chemical shift of the carbonyl carbon (vide infra, ref. 26).

$$\cos^2\phi = \frac{\nu(\mathrm{CO})^x - \nu(\mathrm{CO})^{90}}{\nu(\mathrm{CO})^0 - \nu(\mathrm{CO})^{90}} \tag{1}$$

where $\nu(\mathrm{CO})^x$, $\nu(\mathrm{CO})^{90}$ and $\nu(\mathrm{CO})^0$ are the carbonyl stretching frequencies for the compound in question, a model system where the carbonyl group is orthogonal to the Cp plane, and where the group is coplanar respectively. Equation 1 can be modified slightly to give

$$\cos^2\sigma = \frac{\Delta\nu_x}{\Delta\nu_0} + 1 \tag{2}$$

where $\Delta\nu_x = \nu(\mathrm{CO})^x - \nu(\mathrm{CO})^0$ and $\Delta\nu_0 = \nu(\mathrm{CO})^0 - \nu(\mathrm{CO})^{90}$.

Since the Cp ring and CO group in ferrocene carboxaldehyde are coplanar, the value of $\nu(\mathrm{CO})$ of 1647 cm^{-1} can be taken as $\nu(\mathrm{CO})^0$. Using this value and the value for I, together with the known ϕ value, $\Delta\nu_0$ can be evaluated as -74 cm^{-1}. This in turn gives

$$\cos^2\phi = 1 - 0.0136\Delta\nu_x \tag{3}$$

For the aryl derivatives, if it is assumed that $\nu(\mathrm{CO})$ is only effected by the angle ϕ, it is apparent that such angles must be rather small. Even for the mesitoyl derivative, the calculated ϕ is only 12°. This lends support to the postulate that the Cp ring and carbonyl groups remain sensibly coplanar. The apparently much larger angles for the *ortho*-chloro and -bromo derivatives ($\phi \sim 24°$) must be treated with some caution in view of the known enhancement of $\nu(\mathrm{CO})$ due to the specific dipole–dipole interactions previously referred to. Further complications in using this simple empirical approach are illustrated by considering the t-butyl derivative (FcCO-t-Bu). A value of $\phi = 26°$ is obtained from eq. 3 which is considerably smaller than that calculated from ^{13}C carbonyl shifts (vide infra). One of the major problems is the choice of a suitable model carbonyl, high-lighted by the values of $\nu(\mathrm{CO})$ of 1647 and 1677 cm^{-1} for ferrocenecarboxaldehyde and acetyl ferrocene respectively. The latter should logically be the choice as the reference for alkyl ferrocenyl ketones but obviously gives meaningless results.

^{13}C NMR spectra

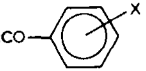
The $\delta(^{13}\mathrm{C})$ values appear in Tables 2, 3 and 4. Using $\mathrm{CDCl_3}$ as a solvent, it was not always possible to detect C(1′) owing to masking by the solvent triplet (δ 77.0 ppm). Accordingly these shifts were also measured in $\mathrm{CS_2}$. The assignments of the aromatic derivatives were made either by direct comparison of relative shifts with those of the corresponding acetophenones [2], or by using the additivity rules described previously for aromatic systems [18,19]. The results of these calculated values appear in parentheses in Table 2. In most cases this proved quite satisfactory but occasionally, particularly with *ortho* substituents, substantial deviations from additivity occurred. Non-additive behaviour has been noted and analysed by Taft [20] and Lynch [21] by the dual substituent parameter approach.

The assignments for 1-adamantyl ferrocenyl ketone (FcCOAd) were made by comparison with 1-AdCHO and 1-$\mathrm{AdCOCH_3}$ [22] and those for 9-anthracyl ferrocenyl ketone (FcCOAn) with reference to 9-AnCHO [23].

As mentioned previously, the geometry of the aromatic ferrocenyl ketones should

TABLE 2

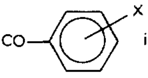
^{13}C CHEMICAL SHIFTS[a,b] FOR AROMATIC FERROCENYL KETONES,



X	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(1′)	C(2′,5′)	C(3′,4′)	C(6′)	C=O	Others
H	139.8	128.0[d]	128.2[d]	131.4	128.2[d]	128.0[d]	–[c]	71.5	72.5	70.2	198.9	–
	(–)	(–)	(–)	(–)	(–)	(–)						
p-Me	137.1	(128.8[d]	128.8[d]	141.9	128.8[d]	128.2[d]	–[c]	71.5	72.3	70.1	198.5	Me 21.5
	(134.9)	(128.1)	(128.7)	(140.3)	(128.7)	(128.1)						
p-OMe	132.4	130.4	113.4	162.4	113.4	(130.4	–[c]	71.5	72.1	70.1	197.2	Me 55.4
	(132.1)	(129.0)	(113.8)	(162.8)	(113.8)	(129.0)						
p-Cl	137.6	129.5	122.5	138.0	128.5	129.5	–[c]	71.4	72.7	70.2	197.5	–
	(137.9)	(129.3)	(128.6)	(137.6)	(128.6)	(129.3)						
p-CN	143.3	128.4	132.1	114.8	132.1	128.4	–[c]	71.3	73.2	70.4	197.5	CN 118.1
	(143.7)	(128.6)	(131.8)	(116.0)	(131.8)	(128.6)						
o-Me	140.0	135.7	129.7	130.9	124.9	127.5	79.4	71.2	72.5	69.9	202.2	Me 19.8
	(140.5)	(136.9)	(128.9)	(131.3)	(125.3)	(127.9)						
o-Cl	139.5	131.3	128.6	130.9	126.2	130.2	–[c]	71.0	72.9	70.1	198.6	–
	(140.2)	(134.2)	(128.6)	(132.7)	(126.3)	(129.3)						
o-Br	141.4	119.5	130.8	133.4	126.7	128.7	78.3	71.1	72.9	70.1	199.4	–
	(143.2)	(122.5)	(131.6)	(133.1)	(126.6)	(129.7)						
mesitoyl	134.3	134.3	128.4	138.3	128.4	134.4	81.9	70.5	71.8	69.8	205.2	Me(C(2)) 19.9
	(138.3)	(136.8)	(126.7)	(140.2)	(126.7)	(136.8)						Me(C(4)) 21.0
m-Me	139.8	128.6[d]	137.9	132.2	128.0[d]	125.2	78.3	71.5	72.4	70.2	199.1	Me 21.4
	(139.7)	(128.7)	(137.1)	(132.1)	(128.1)	(125.1)						
m-Cl	141.3	128.2	134.3	131.4	129.6	126.2	77.7	71.4	72.8	70.3	197.4	–
	(141.2)	(128.4)	(134.4)	(131.8)	(129.5)	(126.1)						
m-Br	141.5	131.2	122.3	134.3	129.8	126.6	77.7	71.4	72.8	70.3	197.3	–
	(141.5)	(131.4)	(122.7)	(134.8)	(129.9)	(126.4)						

[a] 10% solution in $CDCl_3$, δ in ppm, TMS ref. [b] Calculated values using additivity method in parentheses. [c] Masked by solvent. [d] Tentative assignment.

TABLE 3

^{13}C NMR CHEMICAL SHIFTS (δ(ppm)) OF CYCLOPENTADIENYL RING CARBONS FOR SOME AROMATIC FERROCENYL KETONES 

in CS_2

X	C(1′)	C(2′,5′)	C(3′,4′)	C(6′)
H	78.96	71.98	72.72	70.70
o-Me	80.14	71.98	72.72	70.39
o-Cl	79.14	71.47	73.16	70.61
o-Br	78.88	71.55	73.08	70.61
m-Cl	78.49	71.86	72.91	70.77
m-Br	78.47	71.88	72.88	70.78
p-Br	– [a]	71.85	72.77	70.72
p-CN	78.08	71.83	73.24	70.85
Other systems FcCOR				
R	C(1′)	C(2′,5′)	C(3′,4′)	C(6′)
t-Bu	77.55	71.43	71.43	70.26
anthracyl	83.50	71.55	72.45	70.38
mesityl	82.87	70.77	71.84	70.23

[a] Not observed.

approximate to that of the corresponding benzophenones. For the latter series, crystallographic studies reveal that both aromatic rings are inclined to the carbonyl plane. Thus for Ph_2CO, the plane between the rings is 56° [24].

For 4,4′-dimethoxybenzophenone [25], this angle is almost identical (55°), but the two aromatic rings are inclined to the carbonyl plane at different angles (24 and 35°).

In order to compare the two systems, use was made of δ values relative to the unsubstituted compound ($\Delta = \delta_X^n - \delta_H^n, n$ = carbon number). A plot of $\Delta(FcCOC_6H_4X)$ vs. $\Delta(C_6H_5COC_6H_4X)$ for *para* derivatives [3] showed an excellent correlation ($r = 0.997$, 12 points) with a slope close to unity (eq. 4).

$$\Delta(FcCOC_6H_4X) = 0.99\,\Delta(C_6H_5COC_6H_4X) + 0.3 \tag{4}$$

Similar correlations with the ostensibly planar benzaldehydes [4] gave a less satisfactory correlation ($r = 0.980$, 12 points) and a slope of 1.13.

TABLE 4

^{13}C CHEMICAL SHIFTS [a] FOR HINDERED FERROCENYL KETONES (FcCOR)

R	C=O	C(1′)	C(2′,5′)	C(3′,4′)	C(6′)	Others
t-Bu	210.2	76.8	70.9	71.1	69.7	$>$C 44.2; CH_3 28.1
adamantyl	209.6	– [b]	71.0	71.4	69.7	C(1) 48.9; C(2) 39.7; C(3) 36.8; C(4) 28.4
anthracyl [c]	203.8	82.8	71.3	75.4	70.0	C(1) 126.0; C(2) 125.6; C(3) 129.7; C(4) 128.4; C(10) 134.9
[3]-ferroceno-phan-6-one	211.6	88.0	[d]	[d]	[d]	[d]

[a] 10% solution in $CDCl_3$, δ in ppm, TMS ref. [b] Masked by solvent. [c] Other C atoms in anthracene nucleus not detected. [d] C(1) 74.0, other Cp resonances 69.2, 70.2, 71.0, 72.6, C(7) 44.1, C(8) 31.7 ppm cf. refs. 34, 35.

Correlations with acetophenones [2] were better ($r = 0.994$, 12 points) with a slope of 0.98. It was possible to compare the *ortho* derivatives in the latter case, and interestingly the correlation was quite poor ($r = 0.878$, 24 points) with a slope of 0.89 reflecting the much greater departure from coplanarity of the ferrocene system.

Much effort has been devoted to the elucidation of θ, the angle between the carbonyl and phenyl ring planes in aromatic carbonyl derivatives (ref. 6 and references therein). Dhami and Stothers [26] have developed an empirical relationship between θ and ^{13}C carbonyl shifts which is formulated as

$$\cos^2\theta = \frac{\delta(\mathrm{CO})^x - \delta(\mathrm{CO})^{90}}{\delta(\mathrm{CO})^0 - \delta(\mathrm{CO})^{90}} \tag{5}$$

where $\delta(\mathrm{CO})^x$ is the observed carbonyl shift and $\delta(\mathrm{CO})^0$, $\delta(\mathrm{CO})^{90}$ are the shifts when the aromatic ring and the sp^2 carbonyl plane are coplanar and orthogonal respectively. We have used this equation as follows.

Firstly, it is assumed that benzaldehyde is planar (δ(CO) 192.2 ppm as measured in 10% solution in $CDCl_3$ in this work) and that the carbonyl and Cp rings are coplanar for solutions of ferrocenecarboxaldehyde (δ(CO) 193.2 ppm, this work). No value of δ(CO) for formaldehyde has been reported in this medium and at room temperature, though δ(CO) 194.1 ppm was found in cyclopentane at −30° [27]. A value can be deduced by taking δ(CO) for acetone in $CDCl_3$ as 207.5 ppm [18] then subtracting 9.4 ppm for the average deshielding effect of each methyl group (4.7 ppm) to yield 198.1 ppm. This is a very reasonable estimate, since a change from a hydrocarbon solvent to chloroform causes a deshielding of the carbonyl carbon in acetone of 4.7 ppm [18].

Thus the ferrocene and phenyl substituents shield the carbonyl carbon by 4.9 and 5.9 ppm, respectively, leading to a calculated $\delta(\mathrm{CO})^0$ for planar benzoyl ferrocene of 187.3 ppm. $\delta(\mathrm{CO})^{90}$ may be estimated using the value of +17 ppm quoted by Dhami and Stothers (which represents the deshielding due to an orthogonal phenyl group) and the value of δ(CO) for FcCHO quoted above. This yields $\delta(\mathrm{CO})^{90}$ as 210.2 ppm and eq. 5 becomes

$$\cos^2\theta = \frac{210.2 - \delta(\mathrm{CO})^x}{22.9} \tag{6}$$

Table 5 shows values of θ calculated in this manner. These calculated values appear to be quite reasonable and in keeping with crude estimates made from molecular models (cf. 50–55° for the *o*-Me derivative) and also from the known crystal structures of the benzophenones.

For the anthracene derivative (FcCOAn), a large angle of 58° is calculated. It is interesting that the ^{1}H NMR of this compound, unlike most 9-substituted anthracenes, shows a pronounced lack of symmetry of the aromatic proton signals, clearly reflecting the difference in the environments of the two outer rings.

Although the overall correlation between ν(CO) and δ(CO) is not good, ($r = 0.53$, 15 points), if *ortho*-halogen substituents are omitted (since they are known to have a specific dipole–dipole interaction which increases ν(CO) a better, though still not very satisfactory correlation results ($r = 0.83$, 13 points). Thus both ν(CO) and δ(CO) increase with increasing twist angle, confirming that both these parameters can be useful tests of non-coplanarity.

TABLE 5

CALCULATED VALUES OF TWIST ANGLE (θ) FOR AROMATIC FERROCENYL KETONES, $FcCOC_6H_4X$ (after Dhami and Stothers [26])

X	δ^x (ppm)	cos θ	θ (°) [a]
H	198.9	0.702	45
o-Cl	198.6	0.712	45
o-Br	199.4	0.687	47
o-Me	202.2	0.591	54
2,4,6-Me	205.2	0.467	62
m-Me	196.4	0.776	39
m-Cl	196.3	0.779	39
m-Br	196.3	0.779	39
p-Me	198.5	0.715	44
p-OMe	197.2	0.753	41
p-Cl	197.5	0.745	42
p-CN	197.5	0.745	42

[a] For FcCOAn, $\theta = 58°$.

As expected, the chemicals shifts of C(2′,5′); C(3′,4′) and C(6′) are relatively insensitive to phenyl substituents (Table 3). C(1′) on the other hand is a good deal more sensitive, showing marked downfield shifts for *ortho* substituents. Fedin et al. have made a detailed study of factors affecting ^{13}C chemical shifts of a wide range of mono-substituted ferrocenes [28] and have related their findings to electrophilic substituted reactions [29]. They explain the marked sensitivity of C(1′) carbons in terms of the π-inductive mechanism. π-Electron density accumulates and diminishes at successive carbon atoms in alternate systems [30]. This change in electron density is particularly evident at the junction carbon, C(1′). Values of $\delta(C(1'))$ vary systematically (though non-linearly) for benzene and ferrocene derivatives. These values depend not only on the substituent but also on the anisotropy of the aromatic ring, which in turn depends on θ. Thus $\delta(C(1'))$ values should also offer a structural probe in the aromatic ferrocenyl ketones. Pertinently, $\delta(C(1'))$ correlates quite well with $\delta(CO)$ ($r = 0.971$, 9 points) to give the empirical relationship

$$\delta(C(1')) = 0.50\delta(CO) - 19.9 \tag{7}$$

The sterically hindered derivatives (FcCO-t-Bu, FcCOAd) are characterised by large values of both $\delta(CO)$ and $\delta(C(1'))$ which is indicative of substantial twist of the carbonyl out of the Cp plane (ϕ). A value of ϕ_{calc} can be estimated in a manner analogous to that described for the carbonyl stretching frequencies. Thus

$$\cos^2\phi_{calc} = \frac{\Delta_x}{\Delta_0} + 1 \tag{8}$$

where $\Delta_x = \delta(CO)^x - \delta(CO)^0$, $\Delta_0 = \delta(CO)^0 - \delta(CO)^{90}$

Again, using the data for [3]-ferrocenophan-6-one (ϕ 42°, $\delta(CO)^x$ 211.6 ppm) and ferrocene carboxaldehyde (ϕ 0°, $\delta(CO)^0$ 193.2 ppm), the following relationship can be derived

$$\cos^2\phi_{calc} = 1 - 0.0243\Delta_x \tag{9}$$

From eq. 9 values of ϕ of 40 and 39° respectively for FcCO-t-Bu and FcCOAd are found. However, again the problem arises as to which model system is the most appropriate for the case $\phi = 0°$.

If we take acetyl ferrocene (δ(CO) 201.8 ppm, this work) as the reference then eq. 9 becomes

$$\cos^2\phi_{\text{calc}} = 1 - 0.0457\Delta_x \tag{10}$$

and the values of ϕ_{calc} for FcCO-t-Bu and FcCOAd are 38 and 37°. The choice of reference in this particular instance does not therefore markedly alter the ϕ value. This analysis predicts a very substantial out of plane distortion of the carbonyl which should be reflected in the basicity of these species. The ϕ_{calc} values are in reasonable agreement with those predicted from molecular models (~ 40°) and the Van der Waal's radii of the interacting atoms. Complete vindication of this approach must however await the determination of crystal structures of these derivatives. In addition, it would be very instructive to examine the ^{17}O chemical shift of the carbonyl function since the variation in electron density on the oxygen atom would be considerably greater than that on the carbon.

Experimental

^{13}C NMR spectra were run on a Bruker WP80 spectrometer with a probe temperature of 20 ± 1°C. 10% w/v solutions in either $CDCl_3$ or CS_2 (external deuterium lock) were used. All shifts were measured relative to TMS with the conventional positive sign for downfield shifts. ^{1}H NMR spectra were obtained in $CDCl_3$ using a Varian EM360 spectrometer housed in a constant temperature room. δ in ppm from TMS solution infrared spectra were run on 2.5% w/v solutions in CCl_4 on a Perkin–Elmer 257 instrument, using 170μ path length NaCl cells.

Microanalyses were performed by Manchester University Analytical Laboratory.

Preparation of ferrocenyl ketones

These were prepared by standard acylation [31,32] using the corresponding acyl chlorides and ferrocene in CH_2Cl_2 with $AlCl_3$ as catalyst at low temperature. The following method for mesitoylferrocene typifies the procedure. Mesitoyl chloride (5.5 g, 0.03 mol) was dissolved in dry CH_2Cl_2 (30 ml) and cooled to −30°C in a solid CO_2/CCl_4 slurry. Fresh $AlCl_3$ (4.0 g, 0.03 mol) was added rapidly and the whole was stirred for 1 h at −30°C to give a clear amber-orange solution. This was added dropwise by Pasteur pipette to ferrocene (5.6 g, 0.03 mol) in CH_2Cl_2 (30 ml) at room temperature over 20 min. A violet-blue colour developed immediately. The mixture was stirred at room temperature overnight, then quenched by pouring onto crushed ice (50 g). The aqueous phase was extracted twice with 50 ml portions of CH_2Cl_2 and the combined extracts dried with $MgSO_4$. Evaporation yielded a wine-red oil which was dissolved in 60/80 petroleum ether (10 ml) and chromatographed on neutral alumina, eluting first with 60/80 petroleum ether, then gradually replacing this with CH_2Cl_2. A very diffuse mauve band separated which on evaporation gave 3.6 g red-orange solid. A further quantity (3.5 g) was obtained on elution with EtOAc. Yield 70%, (nc) m.p. 115°C. Found: C, 72.1; H, 6.2; $C_{20}H_{20}FeO$ calcd.: C, 72.3; H, 6.1%.

^{1}H NMR δ (ppm) 2.23 s (6H); 2.29 s (3H); 4.24 s (5H); 4.49 t, *J* 1.8 Hz (2H); 4.62 t, *J* 1.8 Hz (2H); 6.84 = 2H.

The following derivatives were prepared by the above method:

m-Methyl benzoyl ferrocene (nc). 66% red oil. Found: C, 71.1; H, 5.1. $C_{18}H_{16}FeO$ calcd.: C, 71.1; H, 5.3%.

^{1}H NMR δ (ppm) 2.40 s (3H); 4.17 s (5H); 4.53 t, *J* 1.8 Hz, (2H) 4.85 t, *J* 1.8 Hz, (2H); 7.2–7.8 m (4H).

m-Bromo benzoyl ferrocene (nc). 20%, m.p. 106–107°C. Found: C, 55.4; H, 3.4. $C_{17}H_{13}BrFeO$ calcd.: C, 55.3; H, 3.5%.

^{1}H NMR δ (ppm) 4.22 s (5H); 4.6 t, *J* 1.9 Hz (2H); 4.88 t *J* 1.9 Hz (2H); 7.2–8.2 m (4H).

m-Chloro benzoyl ferrocene (nc). 54%, m.p. 102–103°C. Found: C, 62.8; H, 3.9. $C_{17}H_{13}ClFeO$ calcd.: C, 62.9; H, 4.0%.

^{1}H NMR δ (ppm) 4.17 s (5H); 4.55 t, *J* 1.9 Hz (2H); 4.85 t, *J* 1.9 Hz (2H); 7.2–8.0 m (4H).

o-Methyl benzoyl ferrocene (nc). 36% red oil. Found: C, 71.3; H, 5.6. $C_{18}H_{16}FeO$ calcd.: C, 71.1; H, 5.3%.

o-Bromobenzoyl ferrocene (nc). 47%, m.p. 109–110°C. Found: C, 55.8; H, 3.7. $C_{17}H_{13}BrFeO$ calcd.: C, 55.3; H, 3.5%.

^{1}H NMR δ (ppm) 4.32 s (5H); 4.60 t, *J* 2.0 Hz (2H); 4.75 t, *J* 2.0 Hz (2H); 7.3–7.9 m (4H).

o-Chlorobenzoyl ferrocene (nc). 43%, m.p. 100–102°C. Found: C, 63.0; H, 4.2. $C_{17}H_{13}ClFeO$ calcd.: C, 62.9; H, 4.0%.

^{1}H NMR δ (ppm) 4.23 s (5H); 4.58 t, *J* 1.8 Hz (2H) 4.72 t, *J* 1.8 Hz (2H); 7.2–7.6 m (4H).

t-Butyl ferrocenyl ketone [33]. 48%, m.p. 93–94°C.

^{1}H NMR δ (ppm) 1.35 s (9H); 4.20 s (5H); 4.47 t, *J* 2.0 Hz (2H); 4.88 t, *J* 2.0 Hz (2H).

9-Anthracyl ferrocenyl ketone (nc). 59%, m.p. 179°C. Found: C, 76.8; H, 4.6; Fe, 14.3. $C_{25}H_{18}FeO$ calcd.: C, 76.9; H, 4.6; Fe, 14.3%.

^{1}H NMR δ (ppm) 4.27 s (5H); 4.55 t, *J* 2.0 Hz (2H); 4.65 t, *J* 2.0 Hz (2H); 7.4–7.7 m (4H), 8.0–8.3 m (4H), 8.57 s (1H).

1-Adamantyl ferrocenyl ketone (nc). 46%, m.p. 137–138°C. Found: C, 72.6; H, 7.3; Fe, 15.8. $C_{21}H_{24}FeO$ calcd.: C, 72.4; H, 7.0; Fe, 16.0%.

^{1}H NMR δ (ppm) 1.87 br.s, 2.15 br.s (15H); 4.28 s (5H); 4.55 t, *J* 2.0 Hz (2H); 4.98 t, *J* 2.0 Hz (2H).

[3]-Ferrocenophan-6-one was prepared by the improved method of Turbitt and Watts [36].

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