A Carbon-13 Nuclear Magnetic Resonance Study of (Arene)(cyclopentadienyl)iron salts

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Carbon-13 n.m.r. data are presented for the complexes [Fe(η-C_5H_5)(η-C_6H_5X)][PF_6] where X is one of 17 substituents. The results are discussed in terms of current theories and are compared with data for other related transition-metal systems. The chemical shifts are qualitatively interpreted by consideration of the ligand–metal interactions. Spectral data are also given for 17 polysubstituted arene complexes of the type [Fe(η-C_5H_5)(η-arene)][PF_6].

THE interpretation of ^{13}C n.m.r. parameters of aromatic systems and of transition-metal complexes in which such systems are present as π-bonded ligands has been the subject of much work and debate.[1-15] Attempts to correlate these parameters with descriptions of the bonding are hampered by the approximations involved in any theoretical approach, but examination of trends in related compounds can lead to certain conclusions.[16-19] Arene–transition-metal complexes are of special interest because of the large upfield complexation shifts of the ring carbons,[4,5] and in this paper we present some results for the mixed-sandwich systems of (arene)(cyclopentadienyl)iron monocations whose chemistry we have been studying for some time.[20]

RESULTS AND DISCUSSION

A number of complexes of the type [Fe(η-C_5H_5)(η-C_6H_5X)][PF_6] were prepared by standard procedures and the substituent X was chosen so as to provide a wide variation of inductive and resonance effects. The ^{13}C n.m.r. data for these complexes are presented in Table 1 and those for the corresponding free ligands in Table 2. The spectra are referenced to external $SiMe_4$, this being found to give closer agreement for test samples examined in [$^2H_3$]nitromethane and [$^2H_6$]acetone than internal $SiMe_4$ (see Experimental section). Literature assignments were assumed for the free ligands.[2,3,21]

For the complexes, the C_5H_5 resonance was generally readily assigned to the most intense signal in the spectrum. The C^1 quaternary carbon was recognizable by the lack of any nuclear overhauser enhancement. The C^4 carbon (*para* to the substituent) was assigned by intensity considerations, its resonance being approximately half as intense as those of C^2 or C^3. The latter assignments were made by comparison with the spectra of the free ligands, except for the series $C_6H_5CH_nMe_{3-n}$ (n = 0—3) for which one of the signals is little affected by increasing methyl substitution (*i.e.* C^3) whereas the other (C^2) shows a regular shift to high field with decrease in n, reflecting an increasing steric and non-bonding anisotropy effect.[22] Where the C^2 and C^3 signals are close together the assignments should be regarded as tentative.

C^1 Chemical Shifts.—As in the free arenes, the largest shifts in monosubstituted systems are found for the carbon at the site of substitution. The magnitude of the upfield complexation shift for C^1 increases in the order C_6H_5X < [Cr(CO)$_3$(C_6H_5X)] < [Fe(C_5H_5)(C_6H_5X)]$^+$ < [Cr(C_6H_5X)$_2$]. Plots of the shift of C^1 (complex) *versus*

TABLE 1

Carbon-13 n.m.r. data [a] for [Fe(C_5H_5)(C_6H_5X)][PF_6]

X	C^1	C^2	C^3	C^4	C_5H_5	α	β	Other data [b]
H	87.27				75.63			^1J(CH) 176 (C_6H_6) ^1J(CH) 177 (C_5H_5)
CH_3	103.06	87.68	86.63	85.39	75.87	18.78		
CH_2CH_3	108.38	86.53	86.53	85.54	75.57	26.75	12.66	
$CH(CH_3)_2$	113.24	84.87	86.40	85.85	75.39	31.80	20.85	
$C(CH_3)_3$	117.49	83.51	86.16	85.73	75.20	33.34	28.66	
CN [c]	73.17	89.92 *	88.32 *	89.36	78.90	115.03		
NH_3^+ [d]	98.61	83.53	87.71	89.07	79.10			
COPh [c]	98.06	88.91 *	87.67 *	89.40	78.22	193.59	135.19	$C^{2'}$ 129.95, $C^{3'}$ 128.94, $C^{4'}$ 134.27
Ph	103.15	85.30 *	87.20 *	86.22	76.68	134.17	126.79	
Cl	106.60	87.88 *	87.21 *	86.16	78.03			
NO_2	127.46	83.45	87.70	90.04	79.33			
NH_2	124.45	69.54	85.18	79.51	75.02			
NMe_2	126.79	65.66	84.56	79.57	73.66		37.90	
OPh [c]	132.70	76.00	85.98	84.01	76.25		152.40	$C^{2'}$ 119.89, $C^{3'}$ 129.87, $C^{4'}$ 125.62
OMe [c]	134.18	73.48	85.79	83.21	75.57		55.07	
F [e]	137.19	77.23	86.34	86.01	77.23			^1J(CF) 272.9, ^2J(CF) 20.4, ^3J(CF) 7.4, ^4J(CF) 2.8
CO_2H	[f]	88.00 *	87.82 *	88.99 *	77.54	165.59		

[a] Chemical shifts in p.p.m. from external $SiMe_4$. In CD_3NO_2 solution unless otherwise stated. Couplings in Hz. For asterisked values the C^2 and C^3 assignments may be reversed. [b] Primes signify ring carbons of non-complexed phenyl substituents. [c] Recorded in perdeuterioacetone. [d] Recorded in D_2SO_4 with dioxan as secondary reference (67.40 p.p.m.). [e] Recorded in $S(CD_3)_2O$. [f] Not observed. Presumably obscured by C^2 or C^3 signal.

TABLE 2

Carbon-13 n.m.r. data for C_6H_5X [a]

X	C^1	C^2	C^3	C^4	α	β
H	127.65					
CH_3	137.44	128.26	127.52	124.51	19.43	
CH_2CH_3	143.90	127.09	127.59	124.82	27.68	14.07
$CH(CH_3)_2$	148.39	125.62	127.59	124.94	33.16	22.32
$C(CH_3)_3$	150.61	124.45	127.28	124.57	33.34	29.59
CN [b]	111.46	131.16	128.45	132.02	117.49	
NH_3^+ [c]	126.99	122.19	130.19	130.31		
COPh [d]	137.17	129.72	128.61	132.74	196.02	
Ph	140.27	126.17	128.14	126.66		
Cl	132.94	129.07	127.53	125.74		
NO_2	147.41	122.29	128.64	133.87		
NH_2	147.23	113.55	128.20	115.95		
NMe_2	150.36	111.77	128.02	115.52		38.70
OPh [b]	156.46	117.80	128.94	122.36		
OMe [b]	159.04	113.00	128.51	119.59		53.60
F [b,e]	162.12	114.76	129.44	123.43		
CO_2H	130.36	129.07	127.53	125.74	166.49	

[a-d] See footnotes *a* and *c*—*e* to Table 1. [e] ^1J(CF) 243.2, ^2J(CF) 21.5, ^3J(CF) 7.4, ^4J(CF) 2.8 Hz.

C^1 (free arene) for these systems (Figure 1) show a general linear correlation with slopes of 1, 1.4, 1.5, and 1.9 respectively. One can relate this effect in simple terms to the various mesomeric forms of C_6H_5X, both free and complexed (see below).

From the well known ability of transition metals to form cyclohexadienyl complexes [22-24] it can be envisaged that forms (II) and (III) would make more significant contributions in complexes than (IV) and (V), and thus result in a correspondingly lower electron density at C^1 giving rise to the observed enhanced deshielding.[25] The effect is predicted to be most noticeable for $+M$ or $-I$ substituents,[26] as is also observed. Although outside the scope of this paper, the preceding argument may also be used to rationalize the orientation of nucleophilic substitution in arene complexes.

C^4 Chemical Shifts.—For monosubstituted benzenes an approximate correlation has been observed between the chemical shift of the carbon *para* to the substituent (C^4) and the Hammett σ parameter [27] or, better, with the constant σ^+.[28] A good correlation is also obtained [9] by using dual substituent parameters such as those given by Swain and Lupton [29] or by Ehrenson *et al.*[30] In this way the change in shift of C^4 when H is replaced by X may be analysed in terms of field and resonance effects by means of expression (1), where F_X and R_X are respectively the

$$\delta(C^4)_X - \delta(C^4)_H = fF_X + rR_X \qquad (1)$$

field and resonance parameters for substituent X and f and r are appropriate weighting coefficients which should be constant within a given series. Using the Swain–Lupton parameters, Bodner and Todd [9] calculated that the relative contributions of field and resonance effects were 10 and 90% for C_6H_5X and 11 and 89% for $[Cr(CO)_3(C_6H_5X)]$. Graves and Lagowski,[13] following this approach, evaluated analogous values of 58 and 42% for $[Cr(C_6H_5X)_2]$ although these are rather approximate due to the very small changes in $\delta(C^4)$. For our data we obtain values of 17 and 83% for f and r with a correlation coefficient of 0.96.

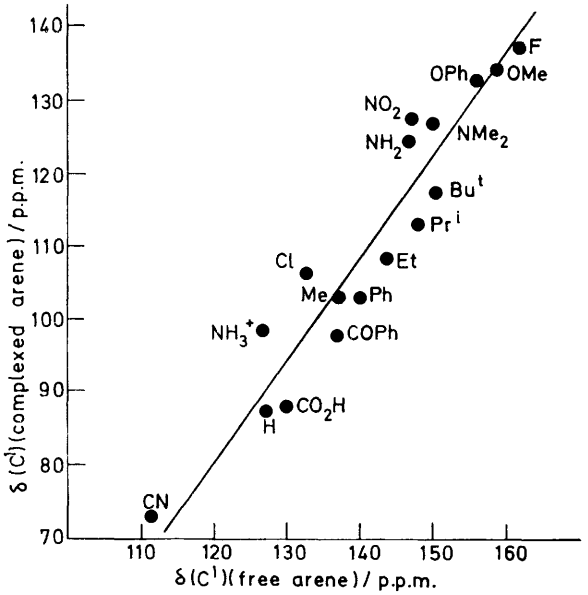
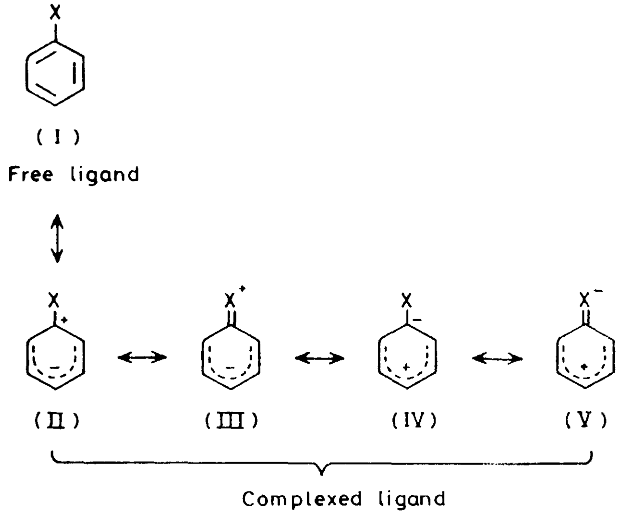


FIGURE 1 Plot of $\delta(C^1)$ for $[Fe(C_5H_5)(C_6H_5X)]^+$ *vs.* $\delta(C^1)$ for C_6H_5X



A plot of the C^4 shift for C_6H_5X *versus* that for $[Fe(C_5H_5)(C_6H_5X)]^+$ also shows a fairly good correlation with

TABLE 3

Selected values of ^1J(CH) in transition-metal π complexes and free ligands

Compound	^1J(CH)/Hz ring	^1J(CH)/Hz CH_3	Ref.
$C_5H_5^-$	157		8
C_6H_6	159		9
1,3,5-$C_6H_3Me_3$	160	126	*a*
[$Fe(C_5H_5)_2$]	175		8
[$Mn(C_5H_5)(CO)_3$]	175		8
[$Pd(C_5H_5)(\eta\text{-}C_3H_5)$]	171		8
[$Cr(C_6H_6)_2$]	164—167		11
[$Cr(CO)_3(C_6H_6)$]	173		9
[$Cr(CO)_3(C_6H_3Me_3)$]	172	129	*a*
[$Fe(C_5H_5)(C_6H_6)$]$^+$	176 (C_6H_6) 177 (C_5H_5)		*b*
[$Fe(C_5H_5)(C_6H_3Me_3)$]$^+$	174 ($C_6H_3Me_3$) 182 (C_5H_5)	129	*b*
[$Rh(C_5Me_5)(C_6H_6)$]$^{2+}$	184 (C_6H_6)		*c*
[$Ir(C_5Me_5)(C_6H_6)$]$^{2+}$	188 (C_6H_6)		*c*

[a] R. V. Emanuel and E. W. Randall, *J. Chem. Soc. A*, 1969, 3002. [b] This work. [c] C. White, S. J. Thompson, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1977, 1654.

a slope of 0.6 (Figure 2). Similar plots for [$Cr(CO)_3$-(C_6H_5X)] and [$Cr(C_6H_5X)_2$] give slopes of 0.8 and 0.05 respectively. The deviation from unit slope illustrates the attenuation in transmission of the effect of the substituent upon complexation. The variation with complex type is discussed below but, qualitatively, the results may be understood in terms of a reduction in the ability of the ring system to fully transmit the substituent effect because of its involvement in the bonding of the ring to the transition metal.

Cyclopentadienyl Resonances.—The cyclopentadienyl ring carbons give a single resonance in all cases indicating rapid rotation of the ring at room temperature. The signal is shifted upfield from $C_5H_5^-$ by *ca.* 25 p.p.m. and lies about 10 p.p.m. downfield from ferrocene. The range of chemical shifts is quite small and the variation of the shift with X can be attributed primarily to the field and steric effects of the substituent (see Figure 3).

Coupling Constants.—The one-bond coupling constants, ^1J(CH), for [$Fe(C_5H_5)(C_6H_6)$]$^+$ are 176 (C_6H_6) and 177 Hz (C_5H_5) and the corresponding values for [$Fe(C_5H_5)$-($C_6H_3Me_3$-1,3,5)]$^+$ are 174 and 182 Hz. These values are comparable to those observed in analogous systems [4,8,9,11] (*cf.* Table 3). Since the observed coupling constants are somewhat larger (by *ca.* 20 Hz) than those for C_6H_6 or $C_5H_5^-$ themselves,[8,9] but relatively constant for similar complexes, it seems unlikely that the factors which influence the complexation shifts, for example, have any direct influence on ^1J(CH).[31]

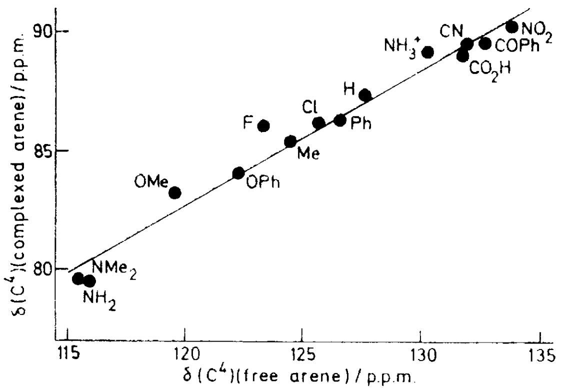


FIGURE 2 Plot of $\delta(C^4)$ as in Figure 1

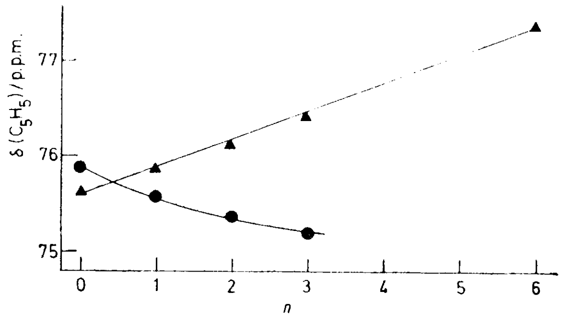


FIGURE 3 Plot of $\delta(C_5H_5)$ *vs.* the number of methyls (*n*) in $C_6H_{6-n}Me_n$ (▲) and $C_6H_5CH_{3-n}Me_n$ (●)

TABLE 4

Carbon-13 n.m.r. data [a] for some polysubstituted complexes [$Fe(C_5H_5)(arene)$][PF_6]

Arene	C^1	C^2	C^3	C^4	C^5	C^6	C_5H_5	Other data
1,2-$C_6H_4Me_2$	(101.92)		87.94	85.23			76.06	CH_3 17.09
1,2-C_6H_4(Me)Cl	(101.92)	(106.96)	87.39 *	85.85 *	85.85 *	87.94 *	77.97	CH_3 17.52
1,2-C_6H_4(Me)OMe [b]	(91.15)	(132.51)	70.09	83.88	82.28	87.76	75.76	C–CH_3 14.45 O–CH_3 55.81
1,2-C_6H_4(Me)NH_2 [b]	(82.96)	(123.28)	69.48	83.88	82.96	86.96	75.26	CH_3 15.55
1,2-C_6H_4(Me)OPh [b]	(92.44)	(130.61)	75.26	87.95	84.19	83.39	76.50	CH_3 14.45, $C^{1'}$ 153.01, $C^{2'}$ 119.46, $C^{3'}$ 129.81, $C^{4'}$ 125.25
1,2-$C_6H_4Cl_2$ [b]	(106.17)		86.90 *	88.01 *			80.25	
1,2-$C_6H_4(NH_2)$Cl	(121.62)	(86.34)	85.42	80.06	84.43	69.66	77.29	
1,2-$C_6H_4(NMe_2)$Cl [b]	(126.2)	(94.5)	87.82	82.04	84.62	72.68	76.80	CH_3 41.41
1,2-$C_6H_4(NMe_2)_2$ [b]	(115.71)		74.28	80.13			73.17	CH_3 39.07
1,3-$C_6H_4Me_2$	(102.47)	85.79		85.79	88.56		76.06	CH_3 18.57
1,3-$C_6H_4(NH_2)$Me [b]	(124.20)	71.14	(100.57)	80.00	84.44	68.00	75.33	CH_3 18.88
1,4-$C_6H_4Me_2$	(101.42)	87.14					76.25	CH_3 18.38
1,4-C_6H_4(Me)Cl	(102.59)	85.45	87.08	(105.24)			78.28	CH_3 18.14
1,4-C_6H_4(Me)NH_2 [b]	(94.90)	(123.59)	68.99	85.54			75.57	CH_3 17.95
1,4-$C_6H_4Cl_2$	(105.55)	87.33					80.31	
1,3,5-$C_6H_3Me_3$	(101.79)	86.65					76.43	CH_3 18.38
C_6Me_6	98.10						77.35	CH_3 15.55

[a] Shifts are in p.p.m. relative to external $SiMe_4$. Recorded in CD_3NO_2 unless otherwise stated. Parentheses indicate substituted carbon; asterisks denote tentative assignments. [b] Recorded in $(CD_3)_2CO$.

Substituent Carbon Shifts.—We shall note here only the shifts for aryl substituents. If we use the relationship observed by Nelson *et al.*[28] between the C^4 shift and the σ^+ constant then we may estimate a σ^+ of 0.3 for the substituent $[Fe(C_5H_5)(C_6H_5)]^+$ thus indicating a moderately deactivating effect (*cf.* Ph 0.0; O_2CMe 0.18; CO_2H 0.47). Similarly values of *ca.* −0.1 and 0.85 are obtained for $[Fe(C_5H_5)(OPh)]^+$ and $[Fe(C_5H_5)(COPh)]^+$ as opposed to −0.45 and 0.6 for the free arenes in the same solvents. In line with this we have so far been unable to acetylate or nitrate the biphenyl complex.[32]

Polysubstituted Benzene Complexes.—Data for some of these systems are presented in Table 4. Additivity relationships hold quite well and may be used to predict shifts to within 1 p.p.m. except for certain *ortho*-disubstituted derivatives. The substituent effects observed in monosubstituted benzene complexes are also apparent in these compounds and do not merit further consideration.

Complexation Shifts.—The ^{13}C n.m.r. shifts for π-bonded carbon atoms are generally observed at higher field than in the free molecules and the origin of this effect has been ascribed to a variety of causes (see, for example, refs. 4, 5, 10, 33, 34, and refs. therein). These include: (*i*) metal-to-ligand π^* back donation,[10,11,13,15,34] (*ii*) ligand π-to-metal donation,[10,15] (*iii*) ligand σ-to-metal donation,[9] and (*iv*) anisotropy of the neighbouring metal atom.[7] Other suggestions based on rehybridization or increased charge density [6,8] may be accommodated by (*i*)—(*iii*).

Semi-empirically, the nuclear screening constant may be expressed in terms of three components [35] [equation (2)] where σ_d is the diamagnetic screening due to electron

$$\sigma = \sigma_d + \sigma_p + \sigma' \qquad (2)$$

circulation on the observed nucleus, σ_p is a paramagnetic term arising from the mixing in of excited electronic states under the influence of the applied magnetic field, and σ' represents the contribution due to non-localized electron circulation (*e.g.* ring currents).

Of these terms σ' is relatively unimportant for conjugated molecules compared to the range of observed chemical shifts.[16] The remaining two terms make significant contributions to σ but, in the theoretical treatment of these terms by Pople,[36,37] σ_d is rather invariant for a given nucleus, especially in closely related compounds (see ref. 18 and refs. therein). Claims that σ_d varies widely, especially in transition-metal compounds, are based on another theoretical approach which also requires an equally wide and opposing variation in σ_p.[33,38,39] Using the Pople treatment, σ_p is seen to be given by equation (3) where K is a constant, ΔE is the

$$\sigma_p = -K(\Delta E)^{-1}\langle r^{-3}\rangle_{2p}\Sigma Q_{AB} \qquad (3)$$

average electronic excitation energy, r is the distance of the carbon $2p$ orbital from the nucleus, and ΣQ_{AB} is a charge-density and bond-order term summed over all neighbouring atoms B. Although these various terms can only be quantified approximately, the prediction of gross trends for transition-metal complexes has been attempted with some success by Brown *et al.*[34] using parameters obtained from semi-empirical calculations. (Good values for ΔE seem to be the major problem for these systems.)

TABLE 5

Ring-carbon complexation shifts [a] for some benzene and mesitylene complexes (L = arene)

		Mesitylene		
Complex	ΔC [b]	$\Delta(C^1)$ [b,c]	$\Delta(C^2)$ [b,c]	Ref.
$[CrL_2]$	53.9	49.4	47.0	13
$[Fe(C_5H_5)L]^+$	40.4	34.8	39.4	*d*
$[Cr(CO)_2L(PPh_3)]$	39.1	32.1	37.0	*e*
$[FeL_2]^{2+}$		26.3	37.6	*d*
$[Cr(CO)_3L]$	35.6	26.6	34.9	12
$[Mo(CO)_3L]$		26.9	32.9	6
$[W(CO)_3L]$		27.5	36.7	6
$[Cr(CO)_2(CS)L]$	29.4			*f*
$[Mn(CO)_3L]^+$	26.7	15.9	30.0	7
$[Ir(C_5Me_5)L]^{2+}$	30.2			*g*
$[Rh(C_5Me_5)]L]^{2+}$	21.2	14.1	21.1	*g*

[a] Free-ligand data for same solvent were used wherever possible. [b] $\Delta C = \delta$ (free ligand) − δ (complexed ligand). [c] C^1 refers to *C*–Me, C^2 to ring C–H. [d] This work. [e] L. A. Fedorov, P. V. Petrovskii, E. I. Fedin, N. K. Baranetskaya, V. I. Zdanovich, V. N. Setkina, and D. N. Kursanov, *Proc. Acad. Sci. USSR*, 1973, **209**, 266; W. R. Jackson, C. F. Pincombe, I. D. Rae, D. Rash, and B. Wilkinson, *Aust. J. Chem.*, 1976, **29**, 2431. [f] D. Cozak, I. S. Butler, J. P. Hickey, and L. J. Todd, *J. Magn. Reson.*, 1979, **33**, 149. [g] C. White, S. J. Thompson, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1977, 1654.

Ab initio and semi-empirical calculations for π-arene complexes are available and although not always in agreement do provide a consistent general description of the bonding involved. Three major metal–arene interactions emerge: (*a*) donation from the ligand σ framework to empty metal *s* and *p* orbitals, (*b*) donation to ligand π^* orbitals of metal $d_{x^2-y^2}$ and d_{xy} electrons, and (*c*) donation of ligand π electrons into metal d_{xz} and d_{yz} orbitals (the *x,y* plane being the plane of the ring system). The d_{z^2} orbital plays only a minor role in the bonding scheme.[15,34,40-43] The dominant interaction is (*b*) followed by (*c*) and (*a*). The last is important in an absolute sense but does not vary greatly in related complexes. In full sandwich complexes (*b*) is more important than in tricarbonyl complexes, and for cyclopentadienyl-to-metal bonding the donation of ligand π-orbital electrons is more important than back donation.[40,41] Brown *et al.* [34] calculate only minor variations in the radial term in equation (3) so that changes in chemical shift may be interpreted in terms of variations in bond order, charge density, and ΔE. Within a given series of complexes, relative changes in shifts can be approximately explained by the appropriate contribution of π donation and back donation. In complexes where the π-to-metal interaction dominates (*e.g.* C_5H_5 complexes) there is a rough overall trend towards lower field with decrease in C–C bond order, whereas an upfield trend is observed for systems where the metal-to-π^* interaction is more significant (*e.g.* arene complexes) although the trend is far from regular (see Table 6).

As a final point we note briefly that there is an approx-

TABLE 6

Chemical-shift and bond-order data for cyclopentadienyl and benzene complexes

Complex	δ(C) ring [a]	ΔP_{ij} [b]	Ref. [c]
$[Fe(C_5H_5)_2]$	40.1	−0.086	8
$[Fe(C_5H_5)(C_6H_6)]^+$	32.4	−0.086	This work
$[Mn(C_5H_5)(CO)_3]$	24.9	−0.100	8
$[Co(C_5H_5)_2]^+$	*ca.* 22	−0.094	*d*
$[Fe(C_5H_5)(CO)_3]^+$	17.1	−0.104	*e*
$[Cr(C_6H_6)_2]$	53.9	0.124	13
$[Fe(C_5H_5)(C_6H_6)]^+$	40.4	−0.088	This work
$[Cr(CO)_3(C_6H_6)]$	35.6	−0.096	12
$[Mn(CO)_3(C_6H_6)]^+$	26.7	−0.090	7

[a] In p.p.m. upfield from uncomplexed ring system. [b] Bond-order data taken from ref. 40. Value given is change relative to uncomplexed ring. [c] For n.m.r. data. [d] Estimated from data of J. E. Sheats, E. J. Sabol, jun., D. Z. Denney, and N. El. Murr, *J. Organomet. Chem.*, 1976, **121**, 73. [e] G. M. Bancroft, K. D. Butler, L. E. Manzer, A. Shaver, and J. E. H. Ward, *Can. J. Chem.*, 1974, **52**, 732.

imate correlation of the complexation shift with the perturbation of the substituent effect as measured by the variation in the C^4 shift. This is shown in Figure 4

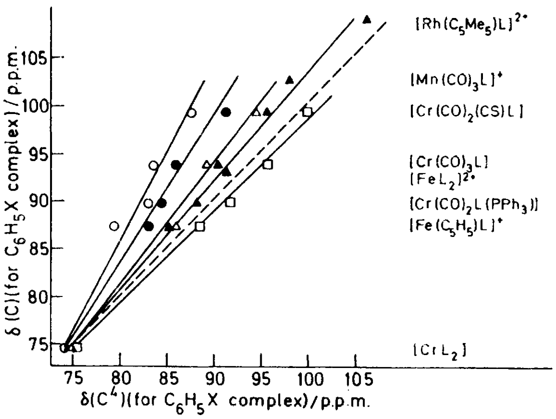


FIGURE 4 Plot of δ(C) for C_6H_6 complex ring carbon *vs.* δ(C^4) for C_6H_5X complex. Data for $[Fe(C_6H_6)_2]^{2+}$ estimated to be *ca.* 93 p.p.m. from values for $[Fe(C_6H_5Me)_2]^{2+}$. X = NMe_2 (○), OMe (●), Cl (△), Me (▲), or CO_2R (□). The broken line represents unit slope, *i.e.* when X = H. Literature data from refs. given in Table 5. L = Arene

and a reasonable correlation with the available data is obtained. More measurements are required to test the validity of this relationship and in view of the sustained interest in arene–transition-metal chemistry[44,45] it is hoped that these will soon be forthcoming.

EXPERIMENTAL

The complexes were prepared following literature prodecures[46-49] or were already available in our laboratory as a consequence of other work.[32,50] The anilinium complex and ion were generated *in situ* by dissolving aniline or its complex in D_2SO_4 using 1,4-dioxan as reference. The spectra were recorded using a Bruker WP-60 instrument with quadrature detection and proton decoupling. Using an 8K transform and a window of 3 800 Hz, a digital resolution of 0.93 Hz was obtained. The complexes were measured as 10—20% w/v solutions of the hexafluorophosphate salts in CD_3NO_3 or $(CD_3)_2CO$, the solvent being used as secondary reference and corrected to an external $SiMe_4$ standard.[51] Test samples measured in both solvents showed only minor concentration and medium effects provided external referencing was used. To correct the given shifts to internal $SiMe_4$, the correction factors +2.3 (CD_3NO_3) and +1.8 [$(CD_3)_2CO$] should be applied. Coupling constants were measured with gated decoupling.

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