# Electronic and Reactivity Effects in $XC_6H_4Fe(CO)(L)C_5H_5$ Complexes

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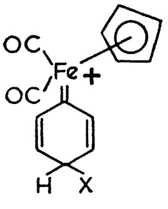
MANY examples are now known where the degree and mode of reaction of a hydrocarbon ligand is completely altered when it is $\pi$-bonded to a metal atom.[1] However, the effect of a $\sigma$-bonded transition-metal atom on the reactivity of an aromatic nucleus has not been investigated. We describe the influence of the groups $C_5H_5Fe(CO)(L)$ [L = CO; $PPh_3$] on a $\sigma$-bonded aryl group.

For a selection of *meta*- and *para*- substituted derivatives $X{\cdot}C_6H_4Fe(CO)_2C_5H_5$ (1)† we have found good linear correlation between the Hammett $\sigma$-constants and (i) the chemical shift of the $^1H$ n.m.r. signals of the $C_5H_5$ ring, and (ii) separately, the values of the symmetric and antisymmetric i.r. stretching frequencies of the FeC–O groups. The small differences in values for (i) and (ii) for groups ranging from CN($\sigma_p = +0{\cdot}63$) to MeO ($\sigma_p = -0{\cdot}27$) suggest very little resonance interaction between these *para*-substituents and the other ligands, CO and $C_5H_5$, bonded to the metal [$\Delta\tau$(CN − MeO) = 0·07; $\Delta\nu_{CO}$ asymm. (CN − MeO) = 15 cm.$^{-1}$; $\Delta\nu_{CO}$ sym. (CN − MeO) = 12 cm.$^{-1}$]. These differences are less than half those found for the related thio-compounds $X{\cdot}C_6H_4SFe(CO)_2C_5H_5$.[2] The $^{19}F$ n.m.r. chemical shift of a monosubstituted fluorobenzene is known to be a sensitive measure of the influence of a substituent.[3] An upfield shift of 1·5 p.p.m. relative to $C_6H_5F$ is produced by a *meta*-$C_5H_5Fe(CO)_2$ substituent; a larger shielding of the $^{19}F$ nucleus [(+10·23 p.p.m.)] is produced by a *para*-$C_5H_5Fe(CO)_2$ substituent, and when one CO is replaced by $PPh_3$ a shift of +14·6 p.p.m. is obtained with $p$-$FC_6H_4Fe(CO)(PPh_3)C_5H_5$. These values are comparable with those given by a $PtX(PEt_3)_2$ group $\sigma$-bonded to fluorobenzene[4] and, like this platinum group, suggests that the $C_5H_5Fe(CO)_2$ moiety is electron-releasing both by inductive and resonance mechanisms. A possible interpretation of these results is that an aryl group directly bonded to the iron atom is able to participate in synergistic $\sigma$-donation–$\pi$-acceptance bonding (using the $\pi^*$-orbitals of the benzene ring) to such a large degree that the bonding of the CO and $C_5H_5$ ligands need hardly be affected.



(3)

An implication of these results would be that the phenyl group in the 'parent' complex (1; X = H) is much more reactive than benzene towards electrophiles. This is supported by experiment. A product balance indicating quantitative conversion into (1; X = $p$-MeCO) is obtained in 1 hr. at 0° using the MeCOCl–$AlCl_3$ Perrier complex. Substitution under Vilsmeier conditions [$POCl_3$–PhN(CHO)Me] produced the formyl derivative (1; X = $p$-CHO), also obtained using $Cl_2CHOEt$ and $AlCl_3$. Competition experiments between (1; X = H) and benzene in homogeneous solution are not possible (*vide infra*), but a lower limit can be placed on the relative reactivity of (1; X = H). Under identical Vilsmeier conditions less than 2% benzene reacted compared with approx. 80% (1; X = H). In Friedel–Crafts experiments where (1; X = H) was totally consumed, up to only 34% acetophenone could be obtained from benzene.

The position of substitution in the complexes was proved by spectroscopic and chemical methods. Thus (1; X = $p$-CHO) was converted ($h\nu/PPh_3$) into $X{\cdot}C_6H_4Fe(CO)(PPh_3)C_5H_5$ (2; X = $p$-CHO) and reduced ($NaBH_4$) to (2; X = $p$-$CH_2OH$) identical with a sample obtained from the terephthaloyl derivative $p$-$MeOCO{\cdot}C_6H_4{\cdot}COFe(CO)_2C_5H_5$ by the successive transformations (i) $h\nu/PPh_3$ and (ii) $LiAlH_4$. Significantly, no substitution can be detected on the $C_5H_5$ ring or at the other positions of the phenyl group. This observation is consistent with resonance stabilisation of the transition state by *ortho–para*-substitution [*e.g.* (3)], but excludes substitution at the *meta*-position or on the $C_5H_5$ ring. This demonstration of enhanced reactivity has considerable preparative importance, since many derivatives (1) where X is a functional group are only accessible with difficulty[5] using conventional methods.[6] Investigations of the organic chemistry of these complexed ligands, also the effect of alternative metal atoms, are therefore now possible.

Substitution of the phosphine complex (2; X = H) is much more rapid than (1; X = H) but the product is decomposed to $C_5H_5Fe(CO)(PPh_3)Cl$ and acetophenone by the HCl generated during Friedel–Crafts acetylation. Both this and the ready cleavage of (1) to $XC_6H_5$ [(X = H; CHO; MeCO)] and $C_5H_5Fe(CO)_2Cl$ by dry HCl is reminiscent of the electrophilic displacement process of protodesilylation.[7]

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† New compounds, X = MeO; Me; F; Cl; $CO_2Me$; and CN have been characterised by usual techniques of analysis and spectrometry.

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