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SUBSTITUENT EFFECTS AND THE STABILITY OF CHROMARENES

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Summary

The chemistry and air stability of the symmetric chromarenes (Ar_2Cr) and the unsymmetric chromarenes of the type $ArCr(C_6H_6)$ can be correlated with the sum of the Hammett σ_m parameters of the substituents. It is proposed that the unsymmetrical chromarenes exhibit an internally compensating stabilisation effect analogous to that of the chromium tricarbonyl moiety. This postulate is supported by NMR and polarographic evidence.

Introduction

The widespread use of metal vapors as synthetic reagents (1-4) has led, among other things, to a resurgence of interest in the chromium - arene sandwicl complexes (chromarenes) (5). The ready incorporation of a wide variety of substituents into this hitherto almost unexplored system has revealed much fascinating new chemistry. Over the past five years, more than 60 substituted chromarenes have been prepared, and some general chemical trends within the system are now becoming apparent.

Discussion

(a) Symmetric chromarenes, Ar_2Cr

The existence of this series of compounds depends upon the subtle interplay of two effects, viz.,(a) the thermodynamic stability of the molecule, which is a reflection of the strength of the arene - chromium bond, and(b) the kinetic barrier to decomposition via the one-electron oxidation of the chromium atom.

The thermodynamic stability could in principle be investigated experimentally by methods such as calorimetry (6) or by a comparison of bond lengths obtained from crystallographic studies (7). Unfortunately, few data are currently available although the situation will undoubtedly change - indeed some workers have already announced this as a long-range goal (8). Valuable predictions are clearly possible with molecular orbital calculations, but again few molecules have actually been studied (9). Perhaps the most readily available technique is that of vibrational spectroscopy, and Klabunde (10) has demonstrated that the incorporation of electron - withdrawing substituents in symmetrical chromarenes of the type $(C_6H_4X_2)_2Cr$ leads to smaller complexation shifts of the aryl in-plane stretching vibrations than is observed for benzene itself. He was thus able to conclude that the chromium to arene back-donation was less pronounced in the case of chromarenes with electronegative substituents, and consequently that the arene-chromium bond was weaker than in $(C_6H_6)_2Cr$ itself. This view is supported by the enhanced thermal stability of chromarenes with increasing alkyl substitution (11) and by the failure to isolate complexes of the type $(C_6F_nH_{6-n})_2Cr$ when n exceeds 2. In essence, the π-basicity of arenes with a multitude of electron-withdrawing substituents is apparently too low to lead to isolable sandwich compounds of the type Ar_2Cr.

In contrast, the presence of electronegative substituents in the arene rings should retard the one-electron oxidation to Ar_2Cr^+ and the activation energy barrier should correlate well with the oxidation potential which is perhaps best measured polarographically (10). Russian workers have shown that the incorporation of alkyl groups into the arene rings leads to a shift of the half-wave potential ($\varepsilon_{\frac{1}{2}}$) towards negative values of the potentials. The change in $\varepsilon_{\frac{1}{2}}$ was found to be directly proportional to the number of alkyl groups introduced and was 0.3V per alkyl group(12).

Another physical technique which might give some information as to the distribution of electron density within the molecule is NMR spectroscopy and ^{1}H (13,14) and ^{19}F (15) spectra have been reported. In this vein, the most comprehensive study is that of Graves and Lagowski (16) who carefully examined the factors influencing the ^{13}C chemical shifts in a large number of symmetrical chromarenes. They showed that the transmission of substituent effects to the C-4 ring carbon was drastically reduced, that the π-electron density was considerably modified from that of the free arene and that enhanced susceptibility to nucleophilic substitution on the ring was to be expected. This prediction, which was also in agreement with an analysis of the ^{19}F NMR shifts (15), was subsequently realised experimentally (17).

Thus, there emerges from these facts a picture of the symmetrical chromarenes in which thermodynamically stable and kinetically inert complexes will only be formed for a somewhat limited range of substituents. The kinetic inertness of the chromarenes is reflected in their resistance to aerial oxidation, and these data have been well documented by a number of laboratories (5,10,13,15-18). It appears that it is the identity of the substituents which is crucial and that positional isomerism is less important. Thus 1, 1', 3, 3' - tetrakis (trifluoromethyl)-chromarene is remarkably air-stable but so also is the 1, 1', 4, 4 isomer (10); in like manner, the oxidative stabilities of the ortho, meta and parafluorotoluene complexes are comparable (15,16). It therefore seemed reasonable to attempt to correlate the oxidative stability of the chromarenes with the sum of the inductive parameters of the substituents. For this purpose we chose the Hammett σ_m values (19) (but the Swain-Lupton (20) $\mathcal{F}$ values also work well). As can be seen from Figure 1, the sum of the Hammett parameters - $\Sigma\sigma_m$ - is an excellent indicator of the oxidative stability of the given chromarene. Using this simple concept, one can now place realistic limits on the substituents one can incorporate and still maintain the desired stability of the complex. It is not an unreasonable prediction that the $\varepsilon_{\frac{1}{2}}$ values obtained polarographically should correlated well with $\Sigma\sigma_m$, and we trust that the appropriate data will soon be available (10).

(b) Unsymmetrical chromarenes, ArCrAr'

While it is clear that the rôle of the substituents is crucial to the behaviour of a given chromarene, it is also noticable that in the unsymmetrical systems of the type $ArCr(C_6H_6)$, it is possible to incorporate more electronegative groups (see Figure 1) than is possible in the Ar_2Cr sandwich molecules Thus, although $(C_6H_3F_3)_2Cr$ has not so far been synthesized, $(C_6F_nH_{6-n})Cr(C_6H_6)$, when n = 4, 5 or 6, are readily available (5, 17, 18, 21) and their chemistry has been extensively studied (5,22). It seems that, in the unsymmetrical chromarenes, there exists a self-compensating mechanism whereby the full effect of the arene substituents need not be tolerated solely by the chromium (as is presumably the case for Ar_2Cr) but can be, to some extent, electronically buffe by the π-C_6H_6 ring. There is clearly electronic interaction between the two rings as is evidenced by the surprisingly large inter-ring J_{HF} coupling constan in the molecules $(C_6F_nH_{6-n})Cr(C_6H_6)$, where n = 4, 5 or 6 (5,17). Furthermore, in $(C_6F_6)Cr(C_6H_6)$, the C_6H_6 ring is readily deprotonated by strong bases (17). has also been shown by a comparison of corresponding ν_{CO} bands in the infrared spectra of the molecules $C_6F_5M(CO)_x$ and $(C_6F_5M(CO)_x)Cr(C_6H_6)$ that the π-$(C_6H_6)C$ moiety pushes electron density into the fluorinated ring (5); this is also consistent with the somewhat reduced susceptibility to nucleophilic attack of $(C_6F_6)Cr(C_6H_6)$ relative to free C_6F_6 (17).

Thus, the π-C_6H_6 ring must be comparable to three PF_3 ligands which can also stabilise the π-$(C_6F_6)Cr$ moiety (18), whereas the analogous molecule $(C_6F_6)Cr(CO)_3$ is currently unknown. Indeed the subtle interplay of thermodynam and kinetic effects is nicely exemplified by the cocondensation reaction of Cr vapor, PF_3 and the equimolar mixture of arenes $C_6F_nH_{6-n}$, where n = 0 through 6, which showed that the difluorobenzene complex was the favored product. One must, however, recall the point made by Timms (18) that the cocondensation meth may not always work even when a more conventional route has been successful; $Cr(NO)_4$ provides a nice example of this phenomenon (18,23).

If the π - C_6H_6 group has the capacity to donate electron density on demand to satisfy the relative electron deficiency of its arene partner which is heavily substituted with electronegative groups, this should be reflected in the NMR spectroscopic properties of the π - C_6H_6 ring. Thus, increasing the withdrawal of electron density from the C_6H_6 ring might be expected to deshield the aromatic protons and this is in fact the case (see Table 1 and Figure 2). Such effects have been noticed previously (24) in a series of ethyl-substituted chromarenes in which the introduction of extra alkyl groups in one ring shields the ring protons in the other. However, the shifts are quite small and it is essential that all the spectra are recorded under identical conditions. Of course, a complicating factor here is that changes in the C_6H_6 to chromium bonding

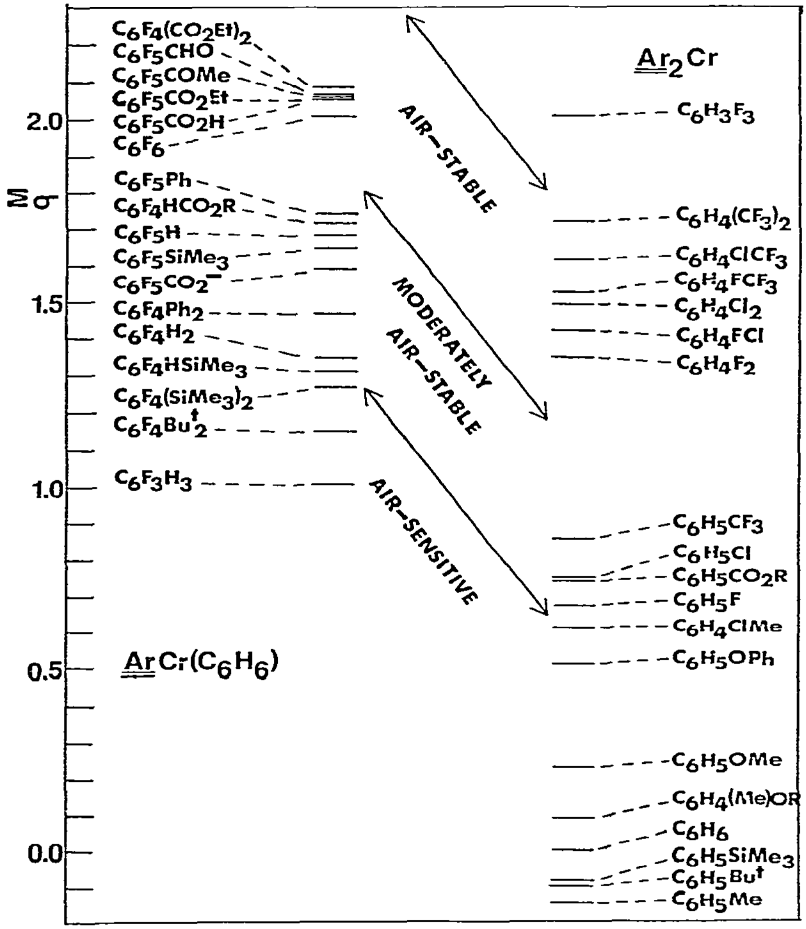

Fig 1. The sum of the σ_m values of a series of symmetrical and unsymmetrical chromarenes.

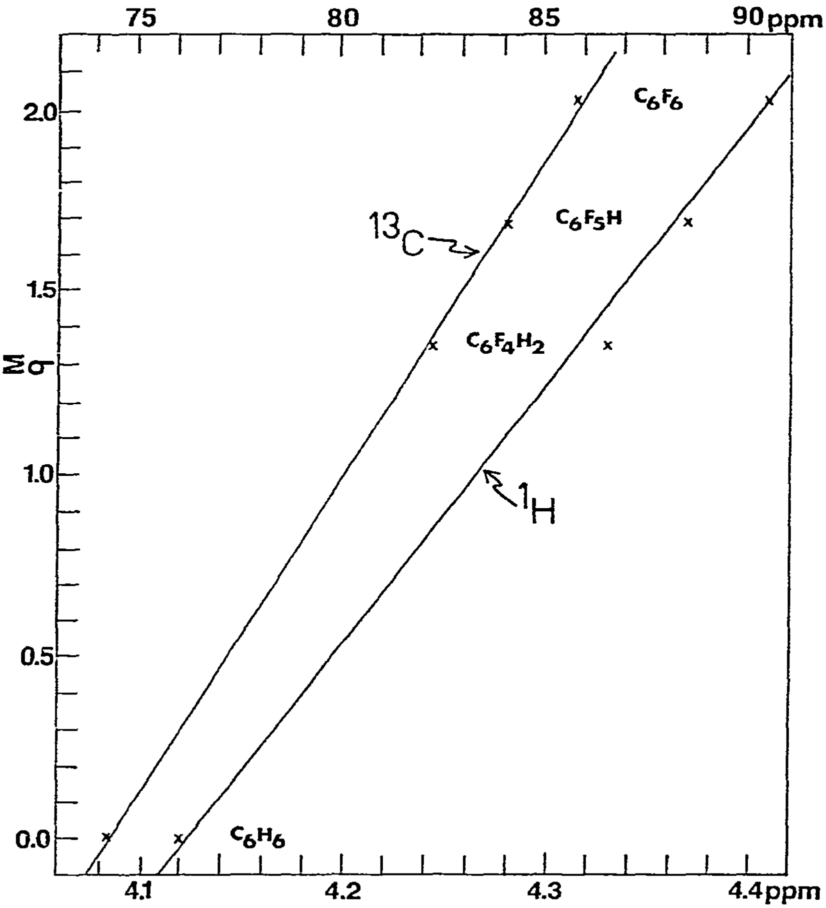

Fig 2. Plots of the sum of the σ_m values of the substituents of $ArCr(C_6H_6)$ versus ^1H and ^{13}C NMR chemical shifts of the C_6H_6 ring.

could also alter the ring current and the local anisotropic contributions to the shi of directly bonded protons (25). In particular, although a withdrawal of electron density should deshield the protons, a diminution of the ring current would lead to an apparent shielding and so these two effects tend to nullify each other to some extent leading to a less than unequivocal result (26).

A much clearer picture emerges from the ^{13}C NMR shifts of the C_6H_6 moiety in the series $(C_6F_nH_{6-n})Cr(C_6H_6)$ in which the correlation (see Figure 2) between the ^{13}C shifts and the number of fluorine atoms in the other ring is remarkably good, ($\bar{r}$ = 0.9997). Although it is true that the use of ^{13}C NMR spectroscopy to interpret changes in bonding in organometallic systems must be treated with some caution (27), nevertheless, with the reservations discussed by Lagowski (16) it can be an excellent probe for a series of closely related molecules. Table 1 lists the ^1H and ^{13}C NMR chemical shifts for a series of molecules $ArCr(C_6H_6)$ and it is noticable that the shifts, in general, correlate with $\Sigma\sigma_m$ and with the oxidative stability of the complex (see Figure 1).

Table 1. NMR Chemical Shifts[a] for the C_6H_6 ring of $ArCr(C_6H_6)$

Ar	^1H	^{13}C
$C_6F_4(CO_2Et)_2$	4.64	88.6
C_6F_5CO-furyl	4.71	87.6
$C_6F_5CO_2Et$	4.54	87.0
C_6F_6	4.41	85.8
C_6F_5H	4.37	84.0
$C_6F_4H_2$	4.33	82.2
C_6H_6[b]	4.12	74.2

[a] All spectra recorded on a Bruker WH-90 spectrometer; all samples run as 5% solutions in C_6D_6 containing TMS as the internal standard and quoted in ppm downfield of this standard.

[b] Data taken from Refs. 14 and 16.

It is thus apparent that ^{13}C NMR spectroscopy provides a measure of the electronic buffering effect of the unsubstituted ring as it tries tc compensate for the electronic effects of the substituents in the other ring of the chromarene. In many ways, this effect parallels the well-known correlation of inductive parameters with ν_{CO} in arene chromium tricarbonyl systems (28).

Epilogue

These relatively simple ideas using substituent parameters to correlate molecular reactivity not only provide a rationale for the ease or difficulty of obtaining certain compounds but may also have some predictive value. Thus, it is now apparent that in the difunctionalisation of 1, 2, 4, 5 - tetrafluorochromarene (22), with a view to producing air-stable organometallic copolymers using a fluorochromarene as one of the monomers, the substituents must be chosen with some forethought. Hence, to prepare a polyamide, the electron - withdrawing acyl linkages, rather than the electron-donating amino groups, would be incorporated in the chromarene-containing monomer. Likewise for polyesters, the chromarene-containing monomer should possess the acid or ester but not the hydroxyl substituents. Progress in this area will be reported in a separate publication (29).

We can also make predictions about the stabilities of as yet unsynthesised chromarenes. Thus, for several years it has been our aim to obtain 2, 3, 4, 5 pentafluorochromarenoic acid with the intent of measuring its pK_a value. The $\Sigma\sigma_m$ value of this molecule, 2.055, would indicate it to be of comparable stability to the known $(C_6F_5CO_2Et)Cr(C_6H_6)$ (22) and hence readily isolable. However, although the desired molecule is probably stable enough, routes to it involving the strongly electron-releasing carboxylate functionality would not be favored. Indeed base hydrolysis of the ethyl ester of pentafluorochromarenoic acid yields not the carboxylate but products derivable from the π-complexed tetrafluorobenzyne (30). This latter intermediate presumably arise by elimination of CO_2 and fluoride ion from the initially produced carboxylate. Thus, other routes to the acid need to be explored and these are discussed elsewhere (22).

In conclusion, substituent parameters provide a useful probe as to the stability and chemistry of chromarenes.

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