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Preliminary communication

Metal carbonyl carbene groups as electron withdrawing substituents in ferrocene, furan, thiophen and pyrrole

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Although much is now known about the physical and chemical properties of hetero-carbenoid complexes of the transition metals in general, and of compounds of the type $(CO)_5CrCYX$ in particular, there has been no determination of the substituent parameters of a carbenoid group such as $[(CO)_5Cr \cdot C(X)—]$. The extent to which both X and Y may both donate electrons to the vacant p_z-orbital of the formally sp^2-carbene carbon atom is uncertain[1].

This study of some ferrocene compounds, $Fc \cdot C(X)Cr(CO)_5$ ($Fc = C_5H_5 \cdot Fe \cdot C_5H_4$; X = OR, NR_2) (I) and 2-substituted, five-membered heterocycles, $C_4H_3Z \cdot C(X)Cr(CO)_5$ (Z = O, S, NMe; X = OEt, NH_2) (II) provides answers to both of these problems.

The chemical shifts of the ferrocenyl protons in I (Table 1), in particular those of the ring directly bonded to the sp^2 carbon atom, show that the group $[(CO)_5Cr \cdot C(X)—]$ exerts a large electron withdrawing effect. From the correlations which have been established between various substituent parameters and the ring proton chemical shifts of monosubstituted ferrocenes[2], the average values of the substituent parameters σ_P and σ_R for the group $[(CO)_5Cr \cdot C(X)—]$ are as follows:

X	σ_P	σ_R
OR	+0.66	+0.67
NR_2	+0.32	+0.30

This shows that there is a large conjugation interaction between the ferrocenyl π-system and the sp^2 carbon atom. This conclusion has considerable bearing upon the problem of carbonium ion stabilisation by the ferrocenyl group[3]. As expected, electron withdrawal from ferrocene decreases from X = OR to X = NR_2. The methyl resonance in I (X = OMe) remained as a sharp singlet at 210°K.

The greater donor character of the ferrocenyl group compared to the phenyl group is shown by the decrease in k_1 from its value in the compounds $Ph \cdot C(X)Cr(CO)_5$ [4] The marked decrease in k_1 from I (X = OMe, OEt) to I (X = NMe_2, NC_4H_8) shows that

TABLE 1

trans-CO STRETCHING FORCE CONSTANT, k_1 (nm^{-1}), AND RING PROTON CHEMICAL SHIFT, δ (Hz), RELATIVE TO UNSUBSTITUTED FERROCENE IN THE COMPOUNDS $C_5H_5FeC_5H_4 \cdot C(X)Cr(CO)_5$

Infrared spectra recorded in hexane solution. NMR spectra (100 MHz) recorded in $CDCl_3$ (internal TMS).

X	k_1	$\delta(H_{2,5})$	$\delta(H_{3,4})$	$\delta(C_5H_5)$
OMe	1562	−84	−63	−9
OEt	1554	−83	−60	−6
NMe_2	1512	−36	−22	−5
NC_4H_8	1497	−32	−32	−2

π-type donation from chromium to the sp^2 carbon atom appears to be less in the latter case. Thus, if Y remained unchanged, electron release to the sp^2 carbon atom would be greater from nitrogen donors than from oxygen donors. However, the NMR evidence suggests that the change in electron donation from Y is in the opposite sense, the net effect implying that nitrogen is a very much better donor than oxygen in these systems.

TABLE 2

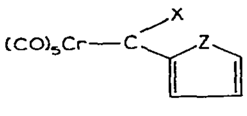
trans-CO STRETCHING FORCE CONSTANT, k_1 (nm^{-1}), AND CHEMICAL SHIFT OF H_3, δ (Hz), RELATIVE TO UNSUBSTITUTED C_4H_4Z IN THE COMPOUNDS $C_4H_3Z \cdot C(X)Cr(CO)_5$

Infrared spectra recorded in hexane solution. NMR spectra (100 MHz) recorded in d_6-acetone (internal TMS).

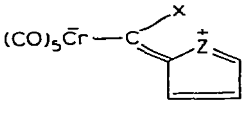
Z	X = OEt		X = NH_2	
	k_1	δ	k_1	δ
O	1580	−78	1550	−112
S	1574	−129	1557	−63
NMe	1557	−159	1509	−72

Similar general conclusions may be drawn from the results (Table 2) concerning the compounds II. The strong electron withdrawing (+*R*) character of the $[(CO)_5Cr \cdot C(X)—]$ group is clearly established by comparison with data for other 2-substituted heterocycles[5]. In this series we can assess the contribution of the tautomeric forms IIa and IIb as a function of the heteroatom, Z. For X = OEt, the contribution of IIb increases in the order Z = O < S < NMe, showing that electron release from Z follows a similar pattern to that from X.

In II (Z = O, X = NH_2) neither k_1 nor δ conform to the expected pattern, k_1 being smaller and δ being larger than expected. There is no evidence of hydrogen bonding (N—H· · ·O) in this or in any of the other compounds II (X = NH_2).



(II a)



(II b)

We have also studied the acylation of I (X = OR) and the quaternisation of I (X = NR_2), as well as the reactions of the compounds II with a variety of nucleophiles. We have also succeeded in isolating the labile vinyl derivatives, $CH_2{=}CH \cdot C(X)Cr(CO)_5$ (X = OR, NR_2). These investigations will be described in detail later.

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REFERENCES

1 E.O. Fischer, H.J. Kollmeier, C.G. Kreiter, J. Müller and R.D. Fischer, *J. Organometal. Chem.*, 22 (1970) C39.
2 D.W. Slocum, T.R. Engelmann, R. Lewis and R.J. Kurland, *J. Chem. Eng. Data*, 13 (1968) 378; G.G. Dvoryantseva, S.L. Portnova, K.I. Grandberg, S.P. Gubin and Y.N. Sheinker, *Doklady Akad. Nauk S.S.S.R*, 160 (1965) 155.
3 M.J. Nugent, R.E. Carter and J.H. Richards, *J. Amer. Chem. Soc.*, 91 (1969) 6145.
4 E.O. Fischer and A. Maasböl, *Chem. Ber.*, 100 (1967) 2445; M.Y. Darensbourg and D.J. Darensbourg, *Inorg. Chem.*, 9 (1970) 32; J.A. Connor, J.P. Lloyd and P.D. Rose, unpublished data.
5 G.A. Cordell, *M.Sc. thesis*, Manchester University, 1968.