The ^{13}C Nuclear Magnetic Resonance Spectra of Carbene and Isonitrile Complexes of Chromium and Tungsten and a Reinvestigation of the ^{1}H Nuclear Magnetic Resonance Spectra of Phenyl Carbene Complexes †

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The effect of changes in the electronic environment of the *sp*² hybridised carbene carbon atom bound to the metal in a series of 18 complexes of the type $(CO)_5MCXY$, where M = Cr or W; X = OR or NR^1R^2, and Y is an organic group, are discussed with the aid of ^{13}C n.m.r. spectroscopy. The chemical shift of the carbene carbon is more strongly influenced by X than by either M or Y. Carbene complexes of the transition metals are better considered as metal-stabilised carbonium ions than as carbonyl (ester or amide) analogues. The resonances of the carbonyl ligands in carbene complexes are compared with those in isonitrile complexes of the type $RNCCr(CO)_5$. Evidence is presented from both ^{13}C and ^{1}H n.m.r. spectra which shows that overall electron release rather than $\pi \rightarrow p$ interaction is important in the stabilisation of the carbene carbon by the group Y.

^{13}C N.M.R. has been shown to be useful in investigations of the electronic environment of *sp*²-hybridised carbon atoms in aromatic,[1] organic carbonyl,[2] and carbonium ion systems.[3] The *sp*² nature of the carbene carbon atom in the complexes $(CO)_5MCXY$, where M = Cr, Mo, or W; X = heteroatom function, *e.g.*, OR, SR, or NR^1R^2; and Y = aryl or alkyl group, has been established by *X*-ray crystallographic studies,[4-6] and π-overlap with the heteroatom function, X, has been suggested as an explanation for the observed hindered rotation around the C–X bond in these systems.[7] Elaboration of the groups X and Y to give a fairly wide range of substituents has been described.[7,8] Spectroscopic studies of these compounds give results which are consistent with the model of the carbene carbon as an electron-deficient *sp*² carbon atom stabilised by dative π-bonding from the heteroatom function X and from the metal together with inductive release from the group Y where this is possible. Additionally, an analogy has been drawn between the metal–carbene carbon bond and the carbonyl group.[7,8] In order to test this bonding model further, we have investigated the ^{13}C n.m.r. spectra of a range of carbene compounds of chromium and tungsten.

RESULTS AND DISCUSSION

Carbene ^{13}C Resonances.—The overall low-field chemical shift of each of the carbene carbon resonances (δ_{carb}) shown in Table 1 is consistent with their formulation as electron-deficient *sp*² carbons. Those recorded for the alkoxy-carbene complexes (X = OR) are, to our knowledge, the lowest field ^{13}C resonances yet found for diamagnetic compounds. They absorb at even lower fields (313—362 p.p.m.) than trialkylcarbonium ions (320—334 p.p.m.),[9] whereas the more closely related hydroxycarbonium ions absorb at higher fields (222—249 p.p.m.).[9] Replacement of the alkoxy-group with an amino-group ($X = NR^1R^2$) or with $O^-NMe_4^+$ causes a large upfield shift in the carbene carbon resonances (*ca.* 70 and 44 p.p.m. respectively; Figures 1 and 2 and Table 1). A much smaller upfield shift (*ca.* 1·5 p.p.m.) is observed[9] for the carbonyl carbon when amides are compared with their analogous esters. Large upfield shifts are observed however on successive substitution of OH for methyl in alkyl carbonium ions.[3]

Carbon chemical shifts are dominated by the second-order paramagnetic term of the screening constant arising from a mixing of the ground and excited states of carbon in the magnetic field. According to the Pople treatment,[10] the paramagnetic contribution to the screening constant may be described by equation (1), where ΔE is

$$\sigma_p = -\frac{k}{\Delta E}\langle r^{-3}\rangle_{2p}\{Q_{AA} + Q_{AB}\} \qquad (1)$$

the average excitation energy, $\langle r^{-3}\rangle_{2p}$ is the mean inverse cube radius of the carbon 2*p* orbital, and the *Q* terms contain elements of the charge density and bond-order matrix. Both $\langle r^{-3}\rangle_{2p}$ and Q_{AA} depend on the local charge density whereas Q_{AB} arises essentially because of a second-order paramagnetic term on the neighbouring atom, B, which induces paramagnetic currents on atom A.[10]

In view of the chemical and physical properties of metal carbene complexes and the evidence for back donation from the group X, it seems unlikely that the carbene carbon could be even more electron-deficient than that in trialkylcarbonium ions. It is probable therefore, that there are other factors which contribute to the large values of δ_{carb}. Indeed other *sp*² carbons

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† A summary of these results was presented at the 4th Northern Inorganic Group Meeting, Leeds, 5th January, 1972.

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bound to transition metals such as the ketonic carbonyl in π-$C_5H_5(CO)_2FeCOMe$ (254·4 p.p.m.)[11] and π-C_5H_5-$(CO)_2FeCOPh$ (255·5 p.p.m.)[11] and the C(1) phenyl carbon in $(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_6H_5)_2$ (192·9 p.p.m.)[11] show similarly large downfield shifts. These downfield shifts could be associated with lower values of ΔE and larger values of Q_{AB} which arise from multiple bonding between the *d*-orbitals of the metal and the sp^2 carbon atoms.† When the metal *d*-orbitals are more diffuse, as for example in tungsten, π-bonding is less effective and the downfield shifts are less pronounced, *cf.* δ_{carb} for compounds (I) and (XVII) (Table 1) and the tungsten analogues of (I) and of (VIII) respectively.[13]

TABLE 1,A

Carbene carbon, δ_{carb}, and carbonyl carbon, δ_{CO}, chemical shifts of carbene complexes, $(CO)_5MCXY$

Compound	M	X	Y	δ_{carb} [a] p.p.m.	δ_{CO}-*cis* [a] p.p.m.	δ_{CO}-*trans* [a] p.p.m.	Ref.[b]
(I)	Cr	OMe	Me	362·3	217·6	223·6	*c*
(II)	Cr	OMe	Ph	354·5	218·4	226·0	*c*
(III)	Cr	OMe	*p*-$Cl{\cdot}C_6H_4^-$	350·1	217·3	224·9	15
(IV)	Cr	OMe	*p*-$MeO{\cdot}C_6H_4^-$	342·8	218·4	225·5	15
(V)	Cr	OEt	Fc	332·0	218·7	224·1	*d*
(VI)	Cr	OEt	Th	319·8	218·7	224·9	8
(VII)	Cr	OEt	Fu	313·6	218·4	225·5	8
(VIII)	Cr	NHMe	Me	284·8	219·2	224·4	*e*
(IX)	Cr	NHC_6H_{11}	Et	284·3	219·8	224·4	26 [f]
(X)	Cr	NMe_2	Ph	277·5	218·7	225·2	23
(XI)	Cr	NH_2	Th	271·8	220·8	226·2	8
(XII)	Cr	NC_4H_8	Ph	271·3	219·2	225·5	17, *g*
(XIII)	Cr	NC_5H_{10}	Ph	270·5	218·4	225·5	17
(XIV)	Cr	NC_4H_8	Th	266·9	218·7	224·9	*f*
(XV)	Cr	NH_2	Fu	255·6	219·5	224·7	8
(XVI)	Cr	NC_4H_8	Fu	253·7	219·2	225·5	8
(XVII)	W	OMe	Ph	321·9	198·6 [h]	204·6	*c*
(XVIII) [i]	Cr	$O^-NMe_4^+$	Th	276·2	223·6	227·6	8

[a] Positive downfield from internal tetramethylsilane. [b] For preparation of compound. [c] E. O. Fischer and A. Maasböl, *Chem. Ber.*, 1967, **100**, 2445. [d] J. A. Connor and J. P. Lloyd, *J.C.S. Dalton*, 1972, 1470. [e] J. A. Connor and E. O. Fischer, *J. Chem. Soc.* (*A*), 1969, 578. [f] This work. [g] J. A. Connor, P. D. Rose, and R. M. Turner, in preparation; see also J. A. Connor and P. D. Rose, *J. Organometallic Chem.*, 1970, **24**, C45. [h] $^1J(^{183}W{-}^{13}CO)$ 125 Hz. [i] Recorded in deuterioacetone solution. Fc = 1-Ferrocenyl; Th = 2-thienyl; and Fu = 2-furyl.

TABLE 1,B

Carbonyl carbon chemical shifts, δ_{CO}, of some compounds of chromium and of tungsten

Compound		δ_{CO}-*cis* p.p.m.		δ_{CO}-*trans* p.p.m.	Ref.*
(XIX)	*p*-$Me{\cdot}C_6H_4{\cdot}NCCr(CO)_5$	216·5		218·7	19
(XX)	$Pr^iNCCr(CO)_5$	216·3		218·2	19
(XXI)	$Cr(CO)_6$		212·1		
(XXII)	$Bu^n_3PW(CO)_5$	198·6 [a]		200·4 [c]	22
(XXIII)	$W(CO)_6$		192·4 [b]		

Coupling constants $^1J(^{183}W{-}^{13}C)$; *a*, (*cis*-) 122 Hz; *b*, (*trans*-) 142 Hz; *c*, 125 Hz.

* Preparation of the compound.

The large upfield shift in δ_{carb} on changing X from OR to O^- or NR_2 is probably due in part at least to differences in π-donation from the heteroatom function causing an increase in $\langle r \rangle_{2p}$. The similarly large upfield shifts observed for carbonium ions on successive substitution of OH groups have been attributed to similar factors and molecular orbital calculations have been carried out which relate $\delta(C^+)$ directly to the π-electron density.[9] Differences in the temperature-independent paramagnetism associated with the groups OR, O^-, and NR_2 could also contribute to the large variation of δ_{carb} with X. Finally, differences in ($d \rightarrow p$) π bonding with the metal would lead to a slightly higher ΔE (or lower Q_{AB}) for the amino-carbenes which would in turn lead to an upfield shift in δ_{carb} with respect to the alkoxycarbenes. This argument is supported by the increase in the M–C (carbene) bond length from alkoxy[4] to amino-carbenes.[5]

Overall electron release ($\sigma + \pi$), which may be related to the concept of vertical stabilisation,[14] rather than distinct $\pi \rightarrow p$ interaction has been shown [7,8] to provide a satisfactory rationalisation of the stabilisation of the carbene carbon by the group Y when this is either a heterocyclic ring[8] or a substituted phenyl group.[7] This view is supported by the observed order of δ_{carb}, which decreases in the order Y = Me > Ph > 1-ferrocenyl > 2-thienyl > 2-furyl for both alkoxy- and amino-carbene complexes, and by the ^{13}C and ^1H n.m.r. of the Y groups which are discussed in greater detail below.

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† A discussion of the relevance to these systems of the Buckingham and Stephens treatment[12] will be discussed elsewhere.

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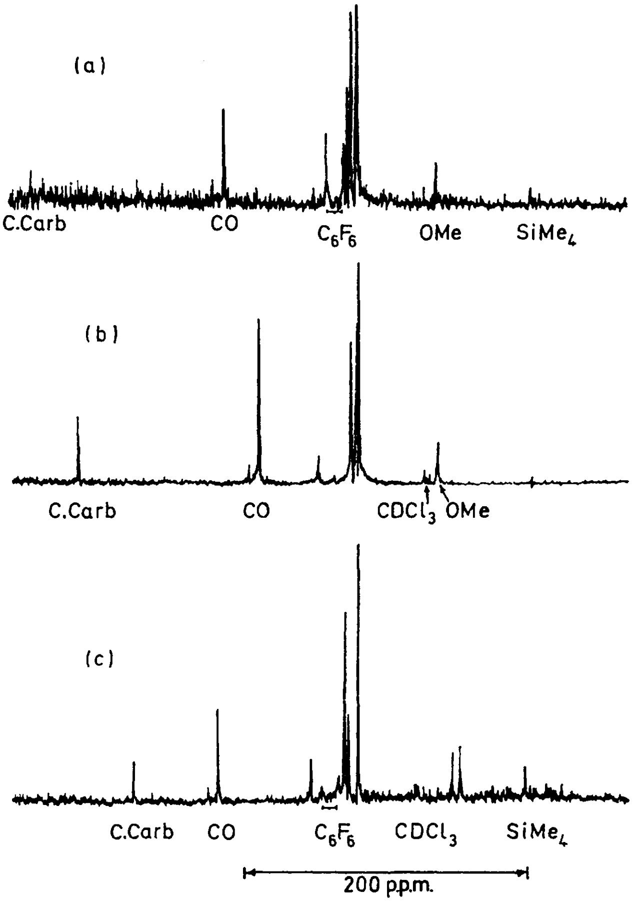

FIGURE 1 12·5 kHz proton noise decoupled ^{13}C n.m.r. spectra of (a) compound (II) (25% w/v), 10 min accumulation time, (b) (XVII) (50% w/v), 10 min accumulation time, and (c) (X) (30% w/v), 1 h accumulation time

The donor and acceptor properties of substituents attached to the benzene ring in carbene complexes containing substituted phenyl groups have been shown to be transmitted through the molecule, for example to the heteroatom substituent, X.[15] This is also borne out by the measurement of δ_{carb} in (III) and (IV) where M^+ substituents cause an upfield shift relative to complex (II). These results are also in good agreement with the *para*-substituent effects of the $-Cl$ and $-OMe$ groups in substituted benzenes.[9] *para*-Substitution in phenyl ketones and methyl benzoates produces only small shifts in the carbonyl resonances.[2]

That the 2-thienyl group is less effective in shielding the carbene carbon than the 2-furyl group is consistent with the greater aromaticity of the thiophen ring system which would make it less likely to give up electron density to the carbene carbon atom. Thus the order of electron releasing ability 2-furyl > 2-thienyl > phenyl varies in exactly the opposite sense to the resonance energies of the parent hydrocarbons.[16]

Further evidence for the presence of vertical stabilisation [14] of the carbene carbon is suggested by the greater effectiveness of the ferrocenyl group in shielding the carbene carbon compared with the phenyl group.

Changes in the steric environment of the heteroatom function also cause marked changes in δ_{carb}. Comparisons of compounds (X) with (XII) and (XIII), of (XI) with (XIV), and of (XV) with (XVI) show that a decrease in δ_{carb} occurs when a cyclic amine replaces NH_2 or NMe_2 as the heteroatom group X. This is most likely to be due to the trigonal planar environment around the nitrogen in the 5- and 6-membered ring system enabling better π-overlap with the nitrogen lone pair.[17] Comparing (VIII) with (IX) we see that long-range steric effects have little influence on δ_{carb}.

Carbonyl ^{13}C *Resonances*.—The variation of δ_{CO} in substituted metal carbonyls has been shown to reflect the charge donor ability of the substituent and has been discussed elsewhere.[11,18] A larger chemical shift and a larger *cis–trans*-separation is expected for the carbonyl resonances in octahedral complexes where the π-acceptor : σ-donor ratio is low since σ-bonding orbitals on the metal are shared by ligands which are mutually *trans*. Thus a good σ-donor such as the carbene ligand shows a larger *cis–trans* separation of carbonyl resonances and larger chemical shift with respect to $Cr(CO)_6$ than the isostructural isonitrile complexes (XIX) and (XX). In spite of repeated efforts, we have been unable to detect the resonance of the isonitrile carbon atom, RNC, in the complexes (XIX) and (XX).[11,19-21] A detailed

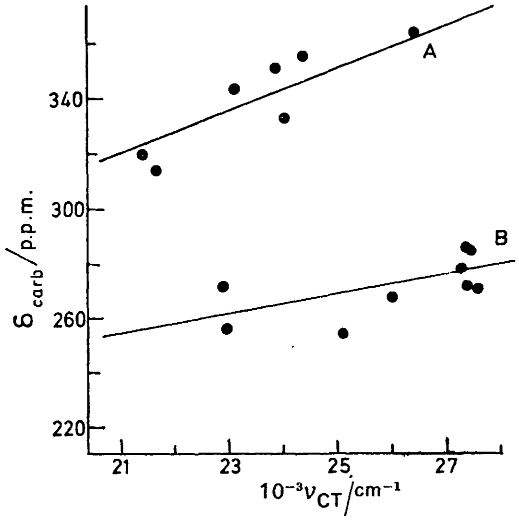

FIGURE 2 Plot of metal-to-ligand charge transfer band frequency/cm^{-1} against $\delta^{13}C$(carbene)/p.p.m. for A, X = OR and B, X = NR^1R^2

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study of isonitrile complexes of the type $(RNC)_nM(CO)_{6-n}$ (R = alkyl or aryl, M = Cr or Mo, n = 1, 2, or 3) has led to the conclusion that in these systems the isonitrile ligands function largely, if not exclusively, as σ-donor ligands, there being no evidence of overall π-acceptor behaviour.[19] Comparison of the tungsten carbene complex (XVII) with the phosphine complex (XXII)[18,22] shows the carbene ligand has a lower π-acceptor : σ-donor ratio than a basic phosphine. Here again the argument that the observed shift differences are brought about by differences in ($d \rightarrow \pi^*$) π overlap is supported by the shortening of M–CO bond lengths *trans* to the carbene ligand.[4,5] The small overall variation in carbonyl chemical shift for the series is consistent with both the relatively small variation in the *trans*-CO i.r. stretching frequency (A_1') and the invariance of the ligand-to-metal charge transfer energy for the series.[8]

Chemical Shifts of the Heteroatom Substituent, X.—The chemical shifts of the methyl and methylene carbons in the methoxy- and ethoxy-carbenes respectively are to lower field of ordinary organic alkoxy-groups (*ca.* 60 p.p.m.) (Table 2,A), reflecting the acceptor character of the carbene carbon. Similar conclusions have been drawn from the ^1H n.m.r. and electronic spectra of heterocyclic carbene compounds.[8]

TABLE 2

Carbon chemical shifts, δ/p.p.m., of heteroatom function (X) groups in the carbene complexes

A. X = OMe, OEt, or $O^-NMe_4^+$

Compound	(CH_2)	(CH_3)
(I)		67·2
(II)		68·0
(III)		67·8
(IV)		67·5
(V)	76·7	15·7
(VI)	77·2	15·5
(VII)	76·7	15·3
(XVII)		70·5
(XVIII)		56·1

B. X = Amino-group

Compound	(N–CH_3)	Ring—C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
(VIII)	35·3						
(IX)		57·7	34·4	25·5	24·9	25·5	24·9
(X)	51·8, 46·1						
(XII)			56·7	26·0	26·0	60·4	
(XIII)			56·1	28·5	24·1	28·5	62·1
(XIV)			56·9	25·7	25·7	60·4	
(XVI)			58·2	25·7	26·6	61·2	

Detailed studies have been made of the barrier to rotation about the C(carbene)–X bond.[7,15] The temperature-dependence of the proton n.m.r. spectra of a number of amino-carbene complexes such as $(CO)_5CrC(Ph)NR^1R^2$ has shown that the barrier to rotation about the C–N bond is *ca.* 84 kJ mol^{-1}, with the result that for $R^1 = R^2$ = Me [23] (X), and comparable systems, the spectra show two signals due to protons on α-carbons attached to the nitrogen. This hindered rotation is also reflected in the observation of two methyl resonances in (X), two ring α-carbon resonances in (XII), (XIII), (XIV), and (XVI) and two α- and two β-ring carbon resonances in (XVI) (see Table 2,B). Compound (XIII) was heated to 65 °C in deuteriochloroform without any noticeable change in the hydrocarbon region of the spectrum, which suggests that the conformation of the cyclic amine is rigid in the temperature range studied.

Chemical Shifts of the Organic Substituent, Y.—The most prominent trend in the shifts arising from the group Y is the large downfield shift observed for the carbon bound to the carbene carbon atom. This reflects the strong electron-withdrawing properties of the groups $(CO)_5MC(X)$–.

In order to compare the effect of changing the substituent X upon the ring carbons of the phenyl, 2-thienyl, and 2-furyl carbon resonances, the results are expressed as $\Delta C(i)$ (i = 1—6) for the individual carbons relative to their values in the unsubstituted ring (benzene, thiophen, and furan).

For Y = Ph, $\Delta C(1)$ is comparable (see Table 3,C) with the values obtained for the monosubstituted benzenes, PhOMe, $PhNMe_2$, and $PhNO_2$ for which $\Delta C(1)$ has the values −30·2, −22·4, and −19·6 p.p.m. respectively;[9] these are substantially larger than for $PhCO_2Me$ (−1·7 p.p.m.).[2] The *ortho*-carbons in all the phenyl carbenes studied show small upfield shifts probably due to steric interactions with the rest of the molecule.[9] The very small values of $\Delta C(3,5)$ illustrate the well known insensitivity of *meta*-carbons to substitution on the phenyl ring.[1] The *para*-position in monosubstituted benzenes is said to be most sensitive to changes in π-density in the ring. Thus the more electronegative alkoxy-carbenes give small negative values for $\Delta C(4)$, while the amino-carbenes give small positive values. This indicates that release of electron density from X *via* a π mechanism is only of secondary importance and that the amino-carbenes are essentially ' flooded ' with electron density relative to the alkoxy-carbenes.

We have reinvestigated the ^1H n.m.r. of the carbene complexes where Y = Ph and find that the results are in good agreement with the ^{13}C data discussed above. Table 4,A shows the shifts, $\delta_{o,m,p}$, of the *ortho*-, *meta*-, and *para*-protons in a number of monosubstituted benzene derivatives relative to the value of benzene in the same solvent, deuterioacetone.[24] A downfield shift is observed (negative δ) for π-electron-withdrawing substituents while π-electron-donor substituents cause a shift to higher field (positive δ). When these values are compared with those for the phenyl carbene complexes, $(CO)_5CrC(X)Ph$ (X = OMe, NH_2, or NC_4H_8), for X = OMe and NH_2 there is evidence for a barely perceptible donation of electrons to the carbene carbon *via* a π-mechanism, indicating that, in solution, the preferred conformation of the phenyl ring is either perpendicular to the [CrCX] plane or with a low barrier to rotation about the ring–carbene carbon bond axis. The value of δ_o for the complex (XII) (X = NC_4H_8) is anomalous

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TABLE 3

Carbon chemical shifts, δ/p.p.m., of organic function (Y) groups in the complexes

A. Y = 2-Furyl

	δC(2)	δC(3)	δC(4)	δC(5)	Δ[a]C(2)	ΔC(3)	ΔC(4)	ΔC(5)
(VII)	165·6	113·5	113·0	150·7	−20·4	−1·4	−1·9	−5·5
(XV)	158·5	129·0	115·2	146·0	−13·3	−17·9	−4·1	−0·8
(XVI)	160·7	110·3	112·5	143·6	−15·5	+0·8	−1·4	+1·6

B. Y = 2-Thienyl

	δC(2)	δC(3)	δC(4)	δC(5)	Δ[a]C(2)	ΔC(3)	ΔC(4)	ΔC(5)
(VI)	157·5	135·8	129·8	141·5	−21·5	−8·2	−2·2	−15·5
(XI)	154·8	134·4	134·4	135·0	−18·8	−6·8	−8·4	−7·4
(XIV)	155·0	124·1	118·4	127·6	−19·0	+3·5	+9·2	−1·7
(XVIII)	162·9	126·6	126·6	129·1	−37·0	+1·0	+1·0	−3·2

C. Y = Phenyl and *para*-substituted phenyl

	δC(1)	δC(2,6)	δC(3,5)	δC(4)	Δ[a]C(1)	ΔC(2,6)	ΔC(3,5)	ΔC(4)
(II)	155·8	124·4	129·5	131·7	−26·8	+4·6	−0·5	−2·7
(III)	152·8	126·2	129·3	137·9	−23·8	+2·8	−0·3	−8·9
(IV)	147·2	130·6	113·8	164·5	−18·2	−1·6	+15·2	−35·5
(X)	154·2	119·8	129·5	126·6	−25·2	+9·2	−0·5	+2·4
(XII)	155·3	119·8	129·8	126·8	−26·3	+9·2	−0·8	+2·2
(XIII)	153·1	119·8	129·3	126·3	−24·1	+9·2	−0·3	+2·7
(XVII)	156·6	126·8	129·0	132·5	−27·6	+2·2	0·0	−3·5
(XIX)	*b*	126·8	131·2	140·9	*b*	+2·2	−2·2	−11·9

D. Y = 1-Ferrocenyl

	δC(1)	δC(2,5)	δC(3,4)	δ(C_5H_5)	Δ[a]C(1)	ΔC(2,5)	ΔC(3,4)	Δ(C_5H_5)
(V)	94·9	73·2	75·3	71·3	−24·5	−2·8	−4·9	−0·9

E. Y = Alkyl

	δCH	δCH_2	δCH_3
(I)			49·1
(VIII)			35·3
(IX)		40·9	11·7
(XX)	49·4		23·5

[a] ΔC(*i*) = δC(*i*) (parent) − δC(*i*) (derivative)/p.p.m. where, for parent: furan δC(2,5) = 145·2, C(3,4) = 111·1; thiophen δC(2,5) = 125·9, C(3,4) = 127·6; benzene δC = 129·0; ferrocene δC = 70·6. [b] Not observed.

although the values of both δ_m and δ_p are clearly in line with those of the other carbene complexes. When the values of δ_i ($i = o, m,$ or p) for complex (XII) are compared with those of the heterocyclic ring protons δ_j (j = 3, 4, or 5) in the pyrrolidinyl complexes (XIV) and (XVI) (Table 4,B), the origin of the anomaly can be attributed to additional steric crowding from the conformationally rigid pyrrolidine ring. This is also reflected in the somewhat higher positive values of Δ*C*(2,6) in (X), (XII), and (XIII) (Table 3,C) and the lower negative and positive values of Δ*C*(3) and Δ*C*(4) in (XIV) and (XVI) respectively (Tables 3,A and 3,B). This information considered with the fact that the β-carbon resonances of the pyrrolidine ring are inequivalent in (XVI), but equivalent in (XII) and (XIV), suggests that the furyl group in (XVI) is more coplanar with the [CrCX] plane than the thienyl group in (XIV).

TABLE 4

A. Proton chemical shifts, δ_i (i = *o*-, *m*-, and *p*-)/p.p.m. for phenyl protons in monosubstituted benzenes, C_6H_5R. Solvent, [$^2H_6$]acetone at 60 MHz relative to benzene

R	δ_o	δ_m	δ_p
NO_2	−0·92	−0·32	−0·29
CO_2Me	−0·67	−0·21	−0·10
COMe	−0·66	−0·22	−0·12
H	0	0	0
Me	+0·16	+0·16	+0·16
NEt_2	+0·65	+0·65	+0·19
$(CO)_5CrC(OMe)$	−0·08	−0·08	−0·05
$(CO)_5CrC(NH_2)$	−0·03	−0·03	+0·04
$(CO)_5CrC(NC_4H_8)$	+0·47	−0·02	−0·02

B. Proton chemical shifts δ_i (i = 3, 4, or 5)/p.p.m. for heterocyclic ring protons in carbene complexes $(CO)_5CrC(X)$-(2-C_4H_3Z) (Z = O or S). Solvent, [$^2H_6$]acetone at 100 MHz relative to C_4H_4Z

X	Z	δ_3	δ_4	δ_5
OEt	O	−0·78	−0·37	−0·66
	S	−1·29	−0·26	−0·65
NH_2	O	−1·12	−0·31	−0·29
	S	−0·63	−0·14	−0·50
NC_4H_8	O	−0·18	−0·18	−0·22
	S	+0·46	+0·04	−0·06

The trends in the other 2-furyl (Table 3,A) and 2-thienyl ring carbon resonances (Table 3,B) also follow closely the observed trends in the proton resonances of these compounds,[8] and probably reflect both electronic and steric situations in a particular compound. Thus conformations favoured by the formation of a N–H · · · S hydrogen bond may be responsible for the anomalous value of Δ*C*(3) in (XV) as compared with (XI).[8]

A rough correlation of δ_{carb} with the frequency of the metal-to-ligand charge transfer band is shown in Figure 2. The energy of this band increases as the electron-donating properties of Y decrease. This is probably due to increasing stabilisation of the carbene carbon p_z orbital with increasing electron delocalisation ($\sigma + \pi$)

from Y. That δ_{carb} increases in the same sense suggests that as Y is varied for a given $(CO)_5MCX$ group, the chemical-shift changes are dominated by variations in the electron density on the carbene carbon rather than by differences in ΔE and implies a static situation with respect to $(d \rightarrow p)$ π-bonding.

General Conclusions.—From the data obtained on this series of compounds it is clear that ^{13}C chemical shifts are sensitive to changes in the electronic environment of an *sp*^{2} carbon bound to a metal. The order of the chemical shifts of the carbene carbon atoms fits well with other spectroscopic data and the known chemistry of these compounds. The metal carbene group $[(CO)_5MC{<}]$ is however rather more sensitive to changes in electronic environment than the carbonyl group to which it has been compared.[8,7] The most important influence on the chemical shift of the carbene carbon is the nature of the heteroatom function, X, with changes in the organic group, Y, and the metal producing smaller but no less significant changes. The low-field chemical shift of the carbene carbon and its sensitivity to changes in substituent are thought to result from its electron-deficient character together with paramagnetic shielding (neighbouring atom effect) and/or a lowering of ΔE caused by the metal atom. The data suggest that the carbene complexes of transition metals can best be thought of as metal-stabilised carbonium ions.[25]

EXPERIMENTAL

Materials.—All compounds were prepared by published methods and details of their physical characterisation are available elsewhere, with the exception of compounds (IX), (XIII), and (XIV). Compound (IX), $(CO)_5CrC(NHC_6H_{11})$-Et, is obtained [26] as pale yellow *needles*, m.p. 74—75 °C, $\nu_{max.}$ 3330 (NH), 2055m, 1968w, and 1936s (CO) cm^{-1}; n.m.r. (C_6D_6) δ 0·84 (3H : t : C*H*$_3$), 1·05 (10H : m : C_6*H*$_{10}$), 2·53 (2H : q : C*H*$_2$), 3·04 (1H : m : C*H*), and 8·30 (1H : br, s : N*H*); $(CDCl_3)$ 1·66 (3H : t : C*H*$_3$), 2·02 (10H : m : C_6*H*$_{10}$), 3·45 (2H : q : C*H*$_2$), 4·17 (1H : m : C*H*), and 9·24 (1H : br. s : N*H*) p.p.m.; $\lambda_{max.}$ (log ε) 253 (4·80) and 363 (4·01) nm (Found: C, 50·6; H, 5·2; N, 4·1; Cr, 16·0. $C_{14}H_{17}CrNO_5$ requires C, 50·7; H, 5·1; N, 4·2; Cr, 15·7%). Compound (XIII), $(CO)_5CrC(NC_5H_{10})Ph$, is obtained [17] as pale yellow *prisms* (69%) m.p. 84—85 °C, $\nu_{max.}$ 2058m, 1976w, 1939vs, and 1935s (hexane) cm^{-1}; n.m.r., see ref. 17; $\lambda_{max.}$ (log ε) 240 (4·80) and 362 (3·86) nm (Found: C, 55·9; H, 4·2; N, 3·8; Cr, 14·5. $C_{17}H_{15}CrNO_5$ requires C, 55·9; H, 4·1; N, 3·8; Cr, 14·3%). Compound (XIV), $(CO)_5CrC(NC_4H_8)Th$, crystallises as yellow *prisms*, m.p. 115—117 °C; $\nu_{max.}$ 2057m, 1977w, 1942s, and 1939m,sh (hexane) cm^{-1}; $\lambda_{max.}$ (log ε) 348 (3·11) (hexane) nm; n.m.r. ([$^2H_6$]acetone) δ 3·61 (2H : t : NC*H*$_2$), 4·33 (2H : t : NC*H*$_2$), 2·14 (4H : m : C*H*$_2$C*H*$_2$) 6·63 (1H : dd : 3-H), 7·04 (1H : dd : 4-H), and 7·44 (1H : dd : 5-H) p.p.m. $^3J_{34}$ 3·5, $^3J_{45}$ 5·0, $^4J_{35}$ 1·2 Hz (Found: C, 47·1; H, 3·2; N, 4·0. $C_{14}H_{11}CrNO_5S$ requires C, 47·1; H, 3·1; N, 3·9%). $CDCl_3$ and C_6F_6 were dried over molecular sieves before use and sample tubes were dried and flushed with nitrogen before being filled. Spectra were obtained on solutions of 25—70% (w/v) in 85% $CDCl_3$ + 10% C_6F_6 + 5% $SiMe_4$.

Spectra.—Spectra were obtained on a Brucker HFX-13 n.m.r. spectrometer operating in the Fourier transform mode at 22·63 MHz. Proton noise decoupling was performed with the use of a 90 MHz broad band decoupler. Spectra were recorded with a spectral width of 12·5 kHz by use of accumulation times of 10 min to 2 h. It was often necessary to run more than one spectrum at different pulse lengths to obtain all the peaks for a given compound in approximately the expected intensity ratios although a 6 μs pulse length (a short pulse length in the single-coil time-sharing mode) was adequate to obtain all the peaks in most compounds. Dielectric heating of the sample in the probe was offset by blowing air at ambient temperature over the sample giving an average probe temperature of 35 °C. All resonances are reported to ±0·3 p.p.m. positive (downfield) with respect to tetramethylsilane.

Spectral Assignments.—Spectral assignments in the hydrocarbon region were made on the basis of off-resonance broadband decoupling experiments (at spectrum widths of 2·5 and 5 kHz) and known substituent parameters.[9] Some of the 2-furyl and 2-thienyl assignments in compounds (VII) and (IX) must be considered as tentative because of the fortuitous overlap of resonances. Carbonyl ligand assignments are based on relative intensities (*cis* : *trans* in the range 4—6).

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