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ELECTRONIC EFFECTS IN OCTAHEDRAL π -ALLYLIRON COMPLEXES: ^{13}C NMR SPECTRA

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Summary

^{13}C NMR spectra have been studied for the three series of allyliron derivatives: (i) $\text{C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{X}$ ($\text{X} = \text{I}, \text{Br}, \text{Cl}, \text{ONO}_2, \text{OCOCH}_3, \text{OCOCF}_3$); (ii) $2\text{-RC}_3\text{H}_4\text{Fe}(\text{CO})_3\text{X}$ ($\text{R} = \text{CH}_3, \text{Br}$; $\text{X} = \text{I}, \text{Br}, \text{Cl}, \text{ONO}_2, \text{OCOCF}_3$), and (iii) $1\text{-RC}_3\text{H}_4\text{Fe}(\text{CO})_3\text{X}$ ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$; $\text{X} = \text{Br}, \text{Cl}, \text{OCOCF}_3$). The spectra reveal the effect of the nature of the ligand X and substituent R on the chemical shifts of the allyl and carbonyl carbon atoms.

Introduction

π -Allyl complexes of iron (and other iron group metals) of the types $\text{AlIM}(\text{CO})_3\text{X}$, $\text{AlIM}(\text{CO})_2\text{XY}$, $\text{AlI}_2\text{M}(\text{CO})_2$, are promising models for the study of the transfer of electronic effects in octahedral complexes, and, in addition, offer examples of isomerism of various types [1]. IR [2,3], Mössbauer [4] and mass spectrometry [5], ^{13}C NMR spectroscopy [6-9] etc. have proved useful tools in studying the transfer of electronic effects over various molecular fragments in π -complexes and coordination compounds of transition metals, including iron derivatives.

Results and discussion

Our results on the shielding of carbon nuclei in compounds I-III (I is $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{X}$, II is $\pi\text{-2-RC}_3\text{H}_4\text{Fe}(\text{CO})_3\text{X}$, and III is $\pi\text{-1-RC}_3\text{H}_4\text{Fe}(\text{CO})_3\text{X}$) show that the ^{13}C chemical shifts from the both indicator functions (CO and π -allyl) possess a pronounced sensitivity towards electronic properties of the substituent X. This makes it possible to analyze the nature and strength of the substituent effects in terms of the relative arrangement of the interacting

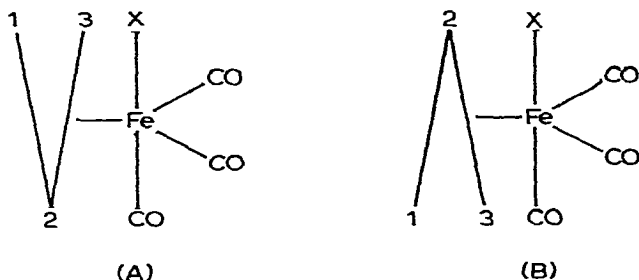
TABLE 1
 ^{13}C CHEMICAL SHIFTS (ppm, in CHCl_3) IN $(\pi\text{-C}_3\text{H}_5)_2\text{Fe}(\text{CO})_3\text{X}$ COMPLEXES

X	$T^\circ\text{C}$	$\delta(^{13}\text{C})$ (vs. TMS)										Isomer ratio IA/IB
		Isomer IA					Isomer IB					
		$\text{C}_{1,3}$	C_2	CO_{eq}	CO_{ax}	$\text{C}_{1,3}$	C_2	CO_{ax}	CO_{eq}	C_2	CO_{ax}	
I	10	59.50	100.56	206.01	208.87	52.41	106.47	209.1	206.6	106.47	209.1	~3/1
Br	10	65.02	101.67	204.78	207.38	54.56	112.78	207.77	205.50	112.78	207.77	4/1
Cl	10	68.20	102.38	204.8	205.95							
OCOCF_3	-40	69.05	104.26	203.22	204.72							
ONO_2	-30	68.79	104.59	202.77	204.26							
OCOCH_3	10	68.07	104.13	204.59	206.08							

TABLE 2
 ^{13}C CHEMICAL SHIFTS (ppm, in CHCl_3 , 10°C) IN $(\pi\text{-1-RC}_3\text{H}_4)_2\text{Fe}(\text{CO})_3\text{X}$ COMPLEXES (IIIA, IIIB)

R	X	Isomer	$\delta(^{13}\text{C})$ (vs. TMS)										Key atom			
			C_1	C_2	C_3	$\text{CO}_{\text{eq}}(1)$	$\text{CO}_{\text{eq}}(2)$	CO_{ax}	CH_3	C_6H_5	C_{ortho}	C_{meta}		C_{para}		
CH_3	Br	IIIA	86.72	102.58	59.24	204.98	204.98	208.23	20.32							
		IIIB	76.07	113.56	48.00				17.59							
CH_3	Cl	IIIA	89.78	103.03	62.23	204.91	204.78	206.41	20.06							
CH_3	OCOCF_3	IIIA	90.88	106.18	63.27	203.42 m	203.42	205.76	20.19							
CH_3	ONO_2	IIIA	91.07	106.24	62.81	203.03	203.03	205.17	19.99							
C_6H_5	Br	IIIA	88.61	96.47	58.52	203.48	205.11	208.09		137.01	129.35	128.71				
		IIIB	82.11	107.51	45.92	208.55				135.69	127.27	128.71				
C_6H_5	Cl	IIIA	91.79	97.12	61.77	203.42	204.41	206.54		137.01	129.35	128.71				
C_6H_5	OCOCF_3	IIIA	93.22	98.94	62.75	201.99	203.35	205.69		136.69	129.61	126				

groups. Prior to the discussion of the experimental results we must note that all the compounds III have a *syn* configuration [10] and a mixture of isomers A and B occurs in solutions of halogeno derivatives of type I (proton NMR data [1] and the results of this work). The isomers differ in the orientation of the allyl group relative to the ligand X:



Stereochemical aspects will be discussed in more detail elsewhere. Here we take into account the data on isomer A in discussing systems comprising the two isomers.

The ^{13}C NMR data of this work (Tables 1-3) show that the shielding of π -allyl nuclei (C_2 and $\text{C}_{1,3}$) gradually decreases in compounds I-III in going from $\text{X} = \text{I}$ to $\text{X} = \text{ONO}_2$, whereas that of carbon atoms of carbonyl functions (both axial and equatorial) increases across the same series. The both effects are related to the change of the substituent perturbation activity, that is to the successive increase of the substituent electron withdrawing power when passing from I to ONO_2 . As for the sign of the effect, it is likely to depend on electron density changes in the case of the allyl ligand and on changes in the sum of bond orders at the carbon atom in the case of the CO function. This assumption will find substantiation in the discussion below.

Collecting data on various types of compounds and on various indicator nuclei in the same compound made it possible to obtain a number of substituent effect sequences and to eliminate change factors that might influence the experimental results. The corresponding data are given in Table 4. As far as the traditional halide series is concerned, one can see that our results are consistent with what one might expect on the basis of changes in halogen electron-withdrawing power:



Next, such oxo ligands as ONO_2 and OCOFCF_3 always exert considerably greater effects than the halide substituents (by the term "oxo ligands" we mean substituents that combine with the metal atom through oxygen). In most cases, the effect of the ONO_2 function is stronger than that of OCOFCF_3 *.

Thus, the NMR spectra furnish data for qualitatively ordering the best

* However, in some cases the effect of OCOFCF_3 on the $\text{C}_{1,3}$ nuclei is somewhat stronger than that of ONO_2 . This discrepancy may be due to close spatial arrangement of $\text{C}_{1,3}$ and X relative to one another and thus attributed to the substituent magnetic anisotropy contribution to the shielding of $\text{C}_{1,3}$.

TABLE 3

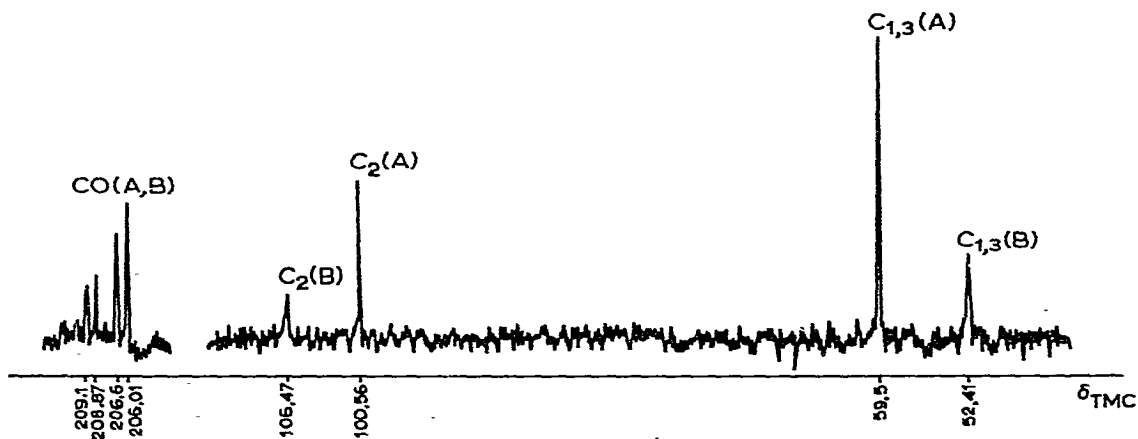
 ^{13}C CHEMICAL SHIFTS (ppm, in CHCl_3 , 10°C) IN $(\pi\text{-}2\text{-RC}_3\text{H}_4)\text{Fe}(\text{CO})_3\text{X}$ COMPLEXES (IIA)

R	X	$\delta(^{13}\text{C})$ (vs. TMS)				
		$\text{C}_{1,3}$	C_2	CO_{eq}	CO_{ax}	CH_3
CH_3	I	59.69	120.12	206.41	210.11	24.60
CH_3	Br	64.95	120.70	204.98	208.62	25.58
CH_3	Cl	67.88	120.83	204.78	206.67	25.90
CH_3	OCOCF_3	68.40	122.52	203.16	205.56	26.29
CH_3	ONO_2	68.33	123.11	202.90	205.30	26.36
Br	Br	69.37	114.14	204.20	205.50	

TABLE 4

SUBSTITUENT EFFECT SEQUENCES IN DERIVATIVES I-III (FROM ^{13}C NMR SPECTRAL DATA)

Type of ligand	Type of carbon atom	Type of compound	Substituent effect sequence	Overall change in $\delta(^{13}\text{C})$ across the series $\Delta\delta(^{13}\text{C})$ (ppm)
$\pi\text{-RC}_3\text{H}_4$	C_2	I, R = H	$\text{I} < \text{Br} < \text{Cl} < \text{OCOCH}_3 < \text{OCOCF}_3 < \text{ONO}_2$	4.03
		II, R = 2- CH_3	$\text{I} < \text{Br} < \text{Cl} < \text{OCOCF}_3 < \text{ONO}_2$	2.99
		III, R = 1- CH_3	$\text{Br} < \text{Cl} < \text{OCOCF}_3 < \text{ONO}_2$	2.66
	$\text{C}_{1,3}$	I, R = H	$\text{I} < \text{Br} < \text{OCOCH}_3 < \text{Cl} < \text{ONO}_2 \leq \text{OCOCF}_3$	9.45
		II, R = 2- CH_3	$\text{I} < \text{Br} < \text{Cl} < \text{ONO}_2 \leq \text{OCOCF}_3$	8.71
	C_3	III, R = 1- CH_3	$\text{Br} < \text{Cl} < \text{OCOCF}_3 \leq \text{ONO}_2$	4.35
			$\text{Br} < \text{Cl} < \text{ONO}_2 \leq \text{OCOCF}_3$	4.03
CO	CO_{ax}	I, R = H	$\text{I} < \text{Br} < \text{OCOCH}_3 < \text{Cl} < \text{OCOCF}_3 < \text{ONO}_2$	4.8
		II, R = 2- CH_3	$\text{I} < \text{Br} < \text{Cl} < \text{OCOCF}_3 < \text{ONO}_2$	4.81
		III, R = 1- CH_3	$\text{Br} < \text{Cl} < \text{OCOCF}_3 < \text{ONO}_2$	3.06
	CO_{eq}	I, R = H	$\text{I} < \text{Br} \approx \text{Cl} < \text{OCOCH}_3 < \text{OCOCF}_3 < \text{ONO}_2$	3.3
		II, R = 2- CH_3	$\text{I} < \text{Br} < \text{Cl} < \text{OCOCF}_3 < \text{ONO}_2$	3.51
		III, R = 1- CH_3	$\text{Br} < \text{Cl} < \text{OCOCF}_3 < \text{ONO}_2$	1.95

Fig. 1. $^{13}\text{C}\text{-}\{^1\text{H}\}$ NMR spectrum of $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{I}$ (A and B).

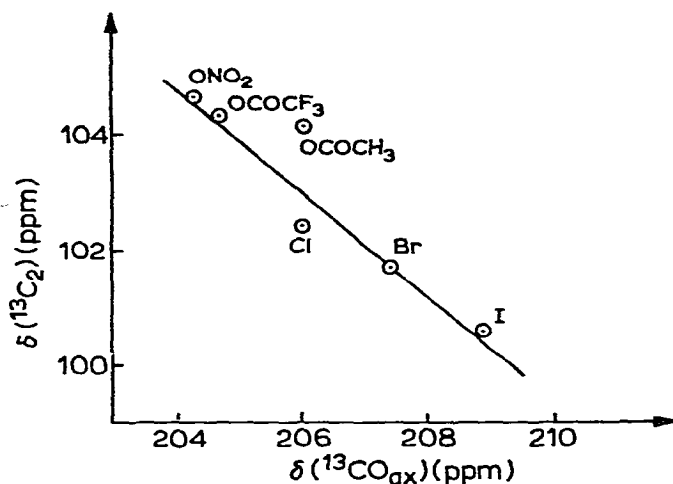


Fig. 2. $^{13}\text{C}_2$ vs. $^{13}\text{CO}_{\text{ax}}$ chemical shifts in derivatives I.

studied substituents* according to their effect on π -allyl as well as carbonyl functions (for both *cis* and *trans* orientations of the latter relative to the perturbing group) in octahedral complexes of iron:



The plots shown in Figs. 2 and 3 demonstrate that in the case of compounds I and II, the π -allyl and CO chemical shifts as well as the chemical shifts from axial and equatorial carbonyl groups form a rather consistent set of data.

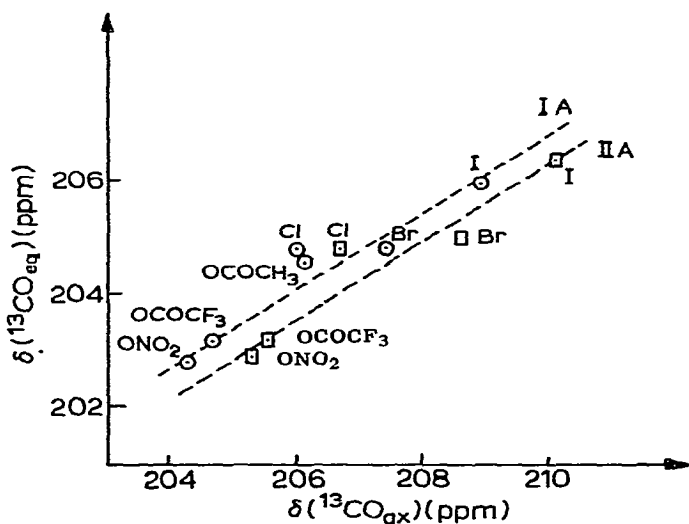


Fig. 3. CO_{ax} vs. CO_{eq} ^{13}C chemical shifts in derivatives IA (\circ) and IIA (\square , R = CH_3).

* As for such an oxo ligand as OCOCH_3 , the available data are insufficient to draw any definite conclusion concerning its electronic properties in the compounds we are discussing.

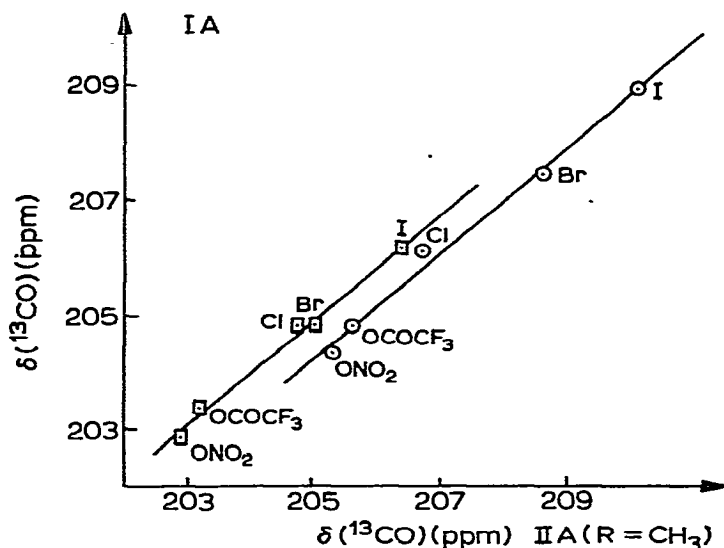


Fig. 4. ^{13}C chemical shifts of carbonyl groups of derivatives IA vs. those of the corresponding derivatives IIA ($\text{R} = \text{CH}_3$) CO_{eq} \square , CO_{ax} \circ .

It should be emphasized that the 2-methyl substituent on the allyl ligand has no pronounced effect on the shielding of ^{13}C nuclei of either π -allyl or CO groups. In this case, the pattern of the ligand X effects remains unaffected. The result is that the chemical shifts from the corresponding indicator nuclei of compounds I and II show a good linear correlation (Figs. 4 and 5). It is noteworthy that the 2-Me substituent perturbation effect is closely related to the orientation of the methyl relative to CO group in octahedral iron complexes. Thus, the occurrence of the methyl substituent gives rise to chemical shifts of

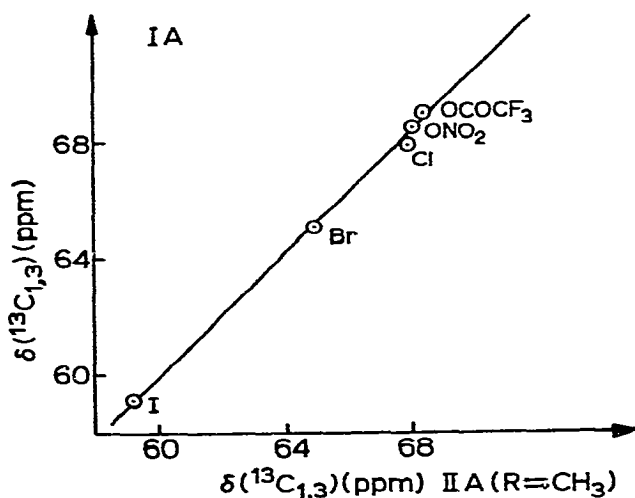


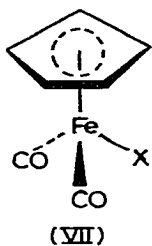
Fig. 5. $^{13}\text{C}_{1,3}$ chemical shifts of derivatives IA vs. those of the corresponding derivatives IIA ($\text{R} = \text{CH}_3$).

0.7 to 1.2 in the case of CO_{ax} , 0.3 or less in the case of CO_{eq} and 0.7 or less for $\text{C}_{1,3}$ (ppm). These results suggest a close spatial arrangement of the methyl relative to CO_{ax} groups (an argument in favour of structure IIA) and indicate a purely steric rather than electronic nature of the methyl-induced shielding of the CO function.

Our data show the *trans* effect to be markedly stronger than the *cis* one. In fact, the shielding of the CO_{ax} group changes in magnitude more drastically than that of the equatorial ones when passing from the weakest electron acceptor (iodine in I and II and bromine in III) to the strongest one (ONO_2) (Table 4).

It should be emphasized that such behaviour is characteristic of compounds I, II and III, bearing substituents in the π -allyl ligands. Thus, the data of this work are in full accord with the well-known *trans* effect patterns for square-planar and octahedral complexes.

The transfer of the substituent effect in octahedral complexes I-III (Tables 1-3) can be compared with that in structurally related pseudo tetrahedral compounds $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ (VII) (for the sake of simplicity, it is assumed that the $\pi\text{-C}_5\text{H}_5$ ligand occupies one coordination site) [7,12]:



It is known that the CO signal from "tetrahedral" iron complexes VII undergoes an upfield shifting in going from $\text{X} = \text{I}$ to Br and to Cl , similar to the case of compounds I and II. However, octahedral and tetrahedral derivatives considerably differ in the magnitude of the effect. The replacement of I with Cl in tetrahedral complexes gives rise to $\Delta\delta(^{13}\text{CO})$ of, according to various authors, 0.3 [7] to 0.9 [12] ppm, whereas in octahedral compounds I and II the effect is much more pronounced, especially in the case of *trans*-groups: $\Delta\delta(^{13}\text{CO}_{\text{eq}}) = 1.3$ (IA) and 1.6 (IIA) ppm, $\Delta\delta(^{13}\text{CO}_{\text{ax}}) = 2.9$ (IA) and 3.4 (IIA) ppm.

Collating ^{13}C NMR data on compounds I (Table 1) and compounds II and III containing substituted π -allyl ligands (Tables 2, 3) makes it possible to discuss the substituent effects in terms of the substituent position in the ligand.

Thus, the data obtained show that the influence of the 2-methyl substituent is chiefly limited to the substituted atom C_2 and appears to be negligible in the case of more distant $\text{C}_{1,3}$ atoms. The substituent causes a pronounced deshielding of the C_2 nucleus, with only a slightly larger downfield shifting of the signal than that observed in ferrocene [13] and benzenechromium tricarbonyl [14] derivatives. On the contrary, the 2-Br substituent influences not only the C_2 , but also $\text{C}_{1,3}$ nuclei. The latter effect is somewhat more pronounced than that observed with ferrocene and benzene derivatives. As for the key C_2 nuclei, the 2-Br substituent causes quite opposite effects in compounds we are discussing and in benzene derivatives [13].

Substituents on the π -allyl terminal carbon produce essentially the same effect as that observed in the case of other organic [15-16] and organometallic [14] compounds: they cause a pronounced downfield shift of the signal from the substituted atom C_1 . However, there are some points to be mentioned concerning the magnitude of the effect. The experimental data summarized in Table 5 demonstrate the difference between organic compounds and organometallics. Thus, the substituents in question cause an 8 to 10 ppm shifting in usual organic compounds, while in organometallic compounds the shifts are twice this value. Note that the substituent contribution to the shielding of the C_1 atom depends on the ligand structure: the value of $\Delta\delta(C_1)$ ranges from 16 to 18 ppm for cyclic ligands against 21 to 24 ppm for open-chain ones.

These results provide some insight into the nature of the substituent effect characteristic of the π -L—M fragment. They strongly indicate a direct participation of the transition metal atom in the redistribution of electron density caused by the substituent.

The above assumptions appear quite realistic in view of the data in Table 6. It is easy to see that the substituent R exerts a pronounced effect on the carbon atoms furthest from it, that is, on the ligand terminal atoms (C_4 in π -butadiene complexes, C_3 in π -allyl complexes, and $C_{2,3}$ in trimethylenemethane derivatives).

TABLE 5

INFLUENCE OF SUBSTITUENTS ON CHEMICAL SHIFTS OF THE SUBSTITUTED ATOMS IN ORGANIC AND ORGANOMETALLIC COMPOUNDS

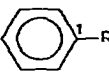
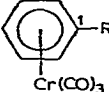
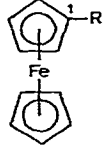

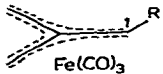



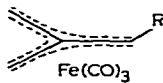
	R	H→R $\Delta\delta(C_1)$ (ppm)	Refs.
	CH ₃ C ₆ H ₅	-8.9 -10.1	15 16,27
	CH ₃ C ₆ H ₅	-17.0 -18.1	14
	CH ₃ CH=CH ₂ C ₆ H ₅	-16.1 -17.4 -17.8	13
	CH=CH ₂	-21.0	24
	CH=CH ₂	-27.0	25,26
	CH ₃ C ₆ H ₅	-21.6 -23.6	

TABLE 6
TRANSMISSION OF THE SUBSTITUENT EFFECTS ALONG THE OPEN-CHAIN LIGANDS

Type of structure	R	$\Delta\delta(^{13}\text{C})$ (ppm)			Refs.
		C ₂	C ₃	C ₄	
	H	0	0	0	24
	CH=CH ₂	4.5	0	1.9	
	H	0	0		
	CH ₃	-0.6	6.0		
	C ₆ H ₅	5.3	6.4		
	H	0	0		25, 26
	CH=CH ₂	0	0.6-1.3		

The data also show that, on the contrary, on the preceding carbon atoms the effect dies down along the chain. It follows that the metal atom involved in π -coordination participates in the transfer of the substituent effect in the ligand. The result is that such ligands as π -allyl, though formally open-chain, behave as π -coordinated cyclic systems in π -L—M fragments, as far as the transfer of the substituent effect is concerned.

Our ^{13}C NMR data on complexes I-III are related to the results obtained with other physico-chemical methods.

The CO stretching frequencies of compounds I-III [2,3] and other transition metal complexes [6-9], as well as the corresponding force constants calculated with certain approximations, appear sensitive to electronic properties of the substituent X at the metal atom. Thus, electronic characteristics of the ligand X in compounds I have been found to correlate with the force constants K_2 determined from stretching vibrations of equatorial carbonyl groups*. Next, it has been shown that a certain relationship exists between changes in electronic properties of the ligand X and changes in peak areas of antisymmetric stretching vibration involving two CO_{eq} groups, ν_2 , and totally symmetric stretching vibration involving all the three CO groups, ν_3 .

One can of course expect a similarity between IR and NMR data on complexes I-III. In fact, equatorial carbonyl force constants K_2 change parallel with the corresponding ^{13}C NMR chemical shifts in compounds I (Fig. 6)**. On the other hand, one can compare the ^{13}C NMR data with other spectral characteristics, such as experimental stretching frequencies (Fig. 7) and the corresponding peak areas (Fig. 8).

There are few cases in which correlations can be drawn between the available mass spectrometric data and ^{13}C NMR data on transition metal complexes. Compounds I-III provide an example. The plot of Fig. 9 shows a linear relationship between the shielding of ^{13}C nuclei of CO_{ax} groups in compounds I

* No such relationship has been found for the axial carbonyl stretching force constants, K_1 [2].

** Other carbonyl complexes of transition metals are discussed in terms of similar relationships between IR and NMR data in refs. 6-9.

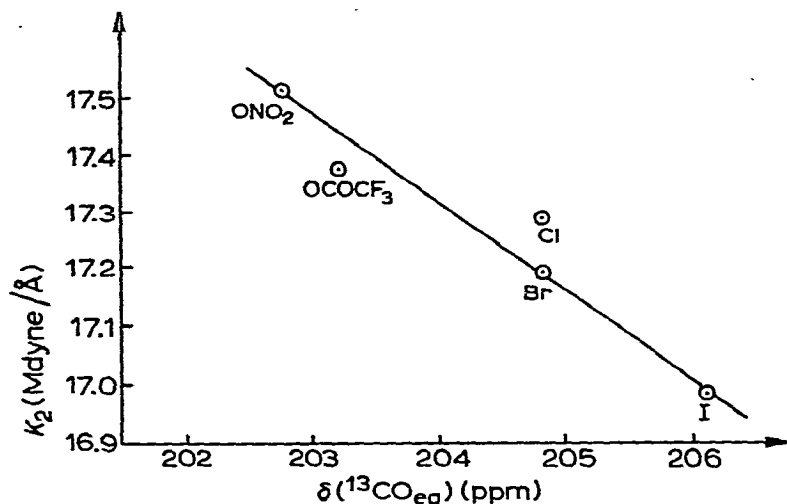


Fig. 6. CO_{eq} force constants K_2 [2] vs. CO_{eq} ^{13}C chemical shifts (Table 1) in compounds I.

and the φ_9/φ_5 values, the peak area ratios of ion currents from $[\text{RC}_3\text{H}_4\text{Fe}(\text{CO})\text{X}]^+$ and $[\text{RC}_3\text{H}_4\text{Fe}(\text{CO})_2\text{X}]^+$, which depend on the substituent X [5].

One could go on by discussing the sequence (2) given above, describing changes of the substituent effect in compounds I-III, in relation to the numerous well known organic and coordination chemistry substituent sequences. Series (2) is a part of the spectrochemical and nepheloxetic series of coordination chemistry [17-20]. There is no qualitative disagreement between this series and the accepted ordering of substituents according to their inductive power ex-

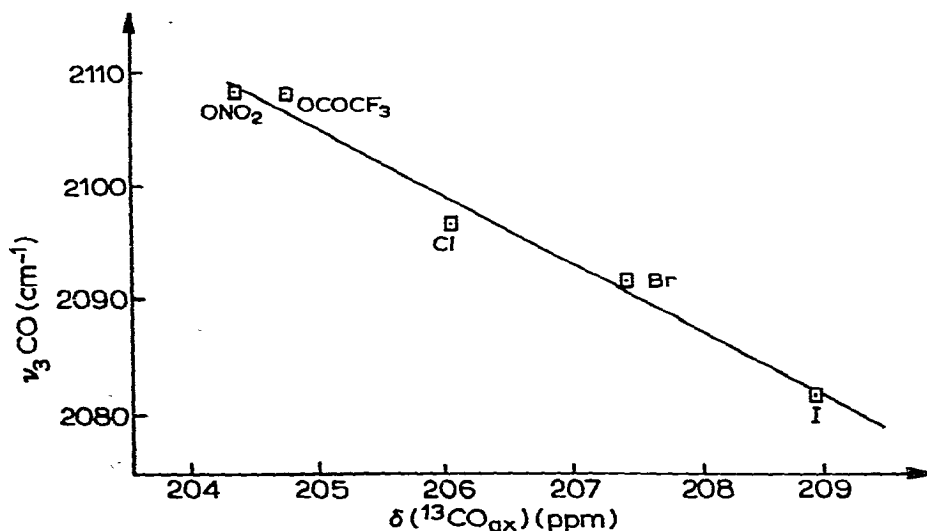


Fig. 7. Frequencies of totally symmetric stretching vibration ν_3 involving three CO groups vs. ^{13}C chemical shifts from axial carbonyl ligands in compounds I.

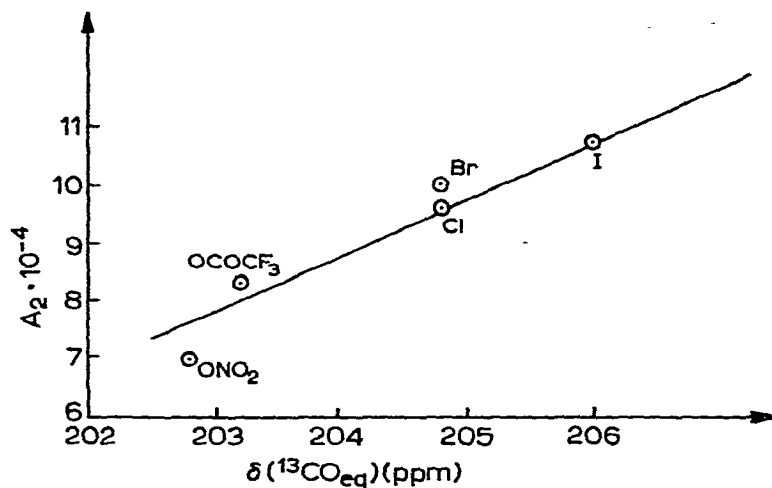


Fig. 8. Peak areas of antisymmetric stretching vibration ν_2 involving two equatorial CO groups vs. ^{13}C chemical shifts from these groups in compounds I.

pressed in terms of parameters σ^* , σ_j etc. [21-23]. However, at present, attempts to derive more basic quantitative relationships would be unjustified, since the number of substituents studied is rather limited.

Therefore we will confine our conclusions to the statement, based on the above discussion of physico-chemical characteristics of compounds I-III, that increase in polarity of the Fe-X bond (without considering π and σ components of the bond separately) across series (2) causes effects which are very important from the point of view of all methods involved in this study. Here belong changes in the stability of fragment ions, in the nature of the π -allyl-Fe and Fe-CO bonding, and hence in the CO bond order. It is likely that increase of

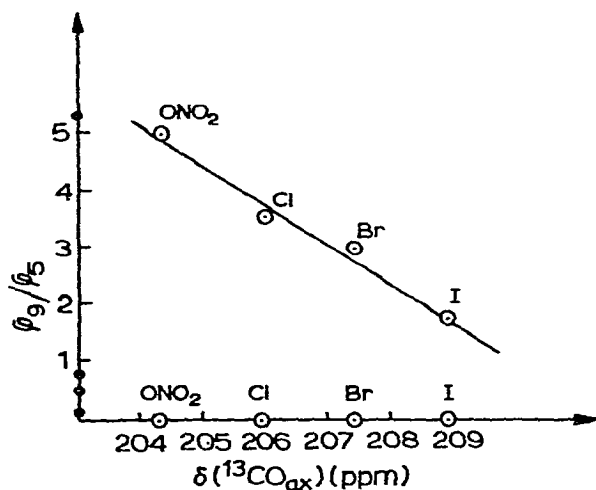


Fig. 9. Ratios ϕ_9/ϕ_5 determining peak area ratio of ion currents from $[\text{C}_3\text{H}_5\text{Fe}(\text{CO})\text{X}]^+$ and $[\text{C}_3\text{H}_5\text{Fe}(\text{CO})_2\text{X}]^+$ in compounds I [5] vs. CO_{ax} ^{13}C chemical shifts of the same derivatives (Table 1).

both the shielding of ^{13}C nuclei and CO force constants along the series is due to increase in the CO bond order.

Experimental

^{13}C NMR spectra were recorded on a 22.63 MHz Bruker HX-90 instrument. Fourier transform mode and noise decoupled (90 MHz) double ^{13}C - $\{^1\text{H}\}$ resonance were applied. Ampoules of a 10 mm external diameter were used. Chemical shifts were referred to tetramethylsilane.

Preparative methods for the compounds under investigation are given in refs. 1, 5, 10.

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