Journal of Organometallic Chemistry, 155 (1978) 221—228

SUBSTITUENT EFFECTS IN THE ^{13}C NMR SPECTRA OF IRON CARBONYL COMPLEXES WITH ORGANIC π-DONORS

DOROTHY H. GIBSON * and TEK-SING ONG
Department of Chemistry, University of Louisville, Louisville, Kentucky 40208 (U.S.A.)
(Received December 20th, 1977)

Summary

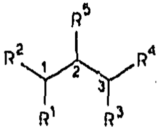
The carbon spectra of nine tetracarbonylallyliron cations and seven acyclic dieneiron tricarbonyl complexes have been obtained. The effects of alkyl substituents (particularly methyl groups) on the chemical shift positions of ligand carbon atoms are described. The CO resonance signals for the cations are not averaged at ambient temperature thus indicating a high barrier to site exchange of these groups.

There have been several recent studies of pentadienyl- (or cyclohexadienyl-) -iron tricarbonyl carbonium ion complexes by means of carbon spectra [1,2,3]. These studies have centered upon the question of charge density-^{13}C chemical shift correlations which have already been established for their uncomplexed counterparts. The bonding model for these complexes consists in part of a back donation component involving ψ_3 of the cation which should have the effect of enhancing the electron density at carbons 1, 3 and 5 relative to 2 and 4. The resonance positions for C(2) and C(4) in these ions are observed at lower field than other ligand carbons of comparable substitution. The tentative conclusion that the electron density of C(2,4) must be lower is supported by the extended Hückel calculations of Hoffmann and Hofmann [4]. The effects are exactly reversed in the uncomplexed ions.

Recent ^{13}C NMR work by Olah [5] demonstrates that allyl carbonium ions are electron deficient at C(1) and C(3); the resonance positions for these centers are at very much lower field than those for C(2). As with the pentadienyl ions, the bonding model for allyl carbonium ion complexes has a back donation component involving a filled metal orbital and an empty non-bonding ligand orbital (ψ_2). This ligand orbital has a node at C(2) and thus C(1) and C(3) can be expected to bear greater electron density than C(2). We have studied the

TABLE 1

^{13}C CHEMICAL SHIFTS AND J(C—H) VALUES FOR TETRACARBONYLALLYLIRON CATIONS [a]



Compound	C(1)	C(2)	C(3)	R(1)	R(2)	R(3)	R(4)	R(5)	CO
I	56.80 (t, 163.25)	99.24 (d, 165.46)	56.80 (t, 163.25)						197.76 196.27
II	82.41 (d, 164.66)	94.30 (d, 164.72)	56.51 (t, 166.93)	CH_3 16.51 (q, 133.12)					195.05 196.60 198.14
III	83.63 (d, 160.31)	98.23 (d, 160.31)	49.07 (t, 165.46)		CH_3 18.85 (q, 129.42)				196.01 196.86 197.31
IV	55.44 (t, 163.99)	124.00 (s)	55.44 (t, 163.99)					CH_3 23.20 (q, 130.92)	197.76 196.14
V	91.05 (d, 160.31)	96.71 (d, 160.31)	49.33 (t, 163.90)		CH_3 13.39 (q, 128.69) CH_2 27.89 (t, 132.36)				196.34 197.18 197.63
VI	115.68 (s)	93.72 (d, 161.78)	47.64 (t, 163.99)	CH_3 23.40 (q, 130.92)	CH_3 29.96 (q, 129.44)				197.96 198.14 200.16
VII	73.89 (d, 169.14)	96.19 (d, 167.67)	82.93 (d, 161.78)	CH_3 17.61 (q, 129.42)			CH_3 19.11 (q, 129.42)		197.25 199.07
VIII	76.36 (d, 158.95)	100.67 (d, 161.33)	76.36 (d, 158.95)		CH_3 18.91 (q, 129.42)		CH_3 18.91 (q, 129.42)		197.57 198.15 198.54
IX	95.93 (d, 155.90)	118.22 (s)	50.89 (t, 166.19)		CH_3, CH_3 18.65, 21.06 (q, 130.90) (q, 127.95) CH 31.46			CH_3 23.01 (q, 128.69)	198.35 197.44 196.47

[a] The anion is tetrafluoroborate in all cases.

^{13}C NMR spectra of a series of alkyl-substituted tetracarbonylallyliron cations and that of the parent compound *; the data are summarized in Table 1.

As shown in Table 1, chemical shift differences between C(2) and a terminal carbon vary over a range of nearly 80 ppm with C(2) being at lower field in all cases except the one in which this position is unsubstituted and a terminal carbon is quaternary (VI). As Lillya has observed with the pentadienyl systems, methyl groups exert significant deshielding effects on the centers to which they are attached. However we note that all alkyl groups exert some effects on other centers in the allyl systems whereas the only long range effect noted with the pentadienyl ions is a slight shielding of the opposite terminal carbon by an *anti* CH_3 group [1] (similar to the γ effect in alkenes). The carbon resonance positions in the cation complexes have been assigned after examination of the off-resonance and broad-band decoupled spectra together with considerations of the molecular symmetry of the ions and internal consistency of the data.

Although the ^{13}C NMR spectra of a number of allyl cations have recently been reported by Olah [5], only a limited number of direct comparisons can be made with the ions studied by us since the substitution patterns of the two groups of compounds differ. The comparisons which can be made are outlined below in the sections which describe α, β and γ effects in the cation complexes:

(a) α-Effects

A *syn-* or *anti*-alkyl group deshields this center by about 30 ppm in the cation and an ethyl group exerts an even larger effect; a methyl group at C(2) deshields it by a much smaller amount [5] (the large negative effect of alkyl groups on trigonal centers has also been studied by Olah in aromatic systems [7]). In the complexes the α-effect of a CH_3 group is deshielding to the extent of 25—26 ppm at either a terminal center or at C(2); the extent of deshielding increases progressively as the alkyl group becomes larger than methyl, but the magnitude of the effect is greater than with the uncomplexed ions. The combined effects of the *gem*-dimethyl groups in VI deshield C(1) more than would be expected from summing the effects of *syn* and *anti* substituents (the combined effects of *gem*-dimethyl groups on carbon resonances in alkenes is usually less than this sum as discussed below).

(b) β-Effects

In the complexes, alkyl groups exert small shielding effects on a β center in all cases except in compound VIII which has *syn*-methyl groups on both C(1) and C(3); in this ion the β center is deshielded slightly. The cations studied by Olah [5] do not allow β-effects to be defined unambiguously.

(c) γ-Effects

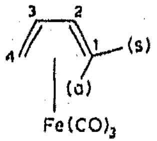
The effects of this type which can be assigned with certainty from the systems studied by Olah [5] are few, but it appears that both *syn-* and *anti*-methyl groups shield the γ center to about the same degree (~20 ppm). The effects seen in the complexes are different: an *anti*-methyl group exerts no effect on C(3) but a

---

* The spectra of compounds I and II have been reported previously [6].

TABLE 2

^{13}C CHEMICAL SHIFTS AND J(C—H) VALUES FOR DIENEIRONTRICARBONYL COMPLEXES



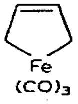
Compound	C(1)	C(2)	C(3)	C(4)	CH$_3$(a)	CH$_3$(s)	CH$_3$(2)	CH$_3$(3)	CO
X	40.68 (t, 161.05) [40.39] [a]	85.51 (d, 169.13) [85.19]	85.51 (d, 169.13) [85.19]	40.68 (t, 161.05) [40.39]					212.00 [211.29]
XI	58.59 (d, 157.37)	93.19 (d, 166.19)	81.27 (d, 169.13)	39.64 (t, 159.57)		19.17 (q, 126.97)			212.77
XII	53.91 (d, 151.49)	88.16 (d, 169.13)	90.43 (d, 166.19)	40.94 (t, 159.57)	13.52 (q, 126.48)				212.06
XIII	44.10 (t, 159.57) [43.86] [a]	103.53 (s) [102.91]	85.07 (d, 167.66) [84.71]	38.21 (t, 159.57) [38.02]			22.58 (q, 125.01) [22.84]		212.19 [211.27]
XIV	58.83 [a] (d, 158.2) [a]	103.37 (s)	81.81 (d, 170.0)	36.36 (t, 159.0)		15.84 (q, 127.0)	18.05 (q, 127.0)		212.19
XV	56.15 (d, 158.85)	90.14 (d, 166.19)	99.43 (s)	43.35 (t, 160.31)		19.50 (q, 129.42)		23.01 (q, 126.48)	213.04
XVI	71.48 (s)	92.32 (d, 163.25)	85.59 (d, 167.66)	41.20 (t, 160.31)	20.57 (q, 129.43)	33.14 (q, 126.49)			212.84
XVII	67.00 (s)	92.94 (d, 163.25)	102.88 (s)	43.67 (t, 157.37)	20.47 (q, 126.48)	33.34 (q, 130.90)		24.57 (q, 129.42)	212.65

[a] Data from Pearson (see ref. 10); spectra obtained in CDCl$_3$ solution.

syn substituent shields it by about 7.5 ppm. However, the γ center in VI which has *gem*-dimethyl groups, is shielded by >9 ppm.

The limiting temperature for site exchange of the CO ligands is a great deal higher for the allyl complexes than the pentadienyl systems. Lillya [1] has observed line broadening of the carbonyl signals for the pentadienyl complexes at −30° C yet we observe two or three CO signals for the allyl compounds at ambient temperature. Takats [8] and Osborn [9] in studying CO site exchange of (alkene)$Fe(CO)_4$ complexes noted that the barrier to exchange was dependent upon the electron-withdrawing characteristics of substituents on the alkene with those systems having the lowest σ donor: π-acceptor values showing the highest barriers to rearrangement. A carbonium ion can be taken as the extreme case of an electron-withdrawing substituent and thus these ions can be expected to have high barriers to CO site exchange.

There has been some recent interest also in establishing the effects of substituents upon the carbon resonance positions in dieneiron tricarbonyl complexes. Pearson [10] has reported the results of a comparative study of some methyl-substituted dienes (both cyclic and acyclic) and their complexes and concluded that the β-effects observed for the complexes support a bonding model having lower π-bond order between C(1)—C(2) and C(3)—C(4). More recently he [11] has studied the effects of methoxy- and methoxy-carbonyl groups in some dienes and their iron tricarbonyl complexes, again concluding from β-effects that there is greater π-bond order in the 2,3-bond of the complexes than in the 1,2- (or 2,4-) -bond. Thus it was concluded that metallocyclic structures, such as the one shown, make strong contributions to the bonding in these complexes.

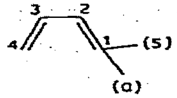


We have obtained the carbon spectra of seven acyclic dieneiron tricarbonyl complexes (the spectra of X and XIII have been reported previously) six of which have methyl substituents; the data, together with that from Pearson [10] on compound XIV is presented in Table 2. Although marked differences are often noted in the chemical shifts of protons in these complexes upon changing from $CHCl_3$ to benzene, the resonance signals for carbon are affected very little as indicated by the comparative data for X and XIII. The carbon spectra of four of the dienes have also been obtained and these data are summarized in Table 3 together with data from Pearson on compounds XVIII and XXII. To make comparison of the data in Tables 2 and 3 easier, *cis*-methyl groups are designated as a (*anti*) and *trans* groups as s (*syn*) at C(1) in both tables.

Help for the assignment of the resonance positions to the various carbon atoms in the complexes is derived from two sources: (a) internal comparisons of the eight diene complexes and (b) the ^3J(C—H) interactions which are in their high resolution gated-^{1}H-decoupled spectra. In compounds XI and XII both C(2) and C(3) should be doublets from first order effects; however C(2) experiences long range coupling with the methyl protons as well as the terminal hydrogens at C(4) while the long range interactions are more limited for C(3) in each compound. The lower intensity broad doublet in each case is then assigned to C(2). With

TABLE 3

^{13}C CHEMICAL SHIFTS FOR DIENES



Compound	C(1)	C(2)	C(3)	C(4)	CH_3(a)	CH_3(s)	CH_3(2)
XVIII	116.6 [a]	137.2	137.2	116.6			
XIX	129.20	133.16	137.65	114.65		17.68	
XX	126.54	132.34	131.02	116.59	13.22		
XXI	116.75	142.46	139.86	113.49			17.79
XXII	127.04 [a]	135.06	141.68	109.99		11.29 or 13.77	11.29 or 13.77
XXIII	134.72	127.06	133.88	114.25	18.13	25.87	

[a] Data from Pearson (see reference 10); spectra obtained in $CDCl_3$ solution.

systems bearing two or more CH_3 groups it is similarly difficult to make proper assignments. Internal comparisons allow clear patterns to emerge; *anti*-methyl groups are more shielded than their *syn* analogs. The position for the methyl group in XIII is lower than that of either a *syn* or *anti* group and thus allows assignments of the two methyl groups in XIV and XV to be made. Additionally, *anti*-methyl groups have lowered signal intensities relative to *syn* groups in the same molecule (XVI, XVII) or when the signal intensity (relative to other carbon centers in the molecule) is compared to that of its *syn* counterpart in molecules which are geometric isomers (XI, XII).

With the assignments firm it is then possible to turn attention to the effects which CH_3 groups exert on the ligand carbon resonances as compared to their counterparts in the uncomplexed dienes. These are considered as α, β, γ and δ effects as follows:

(a) α-Effects. As with olefins [12,13] *cis*- and *trans*-(a and s, respectively)-methyl groups exert strong deshielding effects (10—12.5 ppm) on the diene carbon centers to which they are attached, with a *trans* group exerting a slightly larger effect. The combined effect of *gem*-dimethyl substituents is slightly less than the deshielding expected from summing the two (as is seen with olefins, also ref. 13). A methyl group at the 2-position exerts a much smaller (~5 ppm) deshielding effect. The α-effects of methyl groups in the complexes are in the same direction but larger in magnitude (13—18 ppm) than those in the dienes; the effect exerted by *gem*-dimethyls is roughly the sum of the two. In the complexes, however, a 2-methyl substituent also exerts a strong deshielding effect (18 ppm) on C(2).

(b) β-Effects. Both *cis*- and *trans*-methyl groups shield C(2) (4—5 ppm) in the dienes and the combined effects of these two are seen with the *gem*-dimethyl compound. A methyl group at C(2) exerts a slight shielding effect on C(3) (2.5 ppm) but virtually, no effect on C(1). Reversals of these effects are seen in the complexes: both *cis* and *trans* groups deshield C(2) with the *trans* substituent

exerting a much larger effect. However, the deshielding effect of *gem*-dimethyl groups on C(2) is considerably less than that expected to result from additivity. Also, a 2-methyl group deshields C(1) (7.5 ppm) but has almost no effect on C(3).

(c) γ-Effects. The effects seen here with the dienes parallel the observations on olefins reported by Couperus et al. [13], and others [12]. A *cis*-methyl group shields C(3) (by 6 ppm) and a *trans* group exerts no effect; the effect is diminished (to 4 ppm) when *gem*-dimethyl groups are present. The γ-effects of these groups in the complexes, however, are markedly different from those in the dienes: a *cis* group deshields C(3) by 5 ppm while a *trans* group shields this center by 4 ppm and the two effects are offset when *gem*-dimethyl groups are present. In contrast, the effect of a 2-methyl substituent on C(4) is about the same in the complexed and uncomplexed dienes.

(d) δ-Effects. The effect of a methyl group on the chemical shift of this center is small; *trans* substituents exert a small shielding effect with both groups of compounds. However, in the complex having *gem*-dimethyl substituents a slight deshielding effect is noted whereas the δ center in the uncomplexed diene is shielded.

Consideration of the new spectral data on the dienes and the dieneiron tricarbonyl complexes we have obtained to augment the information currently in the literature leads us to believe that the conclusions of Pearson must be modified. The large α-effects and the unusual γ-effects, in particular, suggest that steric factors play a significant role in determining chemical shift positions of the diene carbon centers in the complexes, *cis*- and *trans*-methyl groups exert opposite effects on the γ center and, furthermore, the effect of a *cis* substituent is reversed with respect to its effect in an olefin or diene. The magnitude and direction of the changes lead us to suggest that there are alterations in the Fe—C bond distances which attend substitution. The substituents could therefore cause shielding to occur as a result of shortening of some metal—carbon bonds while deshielding others as a result of increasing the metal—carbon bond length.

Since large effects are seen with the cation complexes as well, we suggest that the chemical shifts of the ligand-carbons here, also, are governed by changes in metal—carbon bond distances resulting from alkyl substitution. For example, the presence of *gem* substituents in VI should move C(3) closer to iron and push C(1) further away; the chemical shifts of these centers are changed as expected with C(1) being at lower field than would be predicted from combined electronic effects and C(3) having the highest chemical shift of any terminal carbon in the series.

To date there are few studies which demonstrate, unambiguously, a direct correlation between metal—carbon bond distances and ^{13}C chemical shifts. However, the recent work of Lock and Powell et al. [14], does show that upfield shifts of olefinic carbons in a series of rhodium—diene complexes are directly related to the shortening of the metal—carbon bond distances as evidenced from a comparison of X-ray and ^{13}C NMR data.

Whether it is correct to attribute the changes in ^{13}C chemical shifts in the iron complexes to Fe—C bond alterations resulting primarily from steric effects created by alkyl substituents cannot be fully answered at present and will require additional study.

Experimental

The preparations of the carbonium ion complexes have been described previously [15]. The diene complexes (except XVI) were prepared by thermal reactions between diene (in benzene solution) and $Fe_2(CO)_9$; compound XVI was prepared by treatment of the hydrocarbon with $Fe_2(CO)_9$ followed by photolysis of the resulting mixture of η^2-dieneiron tetracarbonyl and η^4-diene-iron tricarbonyl complexes until conversion to the η^4-complex was complete.

The ^{13}C NMR spectra were measured on a Bruker WH-90DS spectrometer at 22.63 MHz with broad-band-, off-resonance- and gated-^1H-decoupled spectra being recorded. The spectra were accumulated and transformed using a Nicolet Model 1180 computer.

The spectra of the carbonium ion complexes were obtained in trifluoroacetic acid solution using external TMS in benzene-d_6 in a coaxial inner tube as reference. The spectra of the dienes and their iron tricarbonyl complexes were obtained in benzene-d_6 with TMS as internal reference.

Acknowledgment

Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We are also grateful to the National Science Foundation (CHE76-05683) for providing matching funds for the purchase of the FT NMR spectrometer.

References

1 P.A. Dobosh, D.G. Gresham, C.P. Lillya and E.S. Magyar, Inorg. Chem., 15 (1976) 2311.
2 A.J. Birch, P.W. Westerman and A.J. Pearson, Aust. J. Chem., 29 (1976) 1671.
3 G.A. Olah, S.H. Yu and G. Liang, J. Org. Chem., 41 (1976) 2383.
4 R. Hoffmann and P. Hofmann, J. Amer. Chem. Soc., 98 (1976) 598.
5 G.A. Olah and H. Mayer, J. Amer. Chem. Soc., 98 (1976) 7333.
6 M. Brookhart, T.H. Whitesides and J.M. Crockett, Inorg. Chem., 15 (1976) 1550.
7 G.A. Olah and D.A. Forsyth, J. Amer. Chem. Soc., 97 (1975) 3137.
8 L. Kruczynski, L.K.K. Li-Shinginan and J. Takats, J. Amer. Chem. Soc., 96 (1974) 4006.
9 S.T. Wilson, M.J. Coville, J.R. Shapley and J.A. Osborn, J. Amer. Chem. Soc., 96 (1974) 4038.
10 A.J. Pearson, Aust. J. Chem., 29 (1976) 1679.
11 A.J. Pearson, Aust. J. Chem., 30 (1977) 407.
12 J.B. Strothers, Carbon-13 NMR Spectroscopy, Academic Press, New York, 1972, Chapter 5.
13 P.A. Couperus, A.D.H. Clague and J.P.C.M. van Dongen, Org. Mag. Res., 8 (1976) 426.
14 R.P. Hughes, N. Krishnamaschari, C.J.L. Lock, J. Powell and G. Turner, Inorg. Chem., 16 (1977) 314.
15 D.H. Gibson and R.L. Vonnahme, J. Amer. Chem. Soc., 94 (1972) 5090; Chem. Commun., (1972) 1021 and J. Organometal. Chem., 70 (1974) C33.