Carbon-13 Nuclear Magnetic Resonance Spectra of σ,η-Binuclear Complexes prepared from Dodecacarbonyltri-iron and Acetylenes

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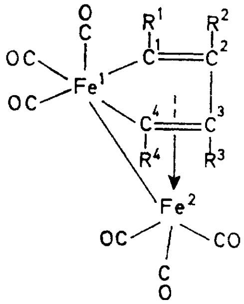
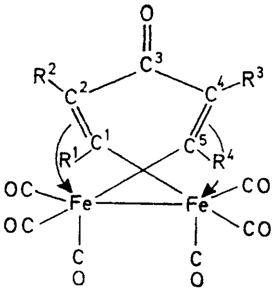
The binuclear complexes $[Fe_2(CR^1{:}CR^2{\cdot}CR^3{:}CR^4)(CO)_6]$, (I), and $[Fe_2(\mu\text{-}CR^1{:}CR^2{\cdot}CO{\cdot}CR^3{:}CR^4)(CO)_6]$, (II), have been investigated by ^{13}C n.m.r. spectroscopy (R^1, R^2, R^3, R^4 = H, Me, Bu^t, Ph, or $CH_2{:}CH{\cdot}CH{:}CH_2$). Low-field absorptions observed for carbon atoms σ- and η-bonded to two iron atoms are discussed for the two classes of complex. Variable-temperature ^{13}C n.m.r. spectra show that these complexes are stereochemically non-rigid; steric effects are important in the fluxional behaviour of the $Fe(CO)_3$ moiety in complexes (II).

SINCE the preparative work of Weiss *et al.*[1] complexes obtained from reactions between iron carbonyls and acetylenes have received much attention in order to better understand their unusual structures. The structures of the binuclear derivatives $[Fe_2(CR^1{:}CR^2{\cdot}CR^3{:}CR^4)(CO)_6]$, (I), and $[Fe_2(\mu\text{-}CR^1{:}CR^2{\cdot}CO{\cdot}CR^3{:}CR^4)(CO)_6]$, (II), are among the new bonding schemes found in the chemistry of organoiron complexes. These derivatives may be obtained in more than one isomeric form.[2] The structure determination[3] of (I) showed: (*i*) the ability of acetylenes to undergo cyclopolymerization–insertion reactions; (*ii*) the presence of sp^2 bridging carbon atoms together with σ- and η-bonded carbon atoms to the two iron atoms; (*iii*) different co-ordination polyhedra for the two iron atoms; and (*iv*) the non-linearity of one of the CO groups on Fe^2, suggesting its interaction with Fe^1. Point (*iv*) has been recently developed by Cotton[4] who suggested that such 'semi-bridging' CO groups are effective in promoting charge transfer from an electron-rich metal atom. The structure of (II), previously thought as being simply derived from (I) by the insertion of a ketonic group in the chelate ring, was shown by *X*-ray analysis[5] to be symmetric with a 'cross' ligand and two carbon atoms σ,η-bonded to two different iron atoms, the latter have the same stereochemistry.





The spectroscopic properties of such complexes have been scarcely investigated. Noteworthy is the ^1H n.m.r. spectrum of (Ia; $R^1 = R^2 = R^3 = R^4 = H$); a difference of only 26 Hz was reported for the two different types of H.[6] The great potential of ^{13}C n.m.r. spectroscopy prompted us to undertake a study of these binuclear iron derivatives in order to obtain more information on their electronic structure. A second aim was a variable-temperature study of the carbonyls since one can easily predict fluxional behaviour on the basis both of the structures of the complexes and the results reported for tricarbonyl(diene)iron systems.[7]

EXPERIMENTAL

All the complexes were prepared according to the literature,[8] and purified by t.l.c. with successive elutions; (Ib)—(Id) and (IIa) and (IIb) could not be obtained as pure samples, only as binary mixtures. Spectral assignments were possible, however, except for the carbonyl region.

^{13}C N.m.r. spectra were recorded on a JEOL-PFT100 spectrometer operating at 25.1 MHz in the Fourier-transform mode; the chemical shifts are downfield positive with respect to internal tetramethylsilane. Accumulations of 2 000—10 000 transients were made at a spectral width of 5 000 or 10 000 Hz. The temperature was monitored by a JEOL JNM-DBT-P-5-H100E temperature control unit with the thermocouple *ca.* 1 cm above the sample [outside of the radio-frequency (r.f.) and decoupling coils]. Solutions were sealed *in vacuo* in 10-mm tubes together with 0.05 mol dm^{-3} $[Cr(pd)_3]$ (pd = pentane-2,4-dionate) as an inert relaxation reagent and $SiMe_4$ as an internal standard. The solvents were $CDCl_3$, CD_2Cl_2, and $C_6D_5CD_3$ for intermediate, low, and high temperatures. Deuteriated solvents were purchased from NMR Ltd. and used immediately after drying over molecular sieves.

RESULTS AND DISCUSSION

The ^{13}C n.m.r. data for complexes (I) and (II) are reported in the Tables 1 and 2. The values of ^1J(H–C) for the carbons in the chelate ring were in the range 160—166 Hz, consistent with their sp^2 hybridization.

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Ligand ^{13}C *Chemical Shifts*.—The shifts of the carbon atoms in the chelate ring cycle were widely different (Δ up to 100 p.p.m.), depending on whether the atoms were σ,η-bonded to two metal atoms, C(σ,η), or η-bonded to only metal atom, C(η). In each complex the upfield resonances for the carbon atoms of the chelate ring were assigned to C(η) on the basis of the upfield co-ordination shift observed for the olefin transition-metal complex.[9] The downfield shift for C(σ,η) is consistent with the reported downfield shift for sp^2 carbon atoms σ-bonded to a transition metal.[9] Theory suggests that variations of the chemical shift for a carbon atom are primarily determined by changes in the paramagnetic contribution [10] to the shielding constant. Changes in the

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

electron density, in ΔE, and in Q_{AB} have been discussed in order to account for the downfield shift of sp^2 carbon atoms σ-bonded to a transition metal.[11] We feel that the electron-withdrawing effect of the metal on C(σ,η) is likely to be on the σ system of the chelate ring because changes in the π system are expected to cause variations in the chemical shift of the *para* carbon atom of the phenyl ring, which were not observed with complex (Ih).* Significant also are the shifts of the substituents on C(σ,η) when compared with the shifts of the same substituents on C(η), suggesting an electron deficiency at C(σ,η). These findings are in good agreement with the acidity of the hydroxo-substituent in $[Fe_2(CO)_6\{C_2(OH)_2C_2Me_2\}]$.[12]

TABLE 1

^{13}C Chemical shifts (p.p.m.) ^{a} of the complexes $[Fe_2(CR^1{:}CR^2{\cdot}CR^3{:}CR^4)(CO)_6]$, (I)

	R^1	R^2	R^3	R^4	Fe^1–CO	Fe^2–CO	C^1	C^2	C^3	C^4	Others
a	H	H	H	H			156.6 ^{b}	114.4 ^{b}			
b	H	Me	Me	H	*c*	*c*	153.6 (160)	130.3			R^2 20.2
c	Me	H	Me	H	*c*	*c*	181.1	113.2 (166)	131.6	150.1 (161)	R^1 32.2, R^3 19.6
d	Me	H	H	Me	*c*	*c*	179.0	110.8 (162)			R^1 32.2
e	Bu^t	H	H	Bu^t	211.6(1), 208.9(2) 211.8(1), 209.1(2) ^{d}	216.7(3) 222.2(1), 214.1(2) ^{d}	197.0	109.7 (166)			R^1: C 43.1; Me 33.7
f	Ph	Ph	Ph	Ph	212.3(1), 204.5(2)	216.2(3)	173.8	129.2 ^{e}			R^1 : C^1 148.6; C^2—C^6 132.0—127.1 R^2 : C^1 136.9; C^2—C^6 132.0—127.1
g	Ph	H	H	Ph	210.0(1), 206.4(2)	214.1(3)	176.5	112.6 (165)			R^1 : C^1 149.9; C^3—C^6 128.9; C^3, C^4,C^5 127.7
h	$CH_2{:}CH{\cdot}CH{:}CH_2$		H	Ph	210.5(1), 207.8(1), 206.6(1)	216.5(3)	149.7 ^{f}	*g*	113.6 (166)	171.8	R^1, R^2 131.2—126.4 R^4 : C^1 147.7 ^{f} C^2—C^6 131.2—126.4

^{a} ^1J(H–C) (±5 Hz) values are given in parentheses. ^{b} I. Fiscler, K. Hildenbrand, and E. Koerner von Gustorff, *Angew. Chem. Internat. Edn.*, 1975, **14**, 54. ^{c} See Experimental section. ^{d} At −100 °C. ^{e} Tentative assignment. ^{f} Assignment could be reversed. ^{g} Not assigned.

TABLE 2

^{13}C Chemical shifts (p.p.m.) ^{a} of the complexes $[Fe_2(\mu\text{-}CR^1{:}CR^2{\cdot}CO{\cdot}CR^3{:}CR^4)(CO)_6]$, (II)

	R^1	R^2	R^3	R^4	Fe–CO	CO	C^1	C^2	C^4	C^5	Others
a	H	Me	Me	H	*b*	199.6	171.1 (161)	100.7			R^2 20.8
b	Me	H	Me	H	*b*	200.1 ^{c}	200.9 ^{c}	83.5 (161)	101.4	169.7 (166)	R^1 37.7, R^3 20.2
c	Bu^t	H	Bu^t	H	212.2(1), 210.5(1), 208.6(3), 206.9(1) ^{d}	197.3	216.3	78.2 (166)	123.9	161.9 (161)	R^1 : C 48.0; Me 32.6 R^3 : C 37.1; Me 29.2
d	H	Bu^t	Bu^t	H	209.9(1), 209.5(1), 205.8(1),^{e} 208.4(3) ^{f}	194.2	163.1 (160)	122.3			R^2 : C 37.8; Me 30.5
e	Ph	Ph	Ph	Ph	210.0(1), 206.9(1), 206.3(1),^{e} 207.7(3) ^{g}	195.5 ^{c}	192.4 ^{c}	94.2			R^1 : C^1 148.7; C^2—C^6 130.4—129.0 R^2 : C^1 137.3, C^2—C^6 130.4—129.0

^{a} ^1J(H–C) (±5 Hz) values are given in parentheses. ^{b} See Experimental section. ^{c} Assignment could be reversed. ^{d} At 25 °C. ^{e} At −25 °C. ^{f} At 65 °C. ^{g} At 50 °C.

The effect of the substituent on the shifts of the carbon atoms of the ligand in (I) and in (II) may be understood in terms of changes in the polarity of the π electrons of the double bonds in the chelate ring, according to the effect of the substituents ($\sigma_I + \sigma_R$). The correlation between the shifts and the ability of the substituent to act on the polarity of the π bond has

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* We thank a referee for having brought this point to our attention.

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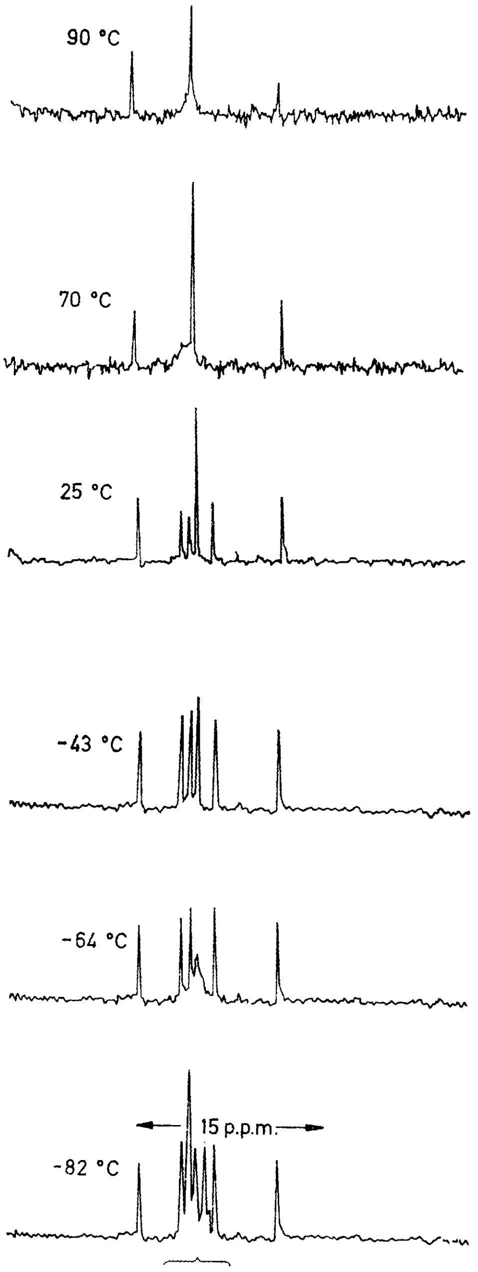
already been shown to be important in the shifts of the carbonyl group in organic derivatives.[13] The above argument is also relevant to the observed concomitant upfield shift of C(η) and downfield shift of C(σ,η) in (II) compared with (I), due to changes in the polarity of the π electrons in the chelate ring on insertion of the ketonic group.



Variable-temperature ^{13}C n.m.r. spectra of the carbonyl region of complex (IIc). The solvents $CDCl_3$, CD_2Cl_2, and $C_6D_5CD_3$ were used

Dynamic Behaviour.—Variable-temperature ^{13}C n.m.r. spectra showed that these iron derivatives are, at least in part, stereochemically non-rigid. The room-temperature spectra of complexes (I) showed a sharp peak of intensity 3 for CO bonded to Fe^2 and two, (Ie)—(Ig), or three resonances, (Ih), for the CO bonded to Fe^1, depending on the position of the substituents in the ligand. On lowering the temperature the low-field signal broadened and eventually split into two peaks (intensities, 1 : 2; T_c −87 °C) for (Ie).* The shift of the apical CO group (222.2 p.p.m.) is at the limit of the range for terminal carbonyl groups, confirming the suggested charge transfer from Fe^1 to this carbonyl[4] and in accordance with the Fe^1–CO bond length observed in similar complexes (2.48 Å).[3] A possible explanation for the exchange of carbonyl groups may be offered by rotation of the $Fe^2(CO)_3$ moiety about the Fe–Fe bond with concomitant bending of the carbonyls. Such rearrangement has been proposed in mononuclear olefin iron carbonyls.[7,14] The high-temperature spectra were unchanged up to 100 °C where decomposition took place. No exchange is therefore occurring at the approximately octahedral Fe^1 or CO scrambling between Fe^1 and Fe^2.

The two broad resonances in the room-temperature spectra of (IId) and (IIe) were resolved into three sharp peaks at −20 °C; increasing the temperature caused these signals to coalesce at 65 (IId) and at 50 °C (IIe). The variable-temperature spectra of complex (IIc) are shown in the Figure. The limiting spectrum showed five resonances (1 : 2 : 1 : 1 : 1): at −64 °C three of these coalesced, the others remaining sharp. We interpret this as caused by CO exchange at one metal atom. The line of intensity 2 is therefore due to a superposition. A second coalescence was observed at 63 °C. Unfortunately the shifts of the carbonyls are such that the still broad unique peak observed may be interpreted as the superposition of the two average peaks of the CO groups of the two $Fe(CO)_3$ moieties (the separation between the calculated peaks is 8 Hz), or as a really unique peak due to CO scrambling between the iron atoms. In recent dynamic ^{13}C n.m.r. studies of binuclear iron olefin complexes it has been shown that intermetal carbonyl exchange does not occur.[15] In any case two, if not three, CO exchange processes are present. If we consider the temperatures at which CO exchange at one metal atom occurs in these complexes, the difference between the energy barrier for this process in (IIc) and those in (IId) and (IIe) is quite remarkable. We feel that steric effects are probably responsible if we ascribe the difference in the energy barriers to the presence of H on one of the C(η) atoms in (IIc) and of large groups on C(η) in (IId) and (IIe).

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* Low solubility prevented recording of the limiting spectra of complexes (If)—(Ih), but significant broadening was observed at −75 °C.

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