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^{13}C NMR SPECTROSCOPY

XI *. 4*H*-INDENEDIIRON PENTACARBONYL COMPLEXES

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Summary

The preparation of 4*H*-indenediiron pentacarbonyl complexes from 1*H*-indenes and diiron enneacarbonyl in hexane solution is described. The structures of the binuclear complexes are based upon spectroscopic analyses, particularly upon ^1H and ^{13}C NMR data. At room temperature the carbonyl groups of the $Fe(CO)_3$ and $Fe(CO)_2$ moieties exhibit very different exchange rates without internuclear scrambling.

It is known that indene [2] and its derivatives [3] form diindenyldiiron tetracarbonyl complexes of type I upon heating for approximately 20 h with $Fe(CO)_5$ at temperatures above 100°C. In order to investigate the possibility of isolating

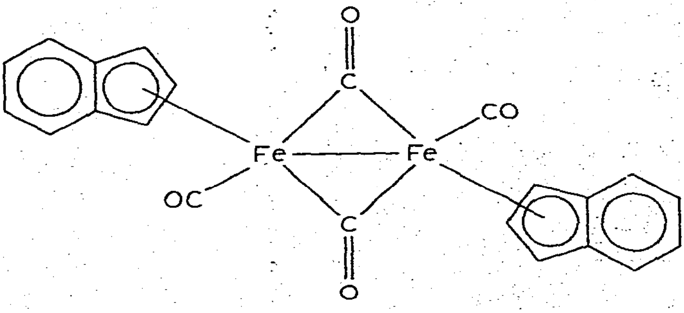

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TABLE 1

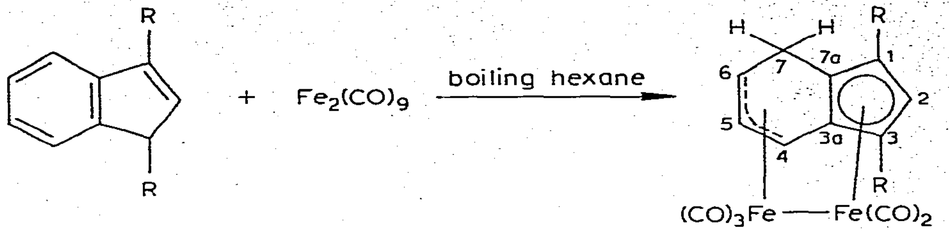
^{1}H NMR DATA FOR IV, V AND VI (100 MHz)

Compound	Chemical shifts δ (ppm) in C_6D_6 [a]							
	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	H(8)
IV	3.06	4.09	3.85	4.13	4.51	2.37	1.37(7a) 0.93(7e)	
V	1.31 [b] 1.18	4.00	[b]	4.14	4.57	2.40	1.22(7a) 0.93(7e)	
VI	2.91	4.20	4.31	3.84	4.44	2.86	5.01	4.77

Compound	Coupling constants J(HH) (±0.1 Hz)														
	1,2	1,3	1,8	2,3	3,4	4,5	4,6	5,6	5,7a	5,7e	6,7a	6,7b	6,7	6,8	7,8	7a,7e
IV	2.7	1.4		2.7	0.7	5.3	1.5	7.0	1.0		2.5	3.8				18.1
V						5.4	1.4	7.1	1.0		2.5	3.8				18.1
VI	2.8	1.7	~0.5	2.8	~0.5	5.8	1.4	8.0					8.0	1.4	10.5	

[a] As compared to $CDCl_3$ solutions [4] IV, V and VI exhibit rather large benzene-induced diamagnetic solvent shifts. [b] Signals of the methyl groups, not assigned.

intermediates or independent species formed under milder conditions indene (II) and its 1,3-dimethyl derivative III were treated with $Fe_2(CO)_9$ in boiling hexane for 3—6 h. Deep red crystalline complexes IV (m.p. 148—150°C; from hexane) * and V (m.p. 134—136°C; from hexane) were isolated from the corresponding indenes, together with minor amounts of the complexes of type I.



(II) R = H
(III) R = CH_3

(IV) R = H
(V) R = CH_3

The structure assignment of IV and V is based on their spectroscopic properties. The mass spectrum (70 eV) of IV shows the parent peak at *m/e* 368 $[C_9H_8Fe_2(CO)_5]$, together with its isotopic satellites of correct intensity ratio, and peaks corresponding to the successive loss of five carbonyl groups. An analogous fragmentation pattern is observed for complex V (parent peak at *m/e* 396 corresponding to $C_{11}H_{12}Fe_2(CO)_5$). The carbon-hydrogen skeleton in the two new complexes follows from a detailed analysis of their ^1H and ^{13}C NMR spectra.

The ^1H NMR spectrum of complex IV (in C_6D_6) ** can be analysed on a first order basis. All assignments were confirmed by double resonance experiments. The results are summarized in Table 1. The resonances of the hydrogens of the five-membered ring in compound IV are particularly indicative. There are three olefinic multiplets (3.06, 3.85 and 4.09 ppm) which exhibit mutual spin coupling below 3 Hz. Thus, H—C(2) (4.09 ppm) is a sharp triplet due to vicinal coupling ($J_{1,2} = J_{2,3} = 2.7$ Hz). None of the three five-membered ring protons is coupled to the methylene protons. Three further olefinic protons are found at 4.51 ppm (H—C(5)), 4.13 ppm (H—C(4)) and 2.37 ppm (H—C(6)). H—C(5) shows vicinal coupling to H—C(4) (5.3 Hz) and H—C(6) (7.0 Hz) and an allylic ^4J coupling to the axial proton at C(7). The methylene protons H_a—C(7) and H_e—C(7) are coupled to H—C(6) with 2.5 and 3.8 Hz, respectively, which proves the location of the methylene group in the six-membered ring. The occurrence of just one allylic $^4J(HH)$ coupling, between H_a—C(7) and H—C(5), indicates non-planarity of the six-membered ring. This result is supported by the different vicinal coupling constants $J_{6,7a}$ and $J_{6,7e}$ on the one hand and $J_{5,4}$ and $J_{5,6}$ on the other hand. The proton spectrum of azulenediiron pentacarbonyl (VI) [5], the structure of which is based on an X-ray analysis [6], reveals essentially the same spin

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* Very recently complex IV (m.p. 135—137°C; from hexane) was also obtained by treatment of *cis*-8,9-dihydroindeneiron tricarbonyl with an excess of $Fe_2(CO)_9$ in boiling xylene [4].

** The chemical shifts in $CDCl_3$ solution correspond to those reported by Deganello and Toniolo [4]; numbering system analogous to [4] and [5].

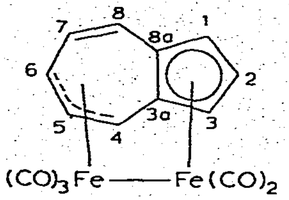
TABLE 2

^{13}C NMR DATA FOR IV, V AND VI IN C_6D_6 (25.2 MHz)

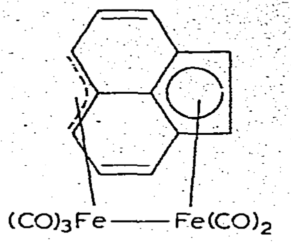
Compound	Chemical shifts δ (ppm)												
	C(1)	C(2)	C(3)	C(3a)	C(4)	C(5)	C(6)	C(7)	C(7a)	C(8)	C(8a)	$Fe(CO)_2$	$Fe(CO)_3$
IV	70.6	78.0	84.2	87.0 [a] 85.8	51.3	79.5	59.8	25.7	[a]			221.3 214.4	217.2
V	84.6 [a] 84.2 83.7 10.8 [b] 10.0	80.0	99.4 [b]	[a]	50.5	78.5	58.4	24.2	[a]				217.7
VI	77.6	81.6	85.8	84.8 [a] 78.3	57.9	80.6	58.2	130.8		118.7	[a]	216.0	

Compound	Coupling constants $^1J(CH)$ (Hz)										
	1	2	3	3a	4	5	6	7	7a	8	8a
IV	178.7	181.2	178.5		173.0	171.6	161.2	127.6 136.0			
VI	178.2	181.2	178.2		167.0	169.6	156.0	159.8		162.5	

[a] Assignments of the quaternary carbon signals were not carried out. [b] Assignments of the methyl carbon signals were not carried out.



(VI)



(VII)

coupling pattern in the cyclopentadienyl and allyl systems. The data for complex V are also consistent with the above analysis (see Table 1).

The proton noise-decoupled ^{13}C NMR spectrum as well as off-resonance decoupling experiments on IV reveal the presence of one methylene group, six =CH carbons and two quaternary carbons in the low-frequency region (Table 2). The carbonyl region exhibits three resonance lines with an approximate intensity ratio of 1 : 3 : 1. $^1J(C,H)$ coupling constants were obtained from the non-decoupled spectrum. The values for the five-membered ring carbons (180 ± 1.5 Hz) are typical for cyclopentadienyl systems π-bonded to transition metals [7] and they correspond closely with the data of the azulene complex VI (Table 2). Smaller $^1J(C,H)$ values ($\approx$170 Hz) have to be expected for a transition metal π-complexed cyclopentadiene system (cf. [8]).

The three line 1 : 3 : 1 pattern of the Fe—CO groups of complex IV remains virtually unchanged in the temperature range between +30 and −50°C (acetone-d_6). Based on the mass-spectrometric information that IV contains five carbonyl groups, which is supported by the relative intensities of the ^{13}C signals, a straightforward interpretation leads to an assignment of the strong line to the carbonyls of the $Fe(CO)_3$ group and of the two weak lines to those of the $Fe(CO)_2$ group. This implies fast exchange of the carbonyl groups in the $Fe(CO)_3$ part, independent of a corresponding process in the $Fe(CO)_2$ group. In the acenaphthylenediiron pentacarbonyl complex VII [9] (X-ray analysis see [10]) the two carbonyl groups of the $Fe(CO)_2$ moiety are equivalent by symmetry of the organic ligand which prevents the observation of separate signals at slow exchange rates. Complex IV enables the demonstration that in this case the two CO groups do undergo a slow exchange. This analysis of the ^{13}C spectrum is in full agreement with the structure of IV.

The close structural relationship between complexes IV, V and VI is further

TABLE 3

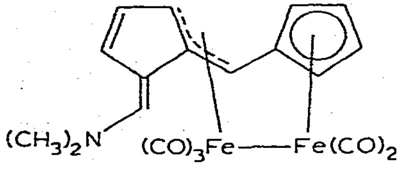
IR DATA FOR THE CARBONYL GROUPS IN IV, V AND VI [a] (HEXANE, cm^{-1})

Compound	IR data		
IV	2038 (2034) [b]	1983 (1988)	1971 (1975)
V	2033	1981	1969
VI	2036	1986	1970

[a] Complex VII, which possesses a plane of symmetry, shows only two carbonyl absorptions ($CHCl_3$) at 2036 and 1984 cm^{-1} [10]. [b] Values in brackets from [4], in CS_2.

demonstrated by their IR spectra. All three complexes exhibit three almost identical absorption bands in the metal—carbonyl region (Table 3).

It should be mentioned that in addition to complexes IV—VII, two further complexes VIII [11] and IX [12] are known with a cyclopentadienyl-allyl moiety bonded to an $Fe_2(CO)_5$ group. The structure of both diiron pentacarbonyl complexes were established by X-ray analysis. Complexes VI—IX may be considered to result, at least formally, from a reorganization of the π-system of the corresponding ligand in the presence of some iron carbonyl moiety. On the other hand, the formation of the 4*H*-indene complexes IV and V from the 1*H*-indenes requires an H-shift from the five-membered to the six-membered ring. At this stage, it is not possible to say how this shift occurs. Complexes of the styrene-iron tri- or tetra-carbonyl type (cf. [13]) may be involved during the rearrangement of the ligand. Deuterium labelling experiments which should reveal the nature of the H-shift are in progress.



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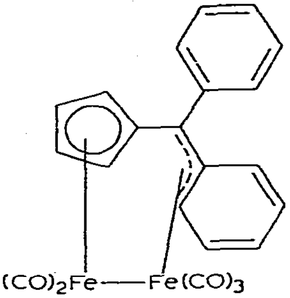

(IX)

Experimental

^1H NMR spectra were measured on an HA-100 spectrometer, ^{13}C NMR spectra on an XL-100-15-FT instrument. Benzene-d_6 with TMS as internal standard was used as solvent. The ^1H NMR spectrum of IV was also recorded in $CDCl_3$ to enable a comparison with the data reported in [4]. IR spectra were recorded on a Perkin—Elmer 457 instrument. Mass spectra were measured on a Dupont-21-491 instrument. The m.p. were measured using a Büchi SMP-15 apparatus.

4H-Indenediiron pentacarbonyl (IV)

A solution of 5.0 g (0.043 mol) indene in 200 ml hexane was refluxed in the presence of 10.0 g (0.0275 mol) diiron enneacarbonyl under nitrogen for 3 h. The solution was cooled, filtered through celite and evaporated under reduced pressure to give a green-brown oil. On cooling the oil to 0°C most of the triiron dodecacarbonyl, formed during the reaction, crystallised out. The remaining oil was chromatographed over 400 g neutral alumina (activity grade II) using 10% ethyl acetate in hexane. The first fraction consisted of 4.5 g non-complexed material, which was not further investigated. A red band was then eluted, which on evaporation of the solvent yielded 0.54 g (3%) of a dark-red solid. A third fraction consisted of 0.12 g of a dark-brown solid (identified by m.p., mass spectra and IR spectra to be compound I [2,14]). The red solid was recrystallised from hexane at —40°C to give dark-red crystals, m.p. 148—150°C, IR (hexane) see Table 3. IR (nujol): 1230m; 1180m; 1035m; 1000w; 955m; 865m; 840s; 810m. NMR. see Tables 1 and 2. Mass spectra (70 eV): 368 (8, M^+); 340 (2, $M^+ - CO$); 312 (31, $M^+ - 2CO$); 284 (16, $M^+ - 3CO$); 256 (6, $M^+ - 4CO$); 228 (100, $M^+ - 5CO$); 172 (15, $M^+ - Fe - 5CO$); 116 (15, $C_9H_8^+$); 115 (20, $C_9H_7^+$). (Analysis found: C, 46.22; H, 2.36. $C_{14}H_8Fe_2O_5$ (calcd.: C, 45.71; H, 2.19%).

1,3-Dimethyl-4H-indenediiron pentacarbonyl (V)

In the same way 5.0 g (0.035 mol) 1,3-dimethylindene afforded 0.82 g (6%) of V as dark red crystals, m.p. 134—136°C, after recrystallisation from hexane. IR (hexane) see Table 3. NMR see Tables 1 and 2. Mass spectra (70 eV): 396 (8, M^+); 368 (1, $M^+ - CO$); 340 (10, $M^+ - 2CO$); 312 (8, $M^+ - 3CO$); 284 (8, $M^+ - 4CO$); 256 (100, $M^+ - 5CO$).

Acknowledgement

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