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(DIETHYL MUCONATE)(1,4-DIAZA-1,3-DIENE)CARBONYLIRON COMPLEXES: SYNTHESES, SPECTRA, AND STRUCTURE DETERMINATION

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Summary

Three examples of a new type of mixed (1,3-diene)(1,4-diaza-1,3-diene)carbonyliron complexes have been prepared. The diene ligand is diethyl muconate, *trans,trans*-$H_5C_2OOC—CH=CH—CH=CH—COOC_2H_5$, and the 1,4-diaza-1,3-diene (DAD) ligands are 2,2'-bipyridyl (BIPY) and the Schiff bases 2-benzoylpyridineanil (BPA) and 2-benzoylpyridine-*p*-methoxyanil (BPpMA). The complexes were made by thermal substitution of one diene ligand of bis(muconate)carbonyliron by the respective DAD ligands, and photochemically from (muconate)tricarbonyliron and DAD by substitution of two CO ligands. The structure of (muconate)(BIPY)Fe(CO) (I) was established by an X-ray analysis (cell data: $a = 9.648(2)$ Å, $b = 11.422(2)$ Å, $c = 19.080(2)$ Å, $\beta = 100.77(2)°$; space group $P2_1/n$, $R = 0.048$). The complex approximates to a square pyramid with one of the BIPY nitrogen atoms occupying the apical position. IR, UV, and mass spectra are reported. The ^1H and ^{13}C NMR spectra reveal the unsymmetrical structure. The complexes II (with BPA) and III (with BPpMA) are mixtures of isomers. The spectral data indicate structures analogous to I.

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Introduction

In recent years a variety of bis(diene)carbonyliron complexes have been prepared and their activity in diene oligomerization investigated [1—3]. It has been shown that the catalytic activity of, e.g., bis(butadiene)carbonyliron [2] can be enhanced and directed towards cyclodimerization by addition of certain n-donating compounds, such as phosphines. Bis(diene)carbonyliron complexes with two identical dienes are conveniently prepared in high yields by low temperature photolysis of pentacarbonyliron in presence of an excess of diene and removal of the evolved carbon monoxide in a stream of inert gas [2]. Complexes with two different diene moieties may be obtained by several methods [2—5]. The most convenient route is from bis(diethyl muconate)carbonyliron, which even at room temperature readily exchanges one of the muconate ligands for a variety of other dienes [5].

Another type of very active iron catalyst for diene cyclodimerization contains nitrogen-containing ligands of the 1,4-diaza-1,3-diene (DAD) type, such as 2,2′-bipyridyl, *o*-phenanthroline [6,7], and Schiff bases [8,9]. They are mostly prepared in situ by reduction of iron salts, e.g., with trialkylaluminium, in the presence of a 1,4-diaza-1,3-diene. Diethyl-bis(2,2′-bipyridyl)iron [6] and the 16 electron complexes $(DAD)_2Fe$ [10] are examples which have been isolated and characterized.

We are interested in the properties and catalytic activities of the hitherto unknown complexes with one diene and one 1,4-diaza-1,3-diene ligand, especially in comparison with the bis(diene)iron compounds mentioned above. We describe below the preparation, spectroscopic data, and structures of the first examples of these mixed (diene)(1,4-diaza-1,3-diene)Fe(CO) complexes, with diethyl muconate as the diene.

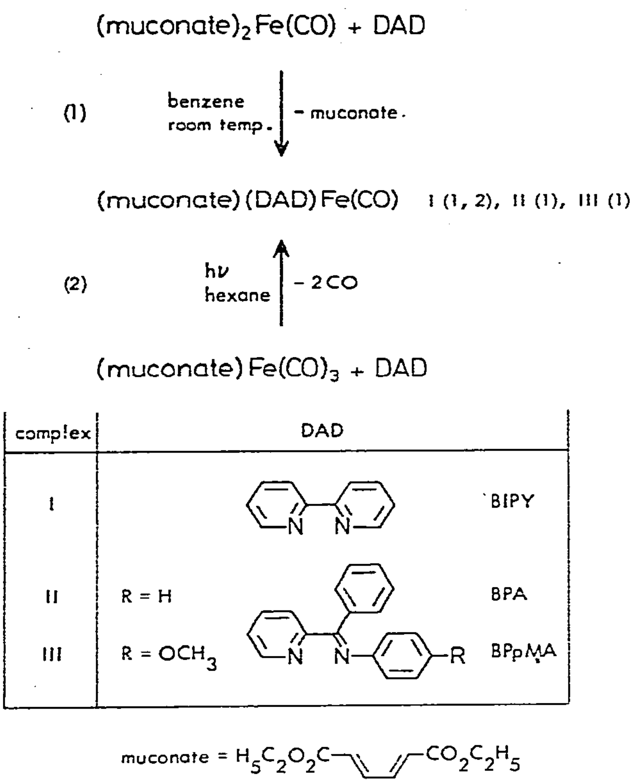
Results

Preparation of the complexes

The complexes I—III have been obtained (1) by thermal exchange of one of the diethyl muconate ligands of $(muconate)_2Fe(CO)$ for a 1,4-diaza-1,3-diene or (2) by photochemical substitution of two carbon monoxide ligands of $(muconate)Fe(CO)_3$ (see Scheme 1).

The photoreaction 2, producing only a gaseous by-product, carbon monoxide, is not as favourable as might at first sight appear. Cleavage of the diene—iron bond, although occurring with a lower quantum yield than CO substitution [11], leads to side reactions, thus reducing the product yields. Moreover, precipitation of insoluble by-products on the immersion lamp cooling jacket may prevent complete conversion of the starting material. In addition, some (muconate)(DAD)Fe(CO) complexes are light sensitive, which disfavours their photochemical preparation. For these reasons the thermal procedure 1 is preferable. The reaction is performed simply by stirring the reactants in degassed benzene at room temperature under argon. Isolation and purification of products is easily achieved by several successive recrystallizations from benzene by addition of hexane.

SCHEME 1



IR spectra

In the infrared spectra of I—III (Table 1) the most intense absorptions are due to the CO stretching vibrations of the carbon monoxide ligands. These bands appear at considerably lower frequencies than those of the bis(diene)carbonyliron complexes [2] as expected for the introduction of an n-donor ligand. On going from I to III the CO bands are shifted to higher frequencies while the ester carbonyl bands show the opposite trend. Spectra were recorded in benzene solution and in nujol or fluorolube suspensions. Solvents normally providing better resolved spectra, such as hexane, could not be used because of the low solubility of the complexes. In benzene all the complexes show one broad unresolved CO stretching band. Ordinate expanded mull spectra reveal two

TABLE 1

IR DATA: CO STRETCHING BANDS OF $(MUCONATE)_2Fe(CO)$ AND I, II AND III (cm^{-1}, in nujol mull)

Compound	$(Muconate)_2Fe(CO)$	I	II	III
CO ligand	2032	1910 1900	1920 1915	1932 1921
Ester CO	1690	1673	1663	1662

bands, which in the case of I are of equal, and in the cases of II and III of unequal intensity. For the two latter compounds this may be attributed to the presence of two isomers due to a positional interchange of the two nonequivalent chelating nitrogen atoms, as confirmed by the ^{1}H NMR spectra of II and III. But since there is no second isomer in I this band splitting may be superficial and caused by a "phase effect" [12].

Electronic spectra

The positions of the observed UV-visible absorption bands are listed in Table 2. Due to the considerable overlapping of numerous bands in the room temperature spectra no assignment is attempted. The band positions are solvent dependent. The hypsochromic shifts observed in going, e.g., from benzene to dimethylsulfoxide, are of the order of 10^3 cm^{-1}.

Mass spectra

With electron impact ionization, no molecular ions are observed in the mass spectra of I—III. I shows peaks corresponding to the loss of CO (*m/e* 410), CO and C_2H_5OH (*m/e* 364), diethyl muconate (*m/e* 240), and to the free ligands (*m/e* 198, 156, 28). Several other peaks (e.g., *m/e* 257 and 213) are probably due to decomposition prior to ionization. The spectra of II and III exhibit corresponding peaks, but indicate increased decomposition. These compounds decompose ca. 60° C below the necessary vaporization temperature of 150° C, whereas I just starts to decompose at that temperature. When the field ionization technique is used, complex I shows a very similar fragmentation pattern, but with clearly recognizable molecular ion. With field desorption ionization the molecular ion is the base peak.

NMR spectra

The ^{1}H NMR spectrum of I (see Fig. 1 and Table 3) exhibits different chemical shifts for all positions which are pairwise identical in the uncoordinated ligands. This indicates an unsymmetrical structure with the two nitrogens of the 2,2′-bipyridyl ligand occupying nonequivalent coordination sites, e.g. the apical and a basal position in a square pyramidal geometry.

The relative assignments (for numbering cf. Fig. 2; protons are numbered according to the adjacent carbon atoms) are based on the double resonance experiments as indicated in Fig. 1. Discrimination between the two halves of the ligands, e.g. H(15) and H(18) of diethyl muconate or H(2) and H(11) of 2,2′-

TABLE 2

UV-VISIBLE BAND POSITIONS [a] OF I—III (10^3 cm^{-1}, in methanol)

Compound	I	II	III
	19.30(sh) 22.60(sh) 29.47 34.44 40.58	17.20(sh) 20.23 31.00(sh) 38.16	20.54 29.06 36.50(sh) 38.24 39.00(sh)

[a] Determined from first derivative spectra; sh = shoulder.

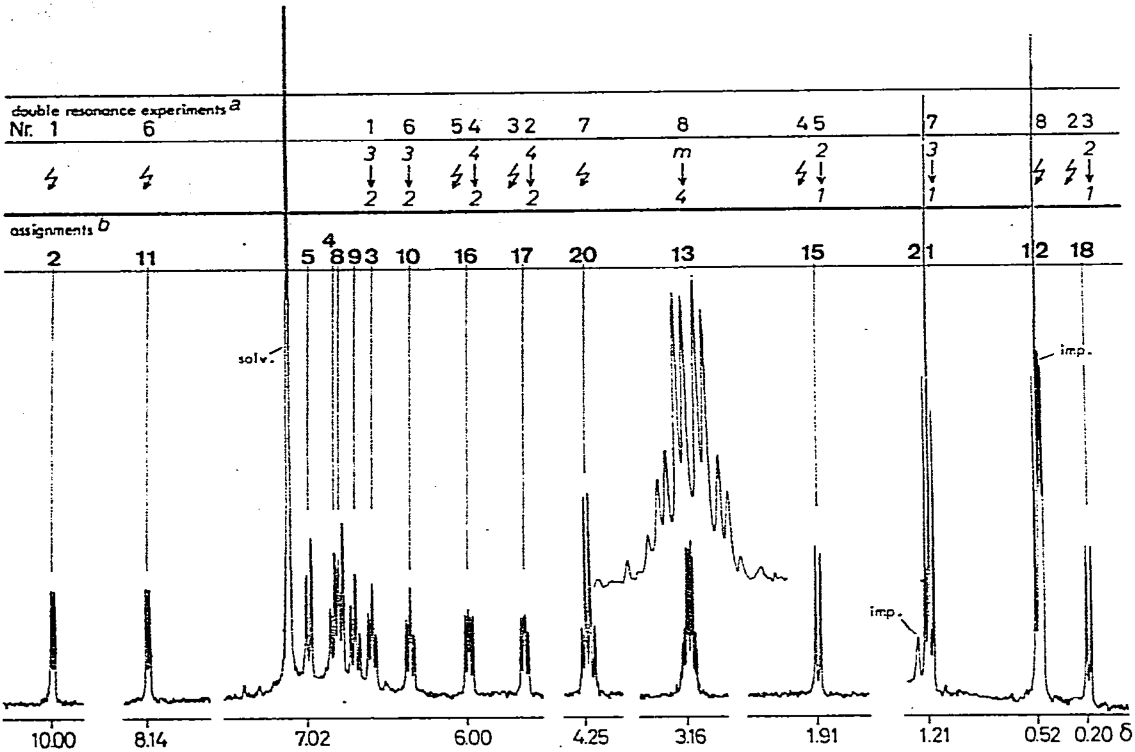


Fig. 1. ^{1}H NMR spectrum of I (in C_6D_6). [a] The numbers correspond to individual double resonance experiments. The flashes indicate the positions of saturation by f_2. The numbers connected by vertical arrows give the change in number of resolved lines observed. [b] For numbering cf. Fig. 2; protons are numbered according to the adjacent carbon atoms.

bipyridyl, is somewhat tentative, and will be discussed after the description of the structure of I.

The ^{13}C NMR spectrum of I again demonstrates the lack of symmetry by exhibiting 21 resonances for the 21 carbon atoms. Chemical shifts from the noise-decoupled spectrum, and the multiplicities and ^{1}H—^{13}C coupling constants from an undecoupled spectrum are listed in Table 4. C(1), C(19), and C(14) are unambiguously assigned to the lowest field resonances. The assignments of C(12), C(21), C(13), C(20), and C(6), C(7) follow from the respective multiplicities. C(2), C(11) should resonate at similar frequencies as C(6), C(7) in *ortho* positions to the nitrogens. The four signals around δ 120 ppm are assigned to the four carbons C(3), C(10), C(5), C(8) in *meta* positions, leaving C(4), C(9) for the nearly identical resonances at δ 135 ppm.

The ^{1}H NMR spectra of II and III (Table 3) indicate the presence of two isomers, A and B, in an approximate ratio of 3 : 1, IIA and IIIA being the major components. The ratio is determined from the integrals of signals which are well resolved, well apart from others and unambiguously assigned, viz. those of the 2-pyridyl protons in the 6-position, those of the diene protons in 1- and 4-positions, and, in the case of III, the methoxy protons. The structures of IIA/IIB and IIIA/IIIB will be discussed below on the basis of the spectral relationships to I.

TABLE 3. ^1H NMR DATA OF I—III AND RELATED COMPOUNDS [a]

Proton [c]	δ (ppm)								
	I	Bipy	L [b]	$LFe(CO)_3$ [d]	$L_2Fe(CO)$ [d]	IIA [e]	IIB [e]	IIIA [e,f]	IIIB [e,g]
H(2)	10.00	8.72					10.01		9.96
H(11)	8.14					8.12		8.09	
H(3)	6.82	6.74							
H(10)	6.88								
H(4)	6.86	7.26							
H(9)	6.73								
H(5)	7.02	8.55							
H(8)	6.82								
H(12)	0.52		0.97	1.00	1.15	0.78	0.65	0.74	0.61
H(21)	1.21					1.07	1.21	1.06	1.17
H(13)	3.16		3.99	3.95	4.10	3.86	2.91	3.85	2.85
H(20)	4.25					4.20	3.44	4.15	3.30
H(15)	1.91		5.87	1.05	0.24	1.97	1.64	1.94	1.61
H(18)	0.20					−0.30	0.45	−0.31	0.38
H(16)	6.00		7.22	5.58	5.90	6.12	buried	6.07	buried
H(17)	5.65					5.90	5.56	5.82	5.60
	$J(H,H)$ [h] (Hz)								
H(15)H(16)	7.8					8.3	8.0	8.4	9.7
H(16)H(17)	4.9								
H(17)H(18)	6.2					7.8	7.8	7.8	8.1
H(12)H(13)	7.0					7.0	7.0	7.0	7.0
H(20)H(21)	7.0					7.0	7.0	7.0	7.0
H(13a)H(13b)	11.0								
H(2)H(3)	5.7						5.0		4.6
H(3)H(4)	6.7								
H(4)H(5)	7.8								
H(10)H(11)	5.4					5.1		5.4	
H(9)H(10)	6.8								
H(8)H(9)	6.2								

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[a] C_6D_6 solution, 10°C. [b] L = diethyl muconate. [c] Numbering according to the adjacent carbon atoms, *cf.* Fig. 2. [d] Taken from [2]. [e] Aromatic protons δ 6.3—7.6 ppm. [f] OCH_3 protons δ 3.16 ppm. [g] OCH_3 protons δ 3.09 ppm. [h] H(3), H(4), H(9), and H(10) exhibit additional splittings of about 1.5 Hz which are not observable, however, at H(2), H(5), H(8), and H(11).

TABLE 4

^{13}C NMR DATA OF I [a]

δ (ppm)	Multiplicity [b]	J [b] (C, H) (Hz)	Assignment [c]
214.5	1	—	C(1)
177.4, 172.1	1, 1	—	C(19), C(14)
157.3, 156.0	1, 1	—	C(6), C(7)
155.9, 154.4	2, 2	186, 186	C(2), C(11)
135.1, 135.0	2, 2	169, 169	C(4), C(9)
124.9, 123.9	2, 2	167, 169	C(3), C(10)
120.8, 119.8	2, 2	163, 163	C(5), C(8)
85.8, 82.3	2, 2	171, 171	C(17), C(16)
58.8, 58.0	3, 3	145, 145	C(13), C(20)
49.2	2	162	C(15)
25.1	2	162	C(18)
14.2, 13.9	4, 4	126, 126	C(12), C(21)

[a] $CDCl_3$ solution. [b] From undecoupled spectrum. [c] See text.

Structure of I

The structure of (diethyl muconate)(2,2'-bipyridyl)carbonyliron (I) has been determined by an X-ray structural analysis. Figure 2 displays a view of the molecule along the plane bisecting the muconate ligand. Selected bond distances and angles are given in Table 5.

There are two possible ways of describing the distorted coordination geometry around the central iron atom. If a trigonal bipyramidal arrangement is assumed, the apical positions are occupied by the carbon monoxide ligand and C(15) of the diene entity [or the midpoint between C(15)—C(16)]. The trigonal plane is then defined by the two nitrogen atoms of 2,2'-bipyridyl and the midpoint between C(17) and C(18). The axial groups, however, deviate considerably from linearity, the angle C(1)—Fe—C(15) being 160.3°

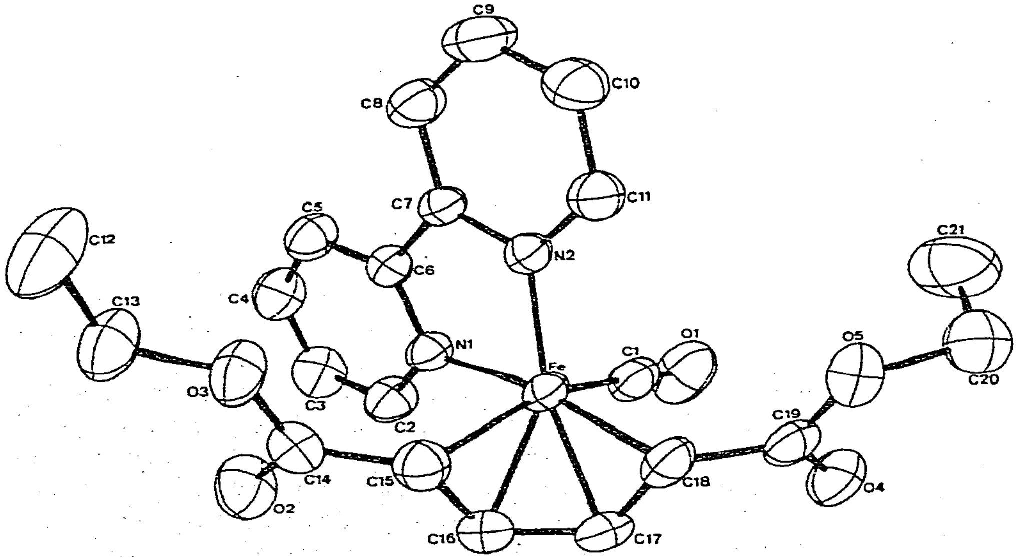


Fig. 2. X-ray molecular structure of (diethyl muconate)(2,2'-bipyridyl)carbonyliron (I).

TABLE 5

SELECTED BOND DISTANCES (Å) AND ANGLES (°) OF I, STANDARD DEVIATIONS IN PARENTHESES

Fe—C(1)	1.750(4)	C(8)—C(9)	1.372(7)
Fe—C(15)	2.133(4)	C(1)—O(1)	1.168(6)
Fe—C(16)	2.029(4)	C(15)—C(14)	1.454(6)
Fe—C(17)	2.020(4)	C(15)—C(16)	1.420(6)
Fe—C(18)	2.096(4)	C(16)—C(17)	1.393(6)
Fe—N(1)	1.977(3)	C(17)—C(18)	1.429(6)
Fe—N(2)	1.979(3)	C(18)—C(19)	1.460(6)
N(1)—C(2)	1.352(6)	C(19)—O(4)	1.220(5)
N(1)—C(6)	1.360(5)	C(19)—O(5)	1.361(5)
C(2)—C(3)	1.370(7)	C(20)—O(5)	1.453(6)
C(3)—C(4)	1.383(8)	C(20)—C(21)	1.498(11)
C(4)—C(5)	1.371(7)	C(14)—O(2)	1.209(5)
C(5)—C(6)	1.394(6)	C(14)—O(3)	1.363(5)
C(6)—C(7)	1.463(5)	C(13)—O(3)	1.462(6)
N(2)—C(7)	1.359(5)	C(13)—C(12)	1.483(9)
N(2)—C(11)	1.345(5)	C(9)—C(10)	1.374(7)
C(7)—C(8)	1.387(5)	C(10)—C(11)	1.379(6)
C(12)—C(13)—O(3)	107.1(5)	Fe—C(18)—C(19)	118.9(3)
C(13)—O(3)—C(14)	115.6(4)	Fe—C(18)—C(17)	66.9(2)
O(3)—C(14)—O(2)	121.9(4)	Fe—C(17)—C(18)	72.6(2)
O(3)—C(14)—C(15)	111.2(4)	Fe—C(17)—C(16)	70.2(2)
O(2)—C(14)—C(15)	126.9(4)	Fe—C(16)—C(17)	69.5(2)
C(14)—C(15)—C(16)	119.4(4)	Fe—C(16)—C(15)	74.1(2)
C(15)—C(16)—C(17)	118.1(4)	Fe—C(15)—C(16)	66.1(2)
C(16)—C(17)—C(18)	118.6(4)	Fe—C(15)—C(14)	119.9(3)
C(17)—C(18)—C(19)	119.1(4)	Fe—C(1)—O(1)	178.1(4)
C(18)—C(19)—O(4)	125.9(4)	Fe—N(1)—C(2)	126.2(3)
C(18)—C(19)—O(5)	111.5(4)	Fe—N(1)—C(6)	115.9(2)
O(4)—C(19)—O(5)	122.5(4)	Fe—N(2)—C(7)	115.5(2)
C(19)—O(5)—C(20)	116.0(4)	Fe—N(2)—C(11)	126.4(3)
O(5)—C(20)—C(21)	109.8(5)	N(1)—Fe—N(2)	80.6(1)
N(1)—C(2)—C(3)	123.2(4)	N(2)—Fe—C(1)	102.6(2)
C(2)—C(3)—C(4)	118.7(5)	N(1)—Fe—C(1)	91.9(2)
C(3)—C(4)—C(5)	119.5(5)	C(1)—Fe—C(18)	94.9(2)
C(4)—C(5)—C(6)	119.3(4)	C(15)—Fe—C(16)	39.8(2)
C(5)—C(6)—C(7)	125.1(4)	C(16)—Fe—C(17)	40.2(2)
C(5)—C(6)—N(1)	121.5(4)	C(17)—Fe—C(18)	40.6(2)
N(1)—C(6)—C(7)	113.4(3)	N(1)—Fe—C(15)	90.4(2)
C(2)—N(1)—C(6)	117.8(3)	N(2)—Fe—C(15)	97.1(1)
C(7)—N(2)—C(11)	118.1(3)	C(15)—Fe—C(1)	160.3(2)
N(2)—C(7)—C(6)	114.2(3)	C(8)—C(9)—C(10)	119.9(4)
N(2)—C(7)—C(8)	121.6(4)	C(9)—C(10)—C(11)	118.6(4)
C(8)—C(7)—C(6)	124.2(3)	C(10)—C(11)—N(2)	122.8(4)
C(7)—C(8)—C(9)	119.1(4)	N(2)—Fe—C(18)	104.3(1)

Distortions are less severe in an assumed square pyramidal configuration. The basal plane in such an arrangement is defined by the terminal carbon atoms C(15) and C(18) of the diene group, C(1) of the carbon monoxide, and the nitrogen atom N(1) of the 2,2'-bipyridyl ligand. The second nitrogen atom N(2) occupies the apical position. This geometry resembles that of (butadiene)tricarbonyliron [13] and of similar compounds, except that two carbonyl groups are replaced by 2,2'-bipyridyl. This ligand is planar within experimental error, with an angle between the best planes through each of the six-membered rings as small as 2.9°. The two Fe—N distances, in despite of the different bonding environments, are identical (1.979 and 1.977 Å). Distances and angles within the 2,2′-bipyridyl ligand are nonexceptional [14].

The planar (±0.008 Å) diene ligand is highly unsymmetrically bonded to the iron, the Fe—C distances ranging from 2.020 to 2.133 Å. The shorter distances are *trans* to the 2,2′-bipyridyl ligand, whereas the longest distance, Fe—C(15), is located opposite the carbon monoxide group. Within the diene entity the bond distances are significantly different. The shortest bond is in the center of the ligand between C(16) and C(17). This indicates a pronounced Fe—C σ-bond character between the terminal carbon atoms and the iron [15], due to the σ-bond stabilizing effect of the 2,2′-bipyridyl ligand [16,17] which may be still enhanced by the electron withdrawing ester groups. This becomes even more evident on comparison with the related carbonylbis(2—5-η^4-methyl sorbate)iron [18] or other bis(diene)carbonyliron complexes [15]. The two carboethoxy groups at the diene 1,4-positions are similar in their geometries. The two planes through the oxygen atoms and the enclosed carbon atom form an angle of 24.99°.

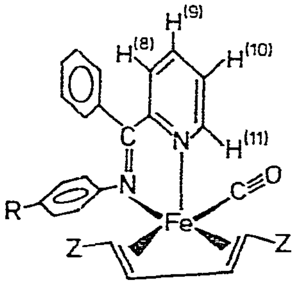
Discussion

Upon replacement of the basal bidentate muconate ligand of bis(diethyl muconate)carbonyliron by 2,2′-bipyridyl the square pyramidal structure is maintained. However, the carbon monoxide moves to a basal position, and the entering 1,4-diaza-1,3-diene ligand occupies the apical and a basal coordination site. An analogous reorganization is also found in some square pyramidal (diene)bis(phosphine)carbonyliron complexes [19,20]. The replacement of one butadiene in bis(butadiene)carbonyliron by the chelating bis(diphenylphosphino)ethane [19] yields a mixture of isomers with basal/basal and apical/basal coordination of the phosphorus atoms. The latter arrangement predominates. In a series of (muconate)$(PR_3)_2Fe(CO)$ complexes [20] the coordination sites occupied by the phosphorus ligands depend strongly on R, changing from basal/basal ($R = OCH_3$) to basal/apical ($R = C_6H_5$) including an example ($R = n\text{-}C_4H_9$) with a temperature dependent equilibrium between the two arrangements. The combination of a strong donor with a good acceptor ligand, such as 2,2′-bipyridyl with muconate, obviously favours apical coordination of one of the donor ligand atoms. While small in number these examples may be revealing with respect to the influence of the electronic donor and acceptor properties of ligands on their geometrical preferences in pentacoordinate transition metal complexes. Rossi and Hoffmann [21] predicted the tendency for donor ligands to prefer a basal site in d^8 complexes of square pyramidal geometry. This may not seem relevant to complexes with a bidentate or two monodentate donor ligands as there is no choice: one of the donors must be basal. Nevertheless, the choice between the apical and another basal position does exist for the second (half of the bidentate) donor ligand. Another degree of freedom, sensitive to electronic (and steric) properties of the ligands, comes into play with unsymmetrical bidentate donor ligands as in II and III. The isomer distribution between structures A and B (vide infra) would be the probe to monitor the influence of varied relative donor strengths of the two different nitrogen atoms. These structural consequences of ligand properties are one aspect of our continued investigation of mixed diene-DAD complexes involving greater variation in diene and DAD ligands.

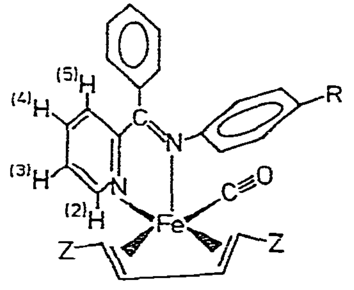
In assigning particular signals in the ^1H NMR spectrum of I (Fig. 1, Table 3) to individual protons, the molecular structure of the complex has to be considered along with the double resonance experiments (Fig. 1) and the comparison with analogous complexes (Table 3 [2]).

The doublets at δ 0.20 and δ 1.91 ppm are associated with the terminal hydrogens of the diene entity. Since the Fe—C(18) distance is shorter than Fe—C(15), H(18) should experience the more effective diamagnetic shielding. Hence, the higher field resonance is assigned to that proton, and consequently the signals at δ 1.91, 5.65, and 6.00 ppm to H(15), H(17), and H(16), respectively. In principle the methylene hydrogens of either ethyl ester group are diastereotopic. However, only the resonance at δ 3.16 ppm exhibits an additional splitting, with 12 of the theoretical 16 lines being observable, whereas the signal at δ 4.25 ppm appears as a normal quartet. Because of the nearness of the basal bipyridyl ring, the C(13)—C(12) ester group is expected to be the more perturbed. This is confirmed by its pronounced shift upfield from normal positions (cf. Table 3), caused by its location right above the center of that pyridyl ring. Hence, the upfield resonances at δ 3.16 and 0.52 ppm are assigned to H(13) and H(12), and those at δ 4.25 and 1.21 ppm to H(20) and H(21), respectively. The relationships between the corresponding CH_2 and CH_3 groups have been confirmed by the double resonance experiments. Assignment of the two low field doublets at δ 10.00 and 8.14 ppm to the *ortho*-protons of the 2,2'-bipyridyl ligand, H(2) and H(11), is in accord with assignments for other 2,2'-bipyridyl-metal complexes [22]. H(2) suffers a pronounced low field coordination shift which must be due to the influence of the close-neighbouring ester carbonyl group C(14)—O(2). The influence of the metal on H(2) and H(11) should be similar because of the nearly identical Fe—N(1) and Fe—N(2) distances. H(3) and H(10) are related to H(2) and H(11) as verified by the double resonance experiments. H(5) and H(8) appear as doublets, and H(4) and H(9) as triplets; the detailed assignments in these cases are somewhat tentative, and are based on the assumption that H(5) and H(4) will resonate at lower field, as do H(2) and H(3).

The ^1H NMR spectra of II and III (Table 3) correlate nicely with that of I and clearly refer to analogous structures. The nitrogen atoms of BPA and BPpMA



A



B

$Z = CO_2C_2H_5$

occupy apical/basal positions in each case. Isomers A and B result from inverted positions of the two nonequivalent nitrogen atoms. The proton in 6-position of the 2-pyridyl ring (H(11) in isomer A, H(2) in isomer B) is the probe to decide which isomer has which nitrogen atom in apical or basal position, respectively. Based on the assignments made for I, the more abundant isomers IIA and IIIA have the pyridyl ring in the apical position, whereas in IIB and IIIB it occupies a basal position.

Experimental

Bis(diethyl muconate)carbonyliron and (diethyl muconate)tricarbonyliron were prepared as previously described [2]. 2,2'-Bipyridyl (Aldrich, analysed reagent) was used as received. 2-Benzoylpyridineanil (m.p. 98—99° C) and 2-benzoylpyridine-*p*-methoxyanil (m.p. 93.5—95° C) were prepared by condensing 2-benzoylpyridine with aniline or *p*-anisidine, and were purified by distillation and recrystallisation from toluene (BPA) or acetone then from ethanol (BPpMA). All solvents (Merck, Darmstadt) used in syntheses and purifications of the iron complexes were refluxed and distilled under argon from lithium aluminium hydride. The complexes were prepared and handled under argon. Elemental analyses were performed by Mikroanalytisches Laboratorium Dornis & Kolbe, Mülheim a.d. Ruhr.

Physical measurements

Spectra were recorded using the following spectrometers: IR, Perkin—Elmer 621; ^{1}H NMR, Bruker WH 270; ^{13}C NMR, Bruker WH 90; UV-visible, Brückl HRS 4001 C; mass spectra, Varian MAT CH-5.

Experimental details for the X-ray structural analysis of I are included in Table 6. The heavy atom position was derived by direct methods, using 210 highest normalized structure factors. Two successive Fourier syntheses revealed

TABLE 6

CRYSTALLOGRAPHIC DATA OF I

$C_{27}H_{22}FeN_2O_5$

mol. weight = 438.23

Crystal habit: red thin plateletts from benzene

a = 9.648(2) Å derived by a least-squares treatment of optimised θ-values of 90 general reflections
b = 11.422(2) Å
c = 19.080(2) Å
β = 100.77(2) °
V = 2065.5 Å^3
Z = 4
D_x = 1.409 g cm^{-3}

Space group: $P2_1/n$, from photographic examination of the crystal.

Nonius-diffractometer CAD-4, equipped with graphite monochromator, λ(Mo-K_α) = 0.71069 Å.

Data collected [a]: 4475 reflections hkl, $\overline{h}kl$, of which 2081 were considered unobserved ($I/\sigma(I) \leqslant 2.0$).

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[a] For details of data collection and computational procedure see [23]. An F_0/F_c list may be obtained on request from the authors (C.K.).

the structure of the rest of the molecule. Isotropic refinement converged at $R = 0.10$, after five cycles of anisotropic full matrix least-squares $R = 0.065$. All hydrogen atoms could be located by a difference Fourier synthesis. They were

TABLE 7

FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS OF I

A. Atom parameters (X10 000) (standard deviations in parentheses)

Atom	x	y	z
Fe	8255(1)	2779(1)	3566(1)
N(1)	7908(3)	3937(2)	4284(1)
N(2)	9673(2)	2244(2)	4391(1)
O(1)	9806(3)	4498(2)	2886(1)
O(2)	4990(2)	2792(2)	4379(1)
O(3)	6324(2)	1337(2)	4943(1)
O(4)	9406(2)	2207(2)	1872(1)
O(5)	10347(3)	672(2)	2548(1)
C(1)	9204(4)	3797(4)	3158(2)
C(2)	6972(4)	4829(3)	4173(2)
C(3)	6717(5)	5553(4)	4707(2)
C(4)	7453(5)	5371(4)	5392(2)
C(5)	8430(4)	4488(4)	5520(2)
C(6)	8644(3)	3776(3)	4957(1)
C(7)	9663(3)	2816(3)	5014(1)
C(8)	10567(4)	2504(4)	5639(2)
C(9)	11507(5)	1608(4)	5624(2)
C(10)	11522(4)	1018(4)	4998(2)
C(11)	10597(4)	1363(4)	4393(2)
C(12)	6370(8)	746(6)	6136(3)
C(13)	5744(6)	1598(5)	5580(2)
C(14)	5854(4)	2031(3)	4366(2)
C(15)	6543(4)	1737(4)	3774(2)
C(16)	6224(4)	2394(3)	3132(2)
C(17)	7086(4)	2249(4)	2629(2)
C(18)	8268(4)	1478(4)	2793(2)
C(19)	9353(4)	1515(4)	2353(2)
C(20)	11551(5)	705(6)	2192(3)
C(21)	12549(7)	1651(8)	2510(4)
H(2)	6432(37)	4889(32)	3679(20)
H(3)	6008(39)	6153(35)	4626(20)
H(4)	7348(37)	5870(34)	5769(20)
H(5)	9040(39)	4381(34)	5986(21)
H(8)	10519(37)	3012(32)	6025(19)
H(9)	12123(38)	1417(34)	6014(20)
H(10)	12148(40)	378(34)	4960(20)
H(11)	10559(37)	981(33)	3950(20)
H(12a)	5909(38)	779(33)	6564(21)
H(12b)	7422(45)	874(42)	6259(23)
H(12c)	6438(50)	−74(41)	6001(24)
H(13a)	6004(43)	2464(38)	5748(23)
H(13b)	4723(46)	1536(37)	5490(21)
H15	6839(33)	978(30)	3771(17)
H16	5448(38)	2969(31)	3069(18)
H17	6991(34)	2681(31)	2192(19)
H18	8156(35)	700(32)	2996(18)
H(20a)	11225(40)	831(37)	1690(23)
H(20b)	11869(48)	−152(42)	2207(24)
H(21a)	12864(45)	1499(38)	3041(25)
H(21b)	13269(75)	2035(54)	2198(32)
H(21c)	13208(72)	1538(69)	2401(39)

included in the four more cycles refinement, which gave a final R-value of 0.048 (R_w = 0.063). Positional and thermal parameters are given in Table 7.

TABLE 7 (continued)

B. Thermal parameters (X1000)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	40	44	24	3	2	−0
N(1)	44	41	33	6	4	1
N(2)	39	46	28	9	5	1
O(1)	110	76	61	−33	25	2
O(2)	61	72	69	30	25	11
O(3)	64	59	44	19	25	6
O(4)	70	79	35	−3	15	4
O(5)	60	65	47	2	20	−4
C(1)	57	60	34	−5	5	−6
C(2)	59	48	45	16	6	3
C(3)	72	51	67	24	20	7
C(4)	75	51	55	6	21	−15
C(5)	63	52	39	8	8	−7
C(6)	39	43	34	0	7	−2
C(7)	39	47	27	8	4	2
C(8)	60	69	32	20	1	−7
C(9)	66	88	39	27	−11	−0
C(10)	58	66	48	29	2	1
C(11)	48	56	38	16	4	−7
C(12)	135	84	53	29	45	11
C(13)	79	79	50	18	32	6
C(14)	37	53	50	−2	11	−0
C(15)	44	44	42	3	8	−1
C(16)	39	59	39	−0	−0	−3
C(17)	47	68	28	−6	−5	−5
C(18)	54	47	30	−10	8	−10
C(19)	50	59	33	−12	2	−19
C(20)	59	93	58	0	19	−4
C(21)	57	147	89	−21	9	13
H(2)	53					
H(3)	62					
H(4)	53					
H(5)	63					
H(8)	54					
H(9)	52					
H(10)	60					
H(11)	56					
H(12a)	59					
H(12b)	79					
H(12c)	88					
H(13a)	76					
H(13b)	70					
H15	27					
H16	51					
H17	44					
H18	40					
H(20a)	66					
H(20b)	90					
H(21a)	76					
H(21b)	128					
H(21c)	89					

Syntheses

(Diethyl muconate)(2,2'-bipyridyl)carbonyliron (I), thermal preparation: 2,2'-Bipyridyl (4.0 g, 26 mmol) was added to a solution of bis(diethyl muconate)-carbonyliron (4.2 g, 8.6 mmol) in benzene (100 ml), and the mixture was stirred at room temperature for 20 h. After evaporation to 40 ml the product was precipitated by addition of hexane (150 ml). The precipitate was separated by inverse filtration under argon pressure. The crude product was dissolved in benzene (200 ml), filtered, and reprecipitated by addition of hexane (150 ml) at —10° C. This procedure was repeated twice to remove free muconate. Yield 2.8 g (80%) I, m.p. 150—155° C (dec.). I analysis, found: C, 57.62; H, 5.01; N, 6.35; Fe, 12.71%; mol. wt. 441 (vaporimetr. in benzene). $C_{21}H_{22}FeN_2O_5$ calcd.: C, 57.55; H, 5.07; N, 6.39; Fe, 12.74%, mol. wt. 438.2.

Photochemical preparation of I: A solution of (diethyl muconate)tricarbonyliron (0.7 g, 2.1 mmol) and 2,2'-bipyridyl (1.0 g, 6.2 mmol) in hexane (70 ml) was irradiated for 3.5 h (Pyrex, immersion lamp apparatus, Philips HPK 125 W lamp). The disappearance of starting tricarbonyliron complex was monitored by IR. The carbon monoxide evolved was removed by bubbling a slow stream of argon through the mixture. Immediately after the irradiation was begun the colour of the solution changed from pale yellow to red, and after 30 min the product began to precipitate at the cooling jacket. After filtration the product was washed several times with hexane. Yield 0.27 g (30 %) I. Analysis, found: C, 57.55; H, 5.06; N, 6.45; Fe, 12.82%; mol. wt. 445 (vaporimetr. in chloroform).

(Diethyl muconate)(2-benzoylpyridineanil)carbonyliron (II): A solution of 2-benzoylpyridineanil (7.8 g, 30 mmol) and bis(diethyl muconate)carbonyliron (3.0 g, 6.2 mmol) in benzene (60 ml) was stirred at room temperature for 6 h. Hexane (100 ml) was added, and the mixture left at —10° C for 10 h. After inverse filtration the precipitate was washed several times with hexane and ether to remove free muconate. For final purification the product was four times dissolved in benzene (50 ml), filtered and reprecipitated by addition of hexane (150 ml) at —10° C. Yield 2.8 g (86%) II, m.p. 86—90° C (dec.). II analysis, found: C, 64.35; H, 5.38; N, 5.14; Fe, 10.42%, mol. wt. 555 (vaporimetr. in benzene). $C_{29}H_{28}FeN_2O_5$ calcd.: C, 64.42; H, 5.18; N, 5.17; Fe, 10.34%; mol. wt. 540.2.

(Diethyl muconate)(2-benzoylpyridine-p-methoxyanil)carbonyliron (III): A solution of 2-benzoylpyridine-*p*-methoxyanil (4.3 g, 15 mmol) and bis(diethyl muconate)carbonyliron (3.0 g, 6.2 mmol) in benzene (60 ml) was stirred at room temperature for 3 h. After filtration and addition of hexane (250 ml) to the filtrate, it was left over night at —10° C. The precipitate was then filtered off and washed with hexane; final purification procedure as for II. Yield 3.0 g (85%) III, m.p. 90—95° C (dec.). III analysis, found: C, 63.30; H, 5.50; N, 4.99; Fe, 10.06%; mol. wt. 578 (vaporimetr. in benzene). $C_{30}H_{30}N_2O_6Fe$ calcd.: C, 63.27; H, 5.30; N, 4.91; Fe, 9.79%; mol. wt. 570.4.

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