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Syn- AND *anti*-SUBSTITUTED (1,3-BUTADIENE)IRON TRICARBONYL COMPOUNDS. SOLID STATE MOLECULAR STRUCTURES

A. IMMIRZI
Istituto di Chimica delle Macromolecole del CNR, via A. Corti 12, 20133 Milano (Italy)

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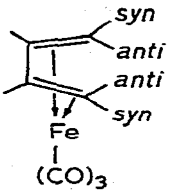
Summary

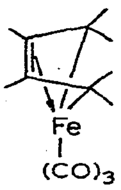
The structures of two diene—iron tricarbonyls having substituents in *syn* and *anti* positions have been determined by X-ray diffraction studies, and provide a reliable model for the parent compound π-butadiene—iron tricarbonyl (which is liquid at room temperature) including hydrogen atom positions. *anti*-H atoms deviate by 30° from the diene plane away from the metal, and *syn*-H atoms deviate by 20° toward the metal.

Introduction

Several (*s*-*cis*-1,3-diene)iron tricarbonyl complexes have been investigated by X-ray diffraction [1—6], electron diffraction [7] and spectroscopic methods [8]. It is well known that unsaturated organic compounds bonded to transition metals exhibit very different geometries and chemical reactivities from those in the free state [9]. In (*s*-*cis*-1,3-diene)$Fe(CO)_3$ compounds the observed structures are in accord with a formulation intermediate between bonding schemes I and II:



(I)



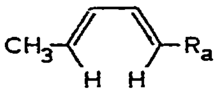
(II)

Mason has suggested [10] that in these compounds the unsaturated ligand is "constrained" in an excited state, *i.e.*, in molecular orbital language, the molecular wave function contains functions representing excited states of the ligand.

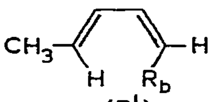
This theory was confirmed by comparing the structure of the coordinated ligand, obtained by X-ray diffraction, with that theoretically calculated for the free excited ligand [11]. When such calculations are not available, the energy of the free ligand in a configuration identical to that observed in the complex may be calculated, *e.g.* by the CNDO method, and compared with the energy of the ground state configuration; the difference between the two calculated energies should be in accord with the UV spectrum [12]. In any case, precise knowledge of the structure of coordinated ligands is desirable.

In the case of coordinated *s-cis*-1,3-dienes, the parent compound $Fe(CO)_3(C_4H_6)$ is a liquid at room temperature and an accurate determination of the structure by X-ray diffraction methods (including location of hydrogen atoms) is impracticable: both low-temperature X-ray diffraction studies [13] and electron diffraction studies [7] gave no definite indication of the hydrogen atom positions. Structural information, however, can be derived from homologous compounds which are solid at room temperature. A great deal of information is available in the literature for the butadiene skeleton, but there is still some uncertainty about the orientation of the substituents. In most reported structures the *s-cis*-diene group is part of a cyclic ligand and in these cases the strain induced by ring closure may cause significant distortion. Moreover, the mutual repulsion of bulky substituents in *anti* positions causes further deviation from the undistorted structure. Hence we believe that a reliable model for the parent compound $Fe(CO)_3(C_4H_6)$ can be obtained only from structures involving acyclic ligands and considering only the hydrogen atom positions.

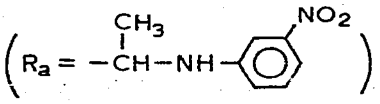
We have undertaken an X-ray diffraction investigation on two (diene)-iron tricarbonyl complexes, A and B, with the ligands A′ and B′ as shown,

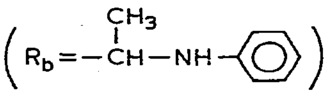


(A')



(B')





mainly to determine which is the *syn* and which the *anti* structure in connection with the study of the reaction of the (*syn, syn*-1,5-dimethylpentadienyl)-iron tricarbonyl cation with amines [14]. In view of the accuracy of the diffraction data and the consequent reliable localization of the hydrogen atoms, we believe it is appropriate to publish detailed structural information.

Results

Crystal data

(A). [2-{(*m*-nitrophenyl)amino}-*trans, trans*-3,5-heptadiene]iron tricarbonyl: $FeC_{16}H_{16}N_2O_5$, mol. wt. 372.17, *a* 11.743(2), *b* 9.755(2), *c* 7.914(1) Å, α 94.66(1), β 89.55(1), γ 109.46(1)°, D_m 1.5 g/cm^3, Z 2, D_c 1.45 g/cm^3, $F(000)$ 384, space group $P\bar{1}$, Mo-K_α radiation, λ 0.71069 Å.

(B). [2-{(phenyl)amino}-*cis, trans*-3,5-heptadiene]iron tricarbonyl:

$FeC_{16}H_{17}NO_3$, mol. wt. 327.17, a 11.789(2), b 14.528(3), c 9.259(2) Å, β 96.61(1)°, D_m 1.4 g/cm^3, Z 4, D_c 1.38 g/cm^3, $F(000)$ 680, space group $P2_1/c$, Mo-K_α radiation, λ 0.71069 Å.

Intensity data, structure determination and refinement

In both cases, single crystals were obtained by slowly cooling n-heptane solutions. Data collection was performed on regularly shaped crystals (of about 0.3 mm in diameter) sealed in glass capillaries.. The intensities of all the independent reflections with $2\theta < 47°$ ($d > 0.89$ Å) were measured by the ω-scan

TABLE 1

ATOMIC COORDINATES

	Complex A			Complex B		
	x/a	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
Fe	0.35130(3)	0.22427(4)	0.01998(4)	0.19354(3)	0.02798(2)	—0.24108(3)
C1	0.34316(25)	0.05181(30)	0.09034(34)	0.05514(18)	0.04472(15)	—0.18702(23)
O1	0.33592(25)	—0.05794(23)	0.13692(31)	—0.03317(14)	0.05920(12)	—0.15186(19)
C2	0.50552(23)	0.29571(28)	—0.03794(35)	0.23696(20)	0.14575(17)	—0.24120(27)
O2	0.60469(17)	0.34228(24)	—0.07249(31)	0.26005(17)	0.22170(12)	—0.24152(26)
C3	0.38532(22)	0.33858(28)	0.21416(33)	0.16236(21)	0.03060(20)	—0.43414(25)
O3	0.41046(20)	0.40991(25)	0.33862(26)	0.14200(20)	0.03317(19)	—0.55701(19)
C4	0.38113(28)	0.10069(37)	—0.36415(37)	0.29869(23)	0.08652(16)	0.8436(26)
C5	0.29448(22)	0.12957(28)	—0.23416(29)	0.26783(17)	0.00833(14)	—0.01932(21)
C6	0.28551(21)	0.26967(28)	—0.20221(29)	0.34186(16)	—0.01784(14)	—0.12176(22)
C7	0.21848(20)	0.29797(25)	—0.06330(27)	0.30659(18)	—0.07993(15)	—0.23372(22)
C8	0.16270(19)	0.18092(24)	0.03732(27)	0.19495(18)	—0.11912(14)	—0.24909(22)
N1	—0.01691(17)	0.21216(21)	0.15969(22)	0.19182(16)	—0.27388(12)	—0.14275(21)
C9	0.10172(20)	0.20365(24)	0.20144(26)	0.14297(18)	—0.18084(14)	—0.14023(23)
C10	0.08825(25)	0.07721(29)	0.31033(32)	0.01509(21)	—0.19043(18)	—0.17748(31)
C11	—0.08277(19)	0.26698(23)	0.27729(26)	0.30467(19)	—0.29428(14)	—0.09552(22)
C12	—0.05306(19)	0.29144(24)	0.44979(27)	0.37005(19)	—0.24281(15)	0.00940(25)
C13	—0.12693(20)	0.33981(24)	0.55872(27)	0.47963(21)	—0.26806(18)	0.06010(28)
C14	—0.22697(23)	0.36833(29)	0.50801(32)	0.52782(22)	—0.34485(21)	0.00673(32)
C15	—0.25482(24)	0.34556(23)	0.33578(33)	0.46432(26)	—0.39720(19)	—0.09690(29)
C16	—0.18439(22)	0.29630(29)	0.22338(29)	0.35362(23)	—0.37356(16)	—0.14744(24)
N2	—0.09360(18)	0.36309(21)	0.74076(23)			
O4	—0.02292(19)	0.30683(24)	0.79067(21)			
O5	—0.13897(17)	0.43606(21)	0.83295(21)			
H4	0.4241(26)	0.0288(32)	—0.3305(37)	0.3517(21)	0.1278(18)	0.0531(27)
H4′	0.4508(26)	0.1908(32)	—0.3843(37)	0.3487(23)	0.0601(19)	0.1772(29)
H4″	0.3344(26)	0.0506(32)	—0.4617(37)	0.2326(22)	0.1160(18)	0.1070(28)
H5	0.2250(20)	0.0445(24)	—0.2108(28)	0.2160(16)	—0.0377(13)	0.0148(20)
H6	0.3319(20)	0.3486(25)	—0.2582(29)	0.4156(15)	0.0168(13)	—0.1228(19)
H7	0.2194(19)	0.3963(23)	—0.0327(26)	0.3572(18)	—0.0883(15)	—0.3022(23)
H8	0.1281(18)	0.0868(22)	—0.0185(25)	0.1664(17)	—0.1406(14)	—0.3428(22)
HN	—0.0221(18)	0.2344(22)	0.0736(26)	0.1569(19)	—0.3069(16)	—0.2120(24)
H9	0.1485(17)	0.2940(21)	0.2628(24)	0.1571(15)	—0.1579(13)	—0.0403(19)
H10	0.1637(23)	0.0784(28)	0.3489(33)	—0.0162(19)	—0.2355(16)	—0.1158(25)
H10′	0.0608(23)	—0.0156(28)	0.2463(33)	—0.0254(21)	—0.1335(18)	—0.1784(26)
H10″	0.0311(24)	0.0705(29)	0.3958(34)	0.0000(23)	—0.2152(18)	—0.2699(28)
H12	0.0166(18)	0.2779(22)	0.4896(26)	0.3395(18)	—0.1911(15)	0.0464(23)
H13				0.5269(21)	—0.2316(18)	0.1373(27)
H14	—0.2762(21)	0.4028(26)	0.5852(30)	0.6011(18)	—0.3585(15)	0.0399(23)
H15	—0.3181(21)	0.3687(25)	0.2951(29)	0.4915(21)	—0.4473(18)	—0.1356(26)
H16	—0.2059(20)	0.2791(25)	0.1147(29)	0.3068(18)	—0.4108(15)	—0.2136(23)

TABLE 2

PRINCIPAL BOND LENGTHS (Å) AND VALENCE ANGLES (°)

Standard deviations for bond lengths are in parentheses. For the valence angles the mean s.d. are 0.12° for angles not involving hydrogen atoms and 0.28° for angles involving one H atom.

Fe—cis-diene group

	A	B		A	B
C4—C5	1.516(4)	1.505(3)	Fe—C7	2.055(2)	2.054(2)
C5—C6	1.407(4)	1.413(3)	Fe—C8	2.117(2)	2.138(2)
C6—C7	1.407(3)	1.401(3)	C5—H5	0.98(2)	0.98(2)
C7—C8	1.417(3)	1.426(3)	C6—H6	0.93(2)	1.00(2)
C8—C9	1.514(3)	1.529(3)	C7—H7	0.97(2)	0.93(2)
Fe—C5	2.156(2)	2.156(2)	C8—H8	0.94(2)	0.95(2)
Fe—C6	2.063(2)	2.068(2)			
C4—C5—C6	121.09	120.58	H6—C6—C5	122.2	118.3
C5—C6—C7	119.47	121.09	H6—C6—C7	117.5	119.9
C6—C7—C8	117.11	121.53	H7—C7—C8	122.5	122.6
C7—C8—C9	121.49	127.14	H7—C7—C6	120.0	115.5
C4—C5—Fe	122.67	123.33	C9—C8—Fe	122.13	123.91
C6—C5—Fe	67.00	67.11	C7—C8—Fe	67.80	66.94
H5—C5—C4	115.4	115.0	H8—C8—C9	113.6	106.4
H5—C5—C6	118.8	119.2	H8—C8—C7	117.9	116.7
H5—C5—Fe	100.8	101.4	H8—C8—Fe	104.3	111.0

Fe—carbonyls

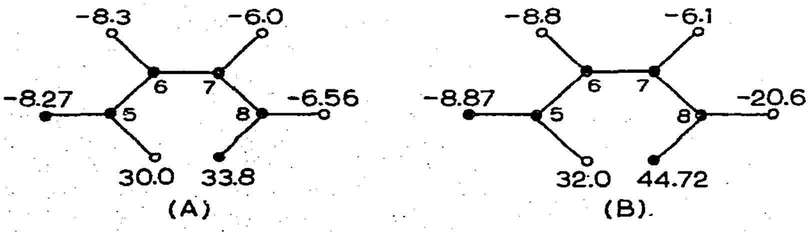
	A	B		A	B
Fe—C1	1.786(2)	1.778(2)	C1—0.1	1.136(3)	1.145(3)
Fe—C2	1.781(2)	1.786(2)	C2—0.2	1.140(3)	1.137(3)
Fe—C3	1.788(2)	1.783(2)	C3—0.3	1.139(3)	1.136(3)
Fe—C1—0.1	178.59	177.27	C1—Fe—C2	101.76	98.14
Fe—C2—0.2	178.95	177.21	C1—Fe—C3	101.54	100.91
Fe—C3—0.3	177.58	179.27	C2—Fe—C3	89.89	90.28

Other C—H and N—H bond lengths

	A	B		A	B
C12—H12	0.93(2)	0.92(2)	C15—H15	0.91(2)	0.89(2)
C13—H13		1.00(2)	C16—H16	0.89(2)	0.95(2)
C14—H14	0.95(2)	0.95(2)	N1 —H.N	0.74(2)	0.87(2)

Angular deviations (°) of the substituents from the cis-diene plane

● = carbon atoms, o = hydrogen atoms; negative values indicate deviation *towards* the metal.



(A) (B).

method on a Philips PW1100 computer-controlled diffractometer with graphite monochromatized Mo-K_α radiation.

In the structure determination and refinement only those reflections with net intensities greater than 3σ were used (σ being the standard error of the net intensity calculated on the basis of count statistics). In both cases the iron atoms were localized by Patterson syntheses and the remaining non-hydrogen atoms by Fourier analyses according to the heavy atom method. Atomic positions and anisotropic thermal vibration parameters were refined by the least squares method with unitary weight factors and using the 9 × 9 block diagonal approximation.

At this point a difference Fourier synthesis revealed, in both cases, all the hydrogen atom positions unambigously. Final refinement of all the atoms, including hydrogen (isotropic), was then performed.

The most significant details of the data collection and refinement are as follows: *Compound A:* 2472 independent reflections measured (those with $l > 0$); 2206 reflections having $I > 3\sigma$ used in the refinement; final R factor 0.026; before introduction of the hydrogen atoms 0.068. *Compound B:* 2341 independent reflections measured (those with $l > 0$ and $k > 0$); 1998 reflections with $I > 3\sigma$ used in the refinement; final R factor 0.024; before introduction of the hydrogen atoms 0.051.

Discussion

The molecular structures are shown in Fig. 1. The structures are projected

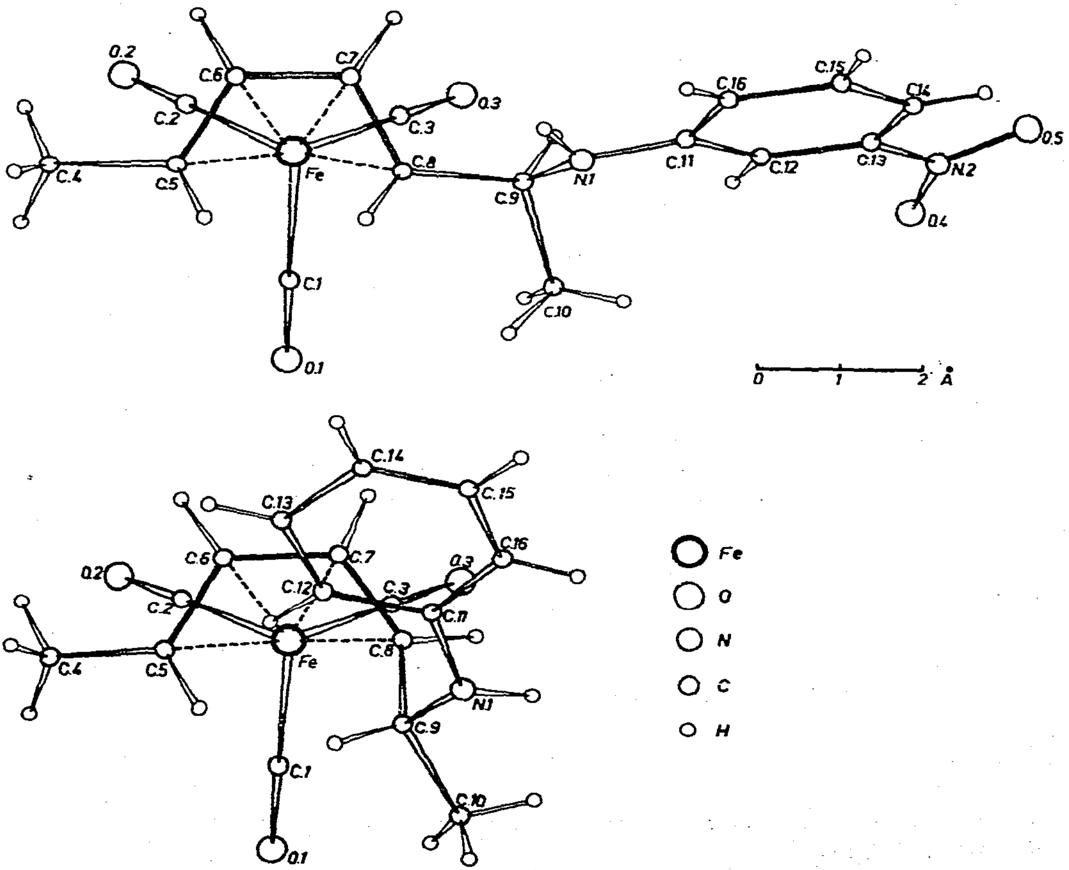


Fig. 1. Molecular models of A (above) and (B) (below) complexes. The structures are projected along the normal to the diene planes.

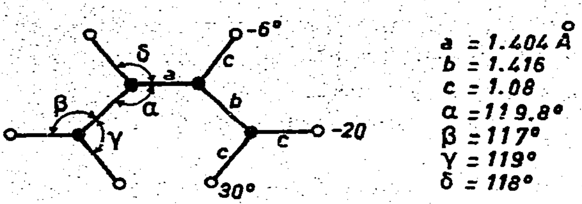


Fig. 2. Proposed model for coordinated butadiene in $Fe(CO)_3(C_4H_6)$ (C_s symmetry).

along the normal to the diene plane in both cases. In both complexes the four carbon atoms of the *cis*-diene group are coplanar within the experimental error (torsion angle for the sequence C5—C6—C7—C8 are —0.24 and 0.069° respectively) and the three bond lengths are essentially equal in both cases.

The substituents attached to the diene moiety are all displaced from the diene plane. The substituents at the inner carbon atoms C6 and C7 and those bonded to the outer carbon atoms C5 and C8 in *syn* positions are displaced *towards* the metal, whereas the outer *anti* substituents are displaced *away* from the metal. For both *syn* and *anti* outer substituents the displacements are clearly dependent on their bulk. Unfortunately we cannot exclude the possibility that the large displacement —20.6° for $H8_{syn}$ in compound B is influenced in part by the large displacement 44.7° of $C9_{anti}$. A study with a ligand of type CH_2=CH—CH=CHR (with both *syn* and *anti* positions occupied by hydrogen atoms, at one side) could give a definite answer to the question. In the actual structures the Fe···$H5_{anti}$ and Fe···$H8_{anti}$ non-bonded distances in complex A, both 2.52 Å, are shorter than Fe···$H8_{syn}$ distance in complex B, 2.61Å indicating that $H.8_{syn}$ atom is not forced over toward the metal.

In conclusion we propose for the butadiene molecule bonded to $Fe(CO)_3$ the model given in Fig. 2 (C_s symmetry).

The reliability of hydrogen atom positions obtained from the least squares refinement may be judged by considering the aromatic H atoms. Although the observed C—H bond lengths are shorter than those obtained by spectroscopic techniques [15] or by neutron diffraction [16], a systematic shortening of this kind is justified by the appreciable difference between the position of the nucleus of a bonded hydrogen atom and the center of gravity of its unique electron [17]. The averaged angular displacement of the nine aromatic H atoms with respect to the expected positions is 2.2° (max 3.6°) and this may be taken as the confidence limit for the deviations of hydrogen atoms in the proposed model.

Acknowledgement

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