Inorg. Chem. **1982**, *21*, 4073–4076

Contribution from the Istituto di Chimica Generale ed Inorganica, Università di Padova, 35100 Padova, Italy,
Istituto di Chimica e Tecnologia dei Radioelementi del CNR, Padova, Italy,
and Istituto di Chimica Generale ed Inorganica, Università di Torino, 10125 Torino, Italy

Theoretical and Spectroscopic Studies of (μ-Butatriene)hexacarbonyldiiron Compounds

GAETANO GRANOZZI,*[1a] MAURIZIO CASARIN,[1b] SILVIO AIME,[1c] and DOMENICO OSELLA[1c]

Received December 29, 1981

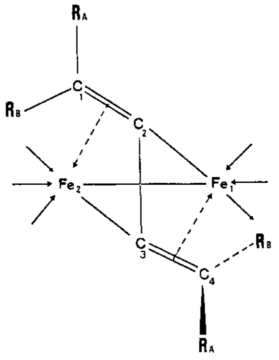
The bonding scheme in (μ-butatriene)hexacarbonyldiiron complexes is discussed on the basis of their ^{13}C NMR and He I excited-gas-phase photoelectron spectra. ^{13}C butatriene resonances have been assigned by using the proton-coupled NMR spectra. At room temperature a single resonance is seen in the carbonyl region, which splits into three resonances at lower temperatures. PE data are analyzed by comparison arguments with related $M_2(CO)_6L$ systems and qualitative quantum-mechanical considerations. CNDO type calculations, which are in qualitative agreement with the proposed assignments, outline the presence of two strong Fe–C bonds accounting for the major $Fe_2(CO)_6$–butatriene interaction.

Introduction

During the last 15 years several stable cumulene diiron complexes have been reported, showing that even less substituted butatrienes, which are not isolable under standard conditions, can be trapped by the $Fe_2(CO)_6$ moiety. They have been synthetized from iron carbonyls according to the following routes: (a) direct reaction of stable cumulenes;[2–4] (b) dehalogenation of unsaturated dihalides;[2,3] (c) dehydroxylation of unsaturated diols.[5]

The EAN formalism requires the interaction of all the six π electrons of the butatriene chain with the two metallic centers and the presence of a direct Fe–Fe bond.

Two crystallographic determinations were reported on [μ-bis(biphenyl-2,2′-ylidene)butatriene]hexacarbonyldiiron[6] and (μ-butatriene)(triphenylphosphine)pentacarbonyldiiron[7] complexes. Both X-ray analyses showed that the butatriene chain assumes a nonlinear configuration (CCC angles: 128–130°), twisted end for end by 80–90°. These structural modifications upon coordination have been related to an optimal overlap of the cumulene π MO's with the iron 3d AO's. The distances in the four-carbon chain are very similar, but, interestingly, Fe_1–C_2 and Fe_1–C_3 distances are quite different (1.94 and 2.04 Å, respectively). On the basis of these structural data two valence-bond descriptions have been postulated.[6,7] In the former (A) the organic chain acts as a *trans*-butadiene, σ bonded via the central carbon atoms and π bonded via the terminal double bonds; in the latter (B) the four-carbon chain is regarded as a bis(η^3-allyl) system.



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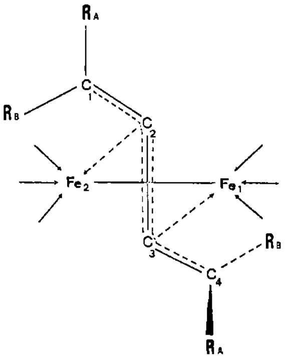

B

Table I. ^{13}C Chemical Shifts (ppm) Measured in the Low-Temperature Limiting Spectra

complex	C_1, C_4	C_2, C_3	R	CO	T_c, °C	$\Delta G^{\ddagger}$, kJ/mol
I	70.4	122.9		214.3, 208.9, 206.6	−24	50.3
II	75.9	120.1	34.5, 26.9	215.9, 211.1, 207.9	−36	47.3

These interesting features prompted us to seek new theoretical and spectroscopic evidence in order to approach a more detailed picture of the bonding system.

We report here ^{13}C NMR and gas-phase UV photoelectron (PE) spectra of the title compound (I, $R_A = R_B = H$; II, $R_A = R_B = CH_3$) together with the results of quantum-mechanical calculations performed following the CNDO[8] scheme.

Experimental Section

$Fe_2(CO)_6(C_4H_4)$ (I) and $Fe_2(CO)_6(C_4Me_4)$ (II) were prepared according to the literature methods.[5] Purity was checked by means of IR and mass spectroscopy. The complexes, dissolved in cyclohexane, were enriched for 4 days in a sealed ampule at +60 °C in the presence of <1 atm of 90%-enriched ^{13}CO. ^{13}C NMR spectra were recorded on a JEOL PS-100 FT NMR spectrometer, operating at 25.1 MHz in the Fourier transform mode. Chemical shifts are reported as downfield positive with respect to $SiMe_4$. The temperature was monitored by a JEOL JNM-DBT-P-5-H-100E temperature-control unit. Solutions of complexes in $CDCl_3$ were sealed in vacuo in 10-mm tubes, with $Cr(acac)_3$ ($\simeq 10^{-3}$ M) added as a shift relaxation agent.

He I excited PE spectra were recorded on a Perkin-Elmer PS-18 spectrometer using a heated inlet probe system at temperatures ranging from 35 to 60 °C with a count rate of about 4000 counts/s. The spectra were calibrated by reference to peaks due to admixed inert gases (Xe, Ar, N_2).

Quantum-mechanical calculations were performed by a version[8] of the CNDO method suitable for compounds containing transition metals. Adopted parameters were taken from ref 9 (for the Fe atoms) or are Pople's standard ones[10] (for the C, H, and O atoms). Geometrical parameters were obtained from the most recent crystallographic determination[7] by assuming a C_2 symmetry axis. The experimental ionization energies (IE's) were connected to the calculated eigenvalues through the Koopmans theorem.[11]

Results and Discussion

NMR Studies. The ^{13}C NMR spectrum of I at +21 °C shows three absorptions respectively at 209.8 (average carbonyl absorption), 122.9, and 70.4 ppm; in the proton-coupled spectrum the two high-field resonances split respectively into

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(1) (a) Università di Padova. (b) Istituto di Chimica e Tecnologia dei Radioelementi del CNR. (c) Università di Torino.

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an apparent doublet (separation 13.4 Hz) and into an apparent triplet (inner separation 166.0 Hz). Since H_A and H_B show different chemical shifts in the ^{1}H NMR spectrum,[2,3] the proton-coupled ^{13}C NMR spectrum of both carbon atoms should appear as the X region of an ABX system. Even if the observed coupling patterns correspond to deceptively simple spectra, they allow an unambiguous assignment of the resonance at 122.9 ppm to C_2 and C_3 and the resonance at 70.4 ppm to C_1 and C_4. On the basis of these observations, the butatriene absorptions are easily assigned also for II (see Table I), where the small changes in the chemical shifts reflect the increased donor ability of the methyl groups.

Although a direct comparison with the ^{13}C NMR data, reported in the literature for η^4-1,3-diene and η^3-allyl mononuclear complexes,[12] shows that the observed behavior of the chemical shifts is more compatible with a bis(η^3-allyl) ligand, we think that a reliable representation of the bonding system in these molecules is not straightforward on the basis of these data.

At +21 °C both compounds show a single absorption in the carbonyl region, which is split into three resonances as the temperature is decreased (see Table I). A dynamic process is then occurring in this range of temperatures, and estimated ΔG^{*} values indicate that the barrier for the CO rearrangement is lower when R = Me by 3 kJ/mol. This effect can be related to an increased electron density on the iron atoms, which in turn causes a labilizing effect for the intramolecular mobility of the carbonyl groups.[13]

The molecular symmetry does not allow us to establish the localized or delocalized nature of the dynamic process observed. We failed to assess it unambiguously by observing ^{57}Fe satellite subspectra as was successfully done for similar cases.[14] It is however likely that the exchange is localized at each metal center since a possible intermediate in the delocalized exchange would involve a high-energy rearrangement of the butatriene chain. Actually, high-temperature spectra (^{1}H and ^{13}C) have shown that the patterns observed at room temperature remain unchanged up to +140 °C.

PE Studies and Quantum-Mechanical Calculations. The He I excited PE spectra of I and II are shown in Figure 1, where the bands are labeled alphabetically.

In the high-IE region (over 13.5 eV) bands E and F, which are present in both spectra, are to be associated with the ionizations from cumulene σ MO's and carbonyl 1π, 5σ, and 4σ MO's. The analysis of this region is not of relevance for the purposes of this paper and will not be considered further. A straightforward assignment of the shoulder E′ in II to the σ CH MO's of the four methyl groups is possible on the basis of (a) the lack of this band in I and (b) the typical IE values of methyl σ MO's (12.5–14.0 eV).

The low-IE region of I (up to 13.5 eV) shows three distinct band envelopes (B, C, D) with two relevant shoulders (A, C′). On going to the methyl-substituted complex II, we detect a general shift of all the bands toward lower IE's. This substitution effect gives rise to different shifts depending on the balance of the inductive and conjugative mechanisms operating in each case.[15] As a consequence, band D splits into two components and the shoulder A is better resolved in II.

Some PE studies on $M_2(CO)_6L$ systems have already been reported (M = Fe, L = S_2, t-C_4H_9NS, (i-$C_3H_7S)_2$;[16] M = Fe, L = B_2H_6;[17] M = Co, L = alkynes[15,18]), showing that the main features are common to all the studied compounds. Actually, their spectra can be analyzed in terms of two regions: a low-IE region corresponding to the ionizations of a "bent" M–M bonding MO and of six 3d "atomlike" MO's (nonbonding) and a higher IE region showing the ionizations of MO's deriving from the mixing between ligand and metal-based orbitals.

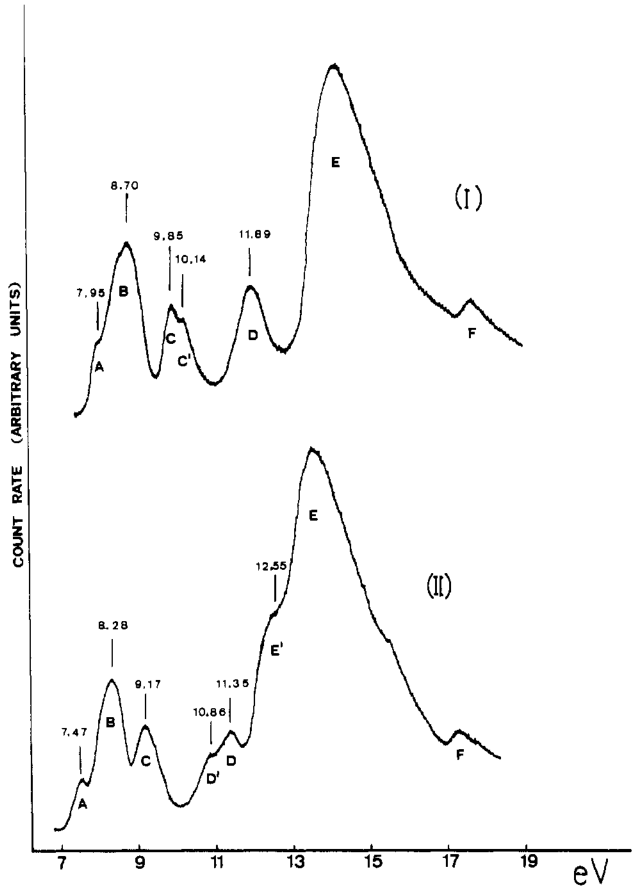

Figure 1. He I excited PE spectra of (μ-butatriene)hexacarbonyldiiron (I) and its tetramethyl derivative (II).

On the basis of these observations the shoulder A in both I and II is to be assigned to the "bent" Fe–Fe bonding MO whereas band B represents six ionizations from the nonbonding 3d MO's. C and D bands (each of them representing two ionizations because of the two components clearly seen in I or in II) are related to the four MO's mainly localized on the butatriene ligand and interacting with the $Fe_2(CO)_6$ moiety.

For some more insight into the bonding system of the title molecules, a first qualitative attempt was to compare this spectral region (C and D bands) with the corresponding ones of related mononuclear systems. Unfortunately, the available data (related to the two isoelectronic (η^4-butadiene)iron tricarbonyl[19] and (η^3-allyl)manganese tetracarbonyl[20] complexes) show a very similar spectral pattern for the two different bonding systems.

A more detailed approach based on quantum-mechanical considerations was then undertaken. A qualitative MO level diagram can be built up by interacting the valence basis set of the $Fe_2(CO)_6$ fragment (as reported by Thorn and Hoffmann[21]) with the valence basis set of a bent butatriene frag-

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Table II. CNDO Results for (μ-Butatriene)hexacarbonyldiiron (I)

		% population					
MO	eigenvalue, eV	$Fe_{1,2}$	$C_{1,4}$	$C_{2,3}$	H	6 × CO	dominant character
25a (HOMO)	−5.54	72	4	1	0	23	"bent" Fe–Fe bond
24a	−7.75	42	16	23	4	15	Fe_1–C_2, Fe_2–C_3 bonding interactions
23b	−8.21	40	27	15	6	12	
23a	−9.23	62	20	3	1	14	3d "iron-like" MO's (nonbonding)
22b	−9.30	75	10	1	0	14	
21b	−9.69	86	2	0	0	12	
22a	−9.70	88	0	0	0	12	
21a	−9.98	84	5	1	0	10	
20b	−10.21	84	1	1	1	13	
20a	−12.31	4	25	40	26	5	ligand-based MO's
19b	−14.07	12	17	14	10	47	

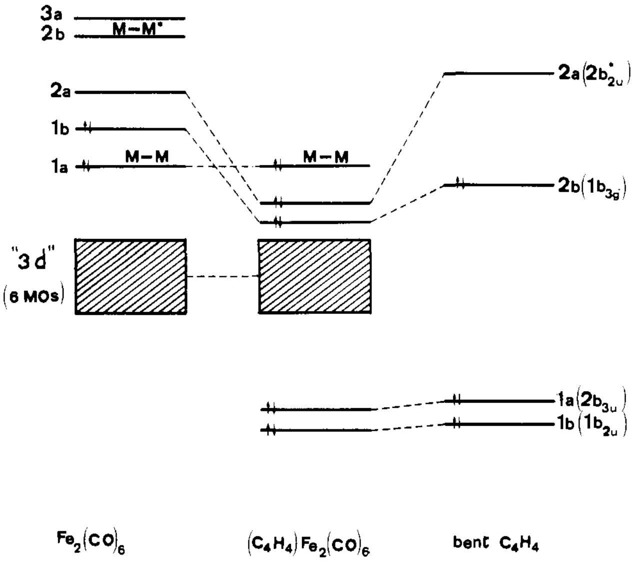

Figure 2. Qualitative energy level diagram for (μ-butatriene)hexacarbonyldiiron and its constitutive fragments (C_2 symmetry point group). The corresponding MO's of the linear butatriene chain are also indicated in parentheses.

ment[22,23] (Figure 2). According to this scheme, the "bent" Fe–Fe bond maintains its HOMO character whereas the interaction between the butatriene ligand and the $Fe_2(CO)_6$ moiety involves mainly the 2b, 2a ligand MO's and the 2a, 1b metallic MO's; this mixing is a consequence of the shape of the relative fragment orbitals,[21,22] which allows good overlapping.

The results of a CNDO type calculation reported in Table II support this view: the 25a HOMO shows a remarkable Fe–Fe bonding character whereas the major $Fe_2(CO)_6$–butatriene bonding character lies in the 24a and 23b MO's. The subsequent six MO's (23a, 22b, 21b, 22a, 21a, 20b) are mainly composed by 3d iron AO's; among them the 23a and 22b MO's show not negligible contributions from $C_{1,4}$ atoms. The inner MO's are mainly localized on the butatriene and carbonyl ligands.

The above considerations lead us to the tentative assignment of band C (and C′) to both 24a and 23b MO's and to relate band D (and D′) to MO's whose metallic contribution is rather scarce. Even if the CNDO IE's calculated within the Koopmans theorem show an unsatisfying agreement with the experimental ones,[24] we think that the analysis of the CNDO eigenvectors can put forward useful indications concerning the bonding mechanism in this molecule. The examination of the 24a and 23b MO's indicates that the major $Fe_2(CO)_6$–butatriene interaction arises from two localized Fe_1–C_2 and Fe_2–C_3 contributions. It is interesting to point out that the C_2 and C_3 atomic contributions to these two MO's look like two lobes pointing directly toward Fe_1 and Fe_2, respectively; it follows that Fe_1–C_3 and Fe_2–C_2 bonding contributions are ruled out in these MO's. The 24a and 23b MO's differ, however, in symmetry properties (symmetric and antisymmetric relative to the C_2 symmetry axis) so that a bonding C_2–C_3 character with the former MO and an antibonding one with the latter is associated.

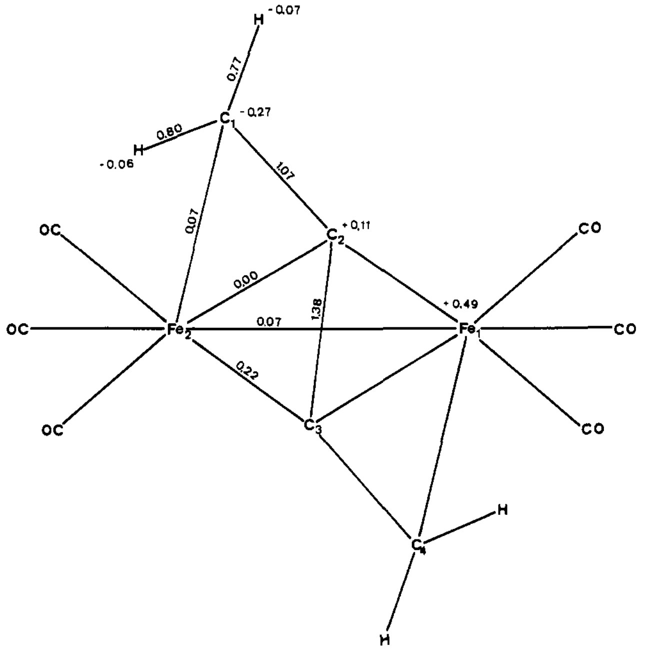

Figure 3. CNDO gross atomic charges and overlap populations of I (in electrons).

In Figure 3 the gross atomic charges and the total overlap populations obtained by the CNDO eigenvectors are reported: the latter parameters can be regarded as a rough estimate of the bonding interactions in this molecule.[25]

This analysis suggests that the main source for the stability of this dimer arises from the two Fe_1–C_2 and Fe_2–C_3 interactions. Furthermore, we note that Fe_1–C_4 shows a larger overlap population with respect to Fe_1–C_3 in spite of the larger

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(25) Even if little significance is attached to the absolute values, the overlap populations can afford a gauge of the relative bond strengths.

bond distance. The smaller electron density of C_2 with respect to C_1 is also an indication of charge donation to the metallic centers via two localized Fe_1–C_2 and Fe_2–C_3 bonds.

Although the body of these results seems to support the A type valence-bond description over the B one, the larger C_2–C_3 overlap population with respect to C_1–C_2 seems to us evidence for the inadequacy of the description of the bonding in terms of the formula A only. It is our opinion that a correct description of the present compounds requires both the A and the B type valence-bond formulas, each of them being too oversimplified, as already suggested by other authors.[6] On the other hand, also the ^{13}C NMR data, which usually furnish very accurate evidence, do not allow us in this case to discriminate with enough confidence between the two formulas.

Registry No. I, 12211-98-2; II, 12212-46-3; Fe, 7439-89-6.

Contribution from the Chemistry Department,
University of Rhode Island, Kingston, Rhode Island 02881

Use of Ligands as Optical Structural Probes. 4. A Solution Kerr Effect Study of Organotin(IV) Tropolonates, Oxinates, and Dibenzoylmethanates

S. K. BRAHMA and W. H. NELSON*

Received March 25, 1982

Molar Kerr constants have been determined for several complexes of the type R_2SnCh_2 (R = methyl, ethyl, or butyl and Ch^- = oxinate, tropolonate, or dibenzoylmethanate) at 25 °C in cyclohexane with use of a 632.8-nm laser source. As expected *cis*-bis(8-quinolinolato)dimethyltin(IV) is strongly negatively birefringent. The other complexes, while polar, are all positively birefringent. Large positive Kerr constants accompanied by nonzero permanent dipole moments in several instances point toward the predominance of distorted trans-type molecules, which in several instances can best be characterized by skew-trapezoidal-bipyramidal structures. Results show that the Kerr effect should be an effective means of determining the structures of complexes of the type R_2SnCh_2 in solution if the ligands Ch^- are planar and highly optically anisotropic.

Introduction

Compounds of the type R_2SnCh_2 have remained objects of considerable interest from the time they were first synthesized.[1-7] This has been true not only because there are a great variety of organic substituents, R, and chelates, Ch^-, that form stable complexes but also because these seemingly simple six-coordinate molecules have some unusual properties. In this paper some of the physical properties will be investigated which are impossible to ascribe to either simple cis or trans isomers.

In several instances there is strong evidence for a regular cis-type geometry in solution. NMR spectra[8] and dipole moments clearly indicate that several complexes of the type X_2SnCh_2 are cis ($X = Cl^-, Br^-, I^-$; Ch^- = β-keto enolate). A Kerr effect study[9] of bis(tropolonato)dimethyltin(IV) has provided additional conclusive evidence for a cis-type structure in solution.

Yet, carefully done Raman studies have strongly demonstrated that many dimethyltin derivatives in solution apparently are trans in solution.[1,2,10,11] There is no doubt that bis(2,4-pentanedionato)dimethyltin(IV) is trans in the solid state.[12] A later infrared study[13] of deuteriomethyl derivatives detected the presence of cis–trans mixtures in carbon disulfide solution. Although some information concerning the mechanism of ligand exchange has been obtained, in the main ^1H NMR studies[14-16] have shown primarily that ligand exchange is very rapid.

Perhaps what has been most difficult to reconcile with the results of the Raman studies has been the very large orientation polarization exhibited by these complexes.[5,14] At first, all of this polarization was attributed to atom polarization,[5] but later studies showed that substantial amounts of orientation polarization[14,17] were exhibited by most of these complexes. Typically permanent dipole moments are fairly large: 2–5 D.

In a recent review Kepert[18] has suggested that many octahedral complexes are of neither a regular cis nor a regular trans geometry but that a related geometry, a skew-trapezoidal bipyramid, should be considered. There is evidence for such structures in the solid state,[19-21] but until now there was no practical means of confirming the presence of such structures in solutions of labile complexes.

In this paper, it will be demonstrated that, by using the Kerr effect, one can distinguish cis, trans, and skew-trapezoidal-bipyramidal structures. Several tin complexes will be assigned a skew-trapezoidal-bipyramidal structure while others will be

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