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THE REACTION OF DIIRON NONACARBONYL WITH *cis*-BICYCLO-[6.2.0]DECA-2,4,6-TRIENE

F. A. COTTON* and G. DEGANELLO**
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (*U.S.A.*)

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SUMMARY

The reaction of diiron nonacarbonyl with *cis*-bicyclo[6.2.0]deca-2,4,6-triene in ether at room temperature produces several products which are separable by chromatography on alumina. Compound (A), $C_{10}H_{12}Fe_2(CO)_6$, obtained in 23% yield, is shown by PMR and IR spectra to have the Fe–Fe bonded $Fe_2(CO)_6$ group attached to the triene portion of the starting bicyclotriene. Compound (B), $C_{10}H_{12}Fe(CO)_3$, obtained both from the initial reaction and by heating (A) in refluxing toluene, is the $Fe(CO)_3$ adduct of tricyclo[4.4.0.0^{2,5}]deca-7,9-diene, a molecule which has not been isolated in the free state. Compound (C), also obtained on pyrolysis of (A) in minute yield, has not yet been characterized. Compound (D), $C_{10}H_{12}Fe_2(CO)_6$, from the original reaction, in small yield, appears to have separate $Fe(CO)_3$ groups bonded to the olefinic portions of a $C_{10}H_{12}$ monocycle, but spectral data alone do not allow a complete specification of the structure.

INTRODUCTION

The work reported here began as an attempt to extend previous studies[1–10] of systems in which the $Fe_2(CO)_6$ or $Ru_2(CO)_6$ groups are bonded to cyclic, conjugated trienes. With cyclooctatriene and cyclooctatetraene, fluxional molecules of the type (I) are obtained[4,5]. These molecules have a skew structure which lacks any element of symmetry, but the appearance of their high-temperature PMR spectra is consistent with the presence of a plane of symmetry. This has been attributed[4] to the rapid intramolecular interconversion of the two enantiomorphous structures of the types shown, and low-temperature PMR spectra support this concept[6,7].

However, several complexes, (II), (III), which do not have temperature-dependent PMR spectra have also been reported[3,8–10]. An X-ray crystallographic study[8] of (II) has shown that it has a transverse orientation of the $Fe_2(CO)_6$ group (IV) which engenders a permanent or static plane of symmetry passing through the

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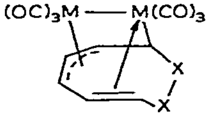
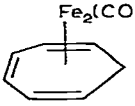
* Address correspondence to this author at the Department of Chemistry, The Texas A and M University, College Station, Texas 77843.

** On leave from Centro di Chimica e Tecnologia dei Composti Metallorganici degli Elementi di Transizione del C.N.R., Bologna, Italy.

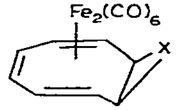
CH_2 group and bisecting the Fe–Fe bond. It is not yet known whether (IIIa) and (IIIb) also have transverse structures. It has been pointed out[8] that the confirmation of a transverse structure in (II) raises a difficult question about what factors determine the relative stabilities of the skew and transverse structures. A corollary question is whether the interconversion of the enantiomers in the case of the skew structures takes place by a small shift across the time-average mirror plane or by a rather large rotation which passes through the transverse configuration.



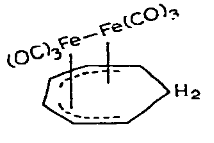
(Ia) M=Fe, X–X=HC=CH
(Ib) M=Fe, X–X=H_2C—CH_2
(Ic) M=Ru, X–X=HC=CH



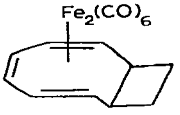
(II)



(IIIa) X=O (ref.9)
(IIIb) X=CH_2(ref.10)



(IV)



(V)

In order to examine the problem further we undertook to prepare (V) and examine its dynamic and structural properties. The chemical and spectroscopic aspects of the work are reported here. Several other interesting compounds which were obtained are also described here.

EXPERIMENTAL

The preparation and all handling of the compounds were carried out in an atmosphere of nitrogen. Infrared spectra were recorded on a Perkin–Elmer model 337 spectrometer. The PMR spectra were measured with Hitachi–Perkin–Elmer R-20B, Varian HA-100 and T-60 spectrometers. Mass spectra were measured by Mr. C. M. Lukehart with a Hitachi–Perkin–Elmer RMU-6D spectrometer. Melting points are uncorrected. Elemental analyses were carried out by Spang Microanalytical Laboratories, Ann Arbor, Michigan, and Meade Microanalytical Laboratories, Amherst, Mass.

cis-Bicyclo[6.2.0]deca-2,4,6-triene, $C_{10}H_{12}$, was prepared by reaction of the lithium salt of $C_8H_8^{2-}$ with 1,2-dibromoethane in liquid ammonia, as described by Staley and Henry[11].

Reaction of $C_{10}H_{12}$ with $Fe_2(CO)_9$

To a solution of *cis*-bicyclo[6.2.0]deca-2,4,6-triene (5.28 g, 40 mmole) in 250 ml of anhydrous ether was added diiron nonacarbonyl (36 g, 99 mmole). The mixture was stirred at room temperature for 90 h. After filtration the red-brown solution was evaporated using a vacuum line. The oily residue was extracted with hexane (3 × 15 ml) and chromatographed on an alumina (Woelm, activity 2) column (4.5 × 85 cm).

Elution with hexane gave a small, pale yellow band (1) containing about 200 mg of starting ligand, followed by a large yellow band (2), while an orange band (3), (4) remained at the top of the column. After removal of bands (1) and (2) with pure hexane, elution was continued using hexane/ether (2/1); this caused bands (3) and (4) to separate, the narrow yellow band (3) moving ahead of the large orange band (4).

Compound (A), $C_{10}H_{12}Fe_2(CO)_6$. The orange solution of band (4) was evaporated to give a red-orange solid. This was sublimed at 75°/0.1 mm and then crystallized from hexane, to afford red-orange crystals,m.p. 110° in 23% yield (3.75 g, 9.1 mmole). The mass spectrum has a very weak parent ion peak at *m/e* 412. The IR spectrum (in cyclohexane) has five strong CO stretching bands at 2063, 2013, 1992, 1978, 1961 cm^{-1}. The PMR spectrum in C_6D_6 has multiplets centered at the following τ values: 6.35 (2 H), 6.77 (2 H), 8.15 (8 H). A spectrum with much less overlapping was obtained in carbon disulfide and is displayed in Fig. 1. The multiplets are centered at τ values of 5.6 (2 H), 6.18 (2 H), 7.48 (2 H), 7.83 (2 H) and 7.98 (4 H). This spectrum showed no evidence of line broadening to temperatures as low as −75°. (Found: C, 46.7; H, 3.01; Fe, 27.3. $C_{16}H_{12}Fe_2O_6$ calcd.: C, 46.64; H, 2.93; Fe, 27.11%.)

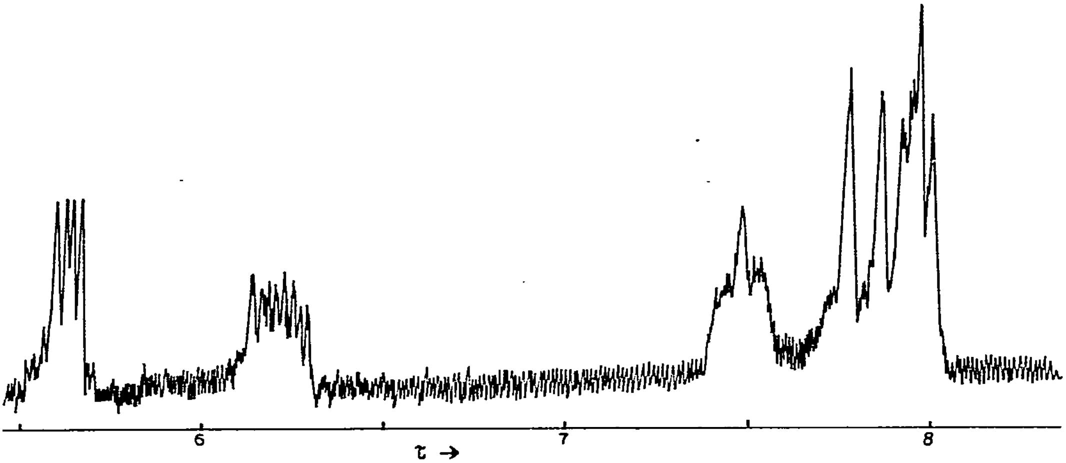


Fig. 1. The PMR spectrum (100 MHz) of $C_{10}H_{12}Fe_2(CO)_6$ (A) in CS_2 solution.

Compound (B), $C_{10}H_{12}Fe(CO)_3$. *Thermolysis of compound (A)*. Compound (A) (0.824 g, 2.00 mmole) was dissolved in 15 ml of dry toluene and the solution was refluxed with efficient stirring for 26 h. The resulting brown mixture was filtered and the filtrate evaporated. The solid residue was extracted with 2 × 5 ml of hexane/ether (1/1) and chromatographed on an alumina (Woelm, activity 2) column (2 × 20 cm). Elution with hexane gave a yellow band while a small brown band remained at the top of the column. The yellow solution was evaporated to give an oily yellow solid which was crystallized from hexane at −78°, as pale yellow crystals, m.p. 64–66% (0.216 g, 0.8 mmole; yield 40%). The IR spectrum (cyclohexane) has strong CO bands at 2042, 1981, 1974 cm^{-1}. The PMR spectrum in C_6D_6 is shown in Fig. 2. The multiplets are centered at τ values of: 5.28 (2 H), 7.03 (2 H), 7.73 (2 H), 8.02 (2 H) and 8.48 (4 H). (Found: C, 57.2; H, 4.5; Fe, 20.6. $C_{13}H_{12}FeO_3$ calcd.: C, 57.35; H, 4.41; Fe, 20.58%.)

The brown band was eluted with hexane/ether (1/1) and on evaporation a few red-black crystals of compound (C) were obtained. The IR spectrum of this substance

(CS_2) has strong bands at 1979, 1935, 1668 cm^{-1}. The quantity obtained did not allow further characterization.

Compound (B), $C_{10}H_{12}Fe(CO)_3$. Isolation from chromatography band (2). The solution of band (2) of the initial chromatogram was evaporated under reduced pressure to give an orange-yellow oil (3.61 g), which has a very complex PMR spectrum and is obviously a complex mixture. Compound (B) can be separated from this mixture by the following procedure. About 0.5 g of the oil was dissolved in 5 ml of hexane and chromatographed on an alumina (Woelm, activity 2) column (2 × 20 cm). A single broad yellow band developed on elution with hexane. This was collected in two fractions and the leading fraction was rechromatographed. The first half of the

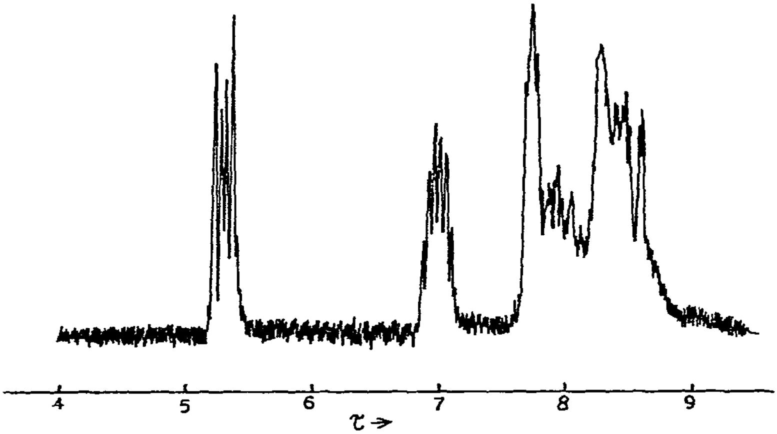


Fig. 2. The PMR spectrum (60 MHz) of $C_{10}H_{12}Fe(CO)_3$ (B) in C_6D_6 solution.

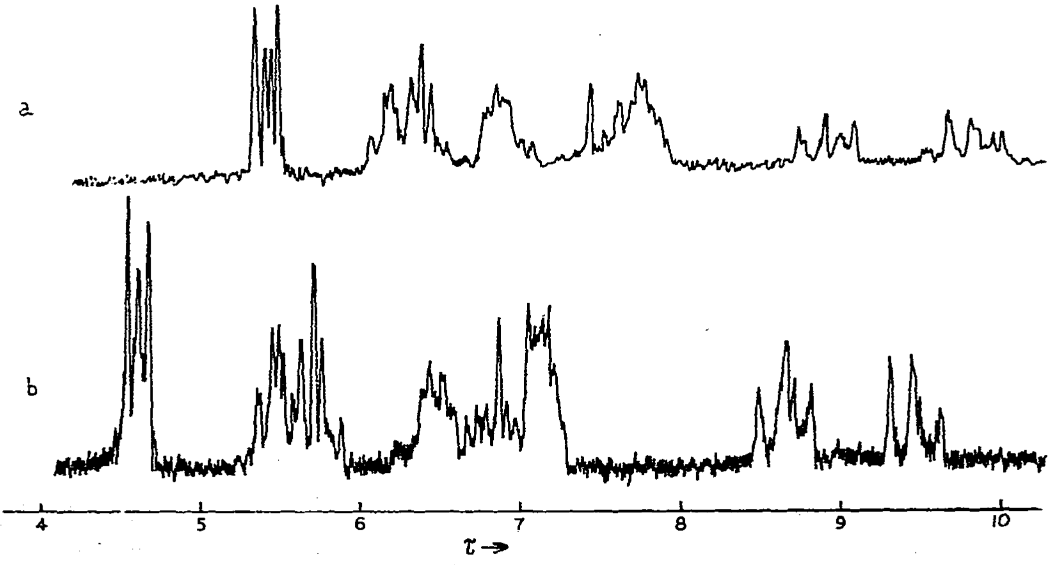


Fig. 3. The PMR spectra (60 MHz) of $C_{10}H_{12}Fe_2(CO)_6$ (D); (a) in C_6D_6 solution, (b) in CS_2 solution.

yellow band which this gave was evaporated in high vacuum to give a waxy yellow solid, which was then crystallized twice from hexane at −78°. Pale yellow crystals of (B) (0.110 g), identified by m.p., IR and PMR, were obtained.

The remaining portions of the rechromatographed material were combined and evaporated. Again a yellow oil was obtained which still had a very complex PMR spectrum. Absorptions from τ 4 to τ 6 and from τ 7 to τ 9 were in an intensity ratio of 1/3.0. No other components of this oil have yet been separated or identified.

Compound (D), $C_{10}H_{12}Fe_2(CO)_6$. The solution of band (3) of the initial chromatogram was evaporated to give a yellow solid, contaminated by some orange solid [compound (A)]. Crystallization from hexane followed by sublimation at 70°/0.1 mm gave pale yellow crystals, m.p. 105°, in 4.3% yield (0.710 g, 1.7 mmole). The mass spectrum has a parent ion peak at *m/e* 412. The IR spectrum in cyclohexane has strong CO stretching bands at 2056, 2043, 1992, 1986, 1979, 1974 cm^{-1}. The PMR spectra in CS_2 and C_6D_6 are shown in Fig. 3. The multiplets are centered at the following τ values: CS_2: 4.60 (2 H), 5.61 (3 H), 6.38 (2 H), 6.78 (1 H), 7.15 (2 H), 8.66 (1 H), 9.50 (1 H); C_6D_6: 5.47 (2 H), 6.35 (3 H), 6.95 (2 H), 7.75 (3 H), 8.99 (1 H), 9.95 (1 H). (Found: C, 46.7; H, 3.10; Fe, 27.2. $C_{16}H_{12}Fe_2O_6$ calcd.: C, 46.64; H, 2.93; Fe, 27.11%.)

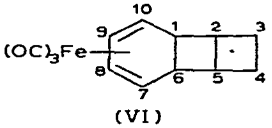
DISCUSSION

Compound (A)

This appears certainly to be the desired substance (V), according to the analytical and spectroscopic data. The presence of five strong, terminal-CO stretching bands in the infrared spectrum is consistent with (in fact, exactly what is expected for) a sawhorse (C_{2v}) $(OC)_3Fe{-}Fe(CO)_3$ group. The PMR spectrum, Fig. 1, indicates that there is a molecular plane of symmetry, and the absence of any line broadening to temperatures as low as −75° suggests that the molecule is not fluxional, but, rather, that it has a structure with a static symmetry plane. The alternative, that the molecule is fluxional with an activation energy so low that the motion is not detectably slowed even at −75°, seems unlikely although it cannot be positively ruled out. An X-ray crystallographic study of this compound is in progress.

Compound (B)

This compound can be assigned the structure shown diagrammatically as (VI) on the basis of analysis and spectroscopic properties. The systematic name for this compound is therefore 7,8,9,10-*tetrahapto*-(tricyclo[4.4.0.$0^{2,5}$]deca-7,9-diene)tricarbonyliron. The analysis and IR spectrum show clearly that there is one trigonal $Fe(CO)_3$ group, whose symmetry is perturbed enough to induce a small splitting of the doubly degenerate CO stretching mode. The observations are very similar to those made on a number of compounds in which the $Fe(CO)_3$ group is bound to a 1,3-



(VI)

butadiene moiety, as, for example, in $C_8H_8Fe(CO)_3$[12,13].

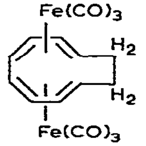
The PMR spectrum, Fig. 2, of compound (B) can be assigned without difficulty to structure (VI), whereas we cannot suggest any other satisfactory alternative. The multiplets at τ 5.28 and τ 7.03 are virtually stereotypic for a 1,3-butadiene moiety bound to an $Fe(CO)_3$ or $Ru(CO)_3$ group. The remaining, upfield signals have credible positions, shapes and relative intensities to be assigned to the bridgehead (τ 7.60–8.13) and methylene (τ 8.14–8.33) protons of structure (VI). There appears to be only negligible coupling between the H(1,6) and the H(7,10) protons. We cannot, of course, determine which multiplet is due to which set. From this we infer that the 6-ring and the external 4-ring are fused to the central 4-ring in an *anti* relationship. An X-ray crystallographic study of this substance has been undertaken to establish this and other structural details with certainty.

The formation of compound (B) is remarkable since the tricyclic olefin which it contains is not, by itself, known, although it has been postulated as an intermediate in the photochemical reaction of benzene with cyclobutene[14]. The normal, thermal rearrangement of bicyclo[6.2.0]deca-2,4,6-triene is to *trans*-bicyclo[4.4.0]deca-2,4,7-triene and then, upon further heating, to bicyclo[4.4.0]deca-3,5,7-triene[15]. We have here an example of the ability of the $Fe(CO)_3$ moiety to stabilize an otherwise unstable hydrocarbon isomer by virtue of its marked affinity for the *cis*-1,3-butadiene moiety.

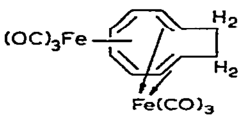
Characterization of compound (C) has been impeded by lack of sufficient quantities of material. From the IR spectrum it appears that it must contain either a bridging CO group or an acyl carbonyl group.

Compound (D)

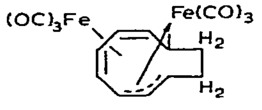
On the spectral evidence at hand we cannot propose a single specific structure for this compound, but some general possibilities may be evaluated. The IR spectrum is indicative of the presence of two similar but non-equivalent $Fe(CO)_3$ groups each in an environment which slightly splits the degeneracy of the nominally *e*-type CO stretching mode. The PMR spectrum has multiplets indicative of the presence of one butadiene moiety bound to an $Fe(CO)_3$ group. The remainder of the spectrum is too complex for us to venture any detailed interpretation. If it is assumed that no hydrogen migration has occurred and that two $Fe(CO)_3$ groups are present, one attached to a 1,3-diene moiety, the three structures shown diagrammatically as (VII)–(IX) seem to be the most likely possibilities.



(VII)



(VIII)



(IX)

Structure (VII) is disfavored by being too regular or symmetrical. The two $Fe(CO)_3$ groups might well be equivalent, or so nearly equivalent, that the appearance of two sets of $Fe(CO)_3$ bands in the IR would not be expected. In addition, with only two equivalent or nearly equivalent butadiene–$Fe(CO)_3$ groups plus aliphatic protons, it is not clear that this structure can account for the PMR spectrum. Structure (VIII) is consistent with the IR spectrum, but it is not clear that it can account for the complex pattern of upfield resonances in the PMR. Structure (IX) is perhaps best able to account for the PMR spectrum, but it is uncertain whether it is consistent with the close similarity of the two sets of $Fe(CO)_3$ IR bands or whether it is sterically feasible. Thus, we feel that only by X-ray crystallography can the structure of compound (D) be convincingly established, and such an investigation will be undertaken.

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