ethyl ether solution containing 3.96 g (44 mmol) of *t*-butyl hydroperoxide. Stirring was continued at −80° for an additional hour. No gas was evolved until the temperature was allowed to rise to −75°, when evolution of oxygen began and did not stop until the temperature reached −65°. No additional evolution of gas took place above −65°, and the temperature was allowed to rise to +5°. A vpc and an infrared investigation of the products formed in this reaction revealed the presence of *t*-butyl alcohol, acetic acid, iodobenzene, ethyl acetate, traces of unreacted *t*-butyl hydroperoxide, and an appreciable amount of a substituted *t*-butyl peroxide, the vpc and infrared spectrum of which were different from those of di-*t*-butyl peroxide.

In order to isolate this peroxide, the ether solution was shaken with 5% potassium hydroxide solution, dried with magnesium sulfate, and filtered. The ether was then removed by distillation, the residue fractionated under reduced pressure, and the fraction boiling at 34–34.5° (7 mm) collected and analyzed; n^{11}D 1.3977.

Anal. Calcd for $C_8H_{18}O_3$: C, 59.25; H, 11.11; (O), 9.88 Found: C, 59.40; H, 11.20; (O), 10.20, 9.68 (HI method at 60°).

This peroxide has a characteristic odor and fails to react with KI solution in acetic acid. Even HI gives low values at room temperature. It gives a single peak on the vapor phase chromatogram with retention time of 27 min as compared to that of *t*-butyl hydroperoxide of 24 min at 60° with helium pressure on the column at 18 psi. The infrared spectrum showed the following bands in cm^{-1}: 2980 vs, 2925 s, 2900 s, 2870 ms, 1475 ms, 1455 ms, 1440 ms, 1375 s, 1360 vs, 1340 w, 1320 m, 1255 w, 1240 m, 1195 vs, 1160 m, 1150 vs broad, 1075 s, 1040 m, 1025 w, 940 s, 925 w, 895 vw, 865 vs, 840 w, and 750 w.

Synthesis of α-*t*-Butylperoxyethyl Ether. Since it was suspected that if one hydrogen atom had been abstracted from ethyl ether by the *t*-butoxy radical, the resulting ethyl ether radical would trap the *t*-butylperoxy radicals to form α-*t*-butylperoxyethylether. It was necessary therefore to synthesize this peroxide by an independent route and show that its properties are identical with those of the peroxide obtained in our free-radical reaction.

The synthesis was accomplished by the following procedure. Acetaldehyde diethyl acetal (8.1 g, 0.05 mol) was mixed with 4.5 g (0.05 mol) of *t*-butyl hydroperoxide. To this mixture was then added three drops of methanesulfonic acid. The reaction became exothermic and had to be cooled with ice. After 3 hr at 0°, the reaction mixture was extracted with three 20-ml portions of ethyl ether. The combined ethyl ether extracts were shaken with 20 ml of 5% potassium hydroxide solution, dried with magnesium sulfate, and filtered. The ether was removed by distillation, the residue fractionated under reduced pressure, and the fraction boiling at 35° (8 mm) collected and analyzed; yield 3.4 g (43%); n^{19}D 1.3976.

Anal. Calcd for $C_8H_{18}O_3$: (O), 9.88. Found: (O), 9.80 (HI method at 60°).

The vpc and infrared spectra of this peroxide were identical with those of α-*t*-butylperoxyethyl ether isolated from our free-radical reaction. This peroxide has also been synthesized in low yields by Rieche and Bischoff[19] using a somewhat different procedure than the one given above.

In experiment 8 the reaction of iodosobenzene diacetate (11 mmol) with *t*-butyl hydroperoxide (22 mmol) at −80° in ethyl ether was carried out in the same way as the experiment described above except that the reaction was kept at −80° for 2 hr before it was allowed to warm up to −75° and both the oxygen evolved and the liquid products formed, with the exception of acetic acid, were determined quantitatively; the results are listed in Table III.

In experiment 9 the reaction of *t*-butyl hydroperoxide (22 mmol) with iodosobenzene (11 mmol) suspended in ethyl ether at −80° was carried out in the same manner as in experiment 8. The gaseous and liquid products, with the exception of water which was detected in the vapor phase chromatogram and by the copper sulfate test, were determined quantitatively; the results are listed in Table III.

Acknowledgment. The authors wish to thank Dr. Nagy for the combustion analyses, Dr. Paul G. Arapakos for assistance in some preliminary experiments, and the Industrial Fund of the Institute for financial support of this investigation.

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Communications to the Editor

Oligomerization Catalysts. II. Spectroscopic Examination of Bis(cyclooctatetraene)iron

Sir:

A new type of valence tautomerism, characterized by simultaneous intra- and internuclear electronic and conformational rearrangements, has been found in bis(cyclooctatetraene)iron, $(COT)_2Fe^0$ (**1**).

This complex, recently described by us,[1] selectively catalyzes the oligomerization of butadiene and the codimerization of butadiene and ethylene to *cis*-1,4-hexadiene. Now we report the first results of spectroscopic examinations, which confirm the assigned structure and elucidate both the conformation of the COT rings and the type of their bonding to iron.

On the basis of our first results,[1] we had excluded for both COT rings the tub conformation, characteristic of $(COT)Ni^0$, as well as the planar conformation of a dianion, found in $(COT)_3Ti_2^{II}$. Moreover, on the basis of a supposed rare gas configuration of the iron, which requires the donation of ten π electrons from the COT rings to the iron, one might expect that the two ligands are differently coordinated to the metal.

The nmr spectrum at room temperature showed only one single peak, indicating equivalence of all protons. In order to reveal a supposed temperature-dependent valence tautomerism, we carried out a nmr examination at various temperatures. The spectra were run (Varian HA, 100 Mc) between −10 and −84° (TMS internal standard), using deuterated toluene as solvent (Figure 1). The spectrum at −10° still exhibits one peak at τ 5.00. Down to −35° this signal broadens and, below the coalescence temperature (between −35 and −45°), it begins to split off. At −84° we observe four signals at τ 4.60, 4.91, 5.42, and 5.50. (The doublet at τ 5.46 and 5.55 (J = 9 cps) is centered at τ 5.50.) The relative intensities of the four signals are 1:5:1:1. Spin-decoupling experiments were carried out at all the above positions and at τ 5.02. A decoupling was observed only by irradiating at this last position: the τ 4.60 signal (presumably a multiplet) sharpens markedly and the τ 5.50 doublet becomes a singlet (Figure 1). This proves that the τ 4.91 signal is composite and results from the superposition of a

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[1] A. Carbonaro, A. Greco, and G. Dall'Asta, *Tetrahedron Lett.*, **22**, 2037 (1967).

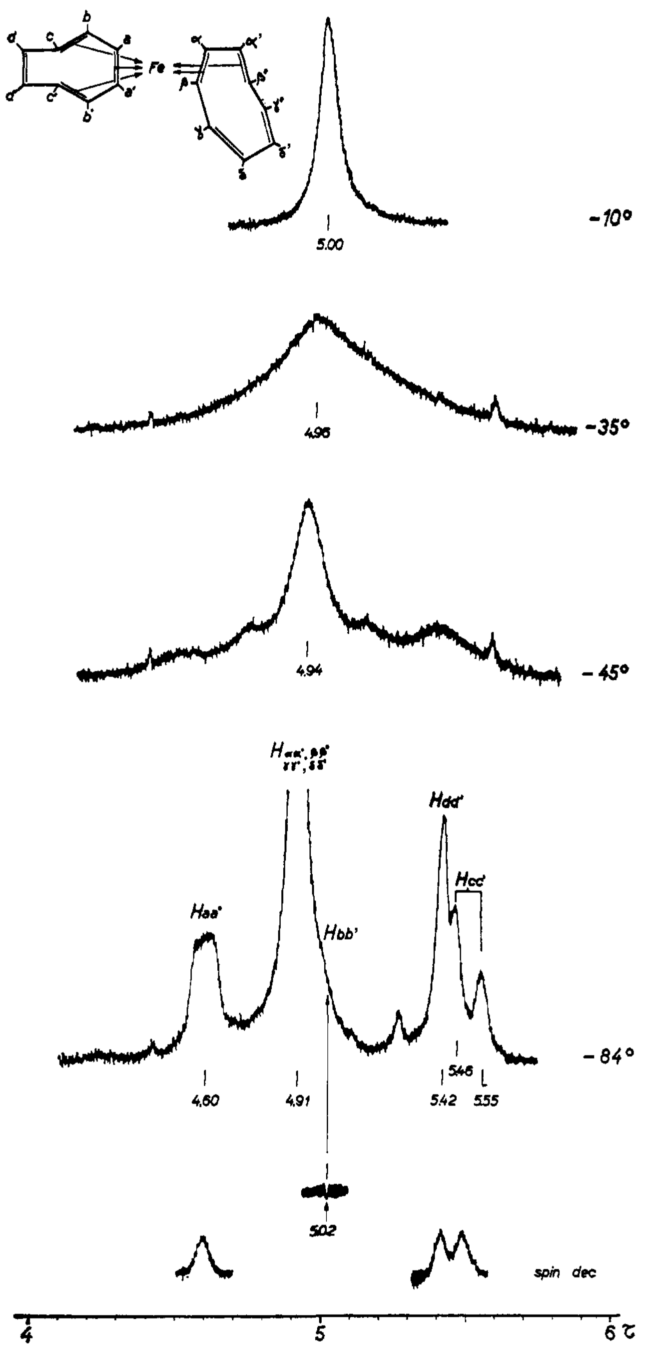

Figure 1. Nmr spectra of $(COT)_2Fe$ in deuterated toluene at various temperatures (°C) and spin-decoupling spectrum obtained by irradiating at −84° with τ 5.02 radiation (Varian HA 100 Mc).

strong signal on a smaller one (at τ 5.02). On the basis of the shape of the composite peak and of analogies with other COT–metal complexes, we tentatively attribute to this last signal a relative intensity of 1. Thus, the relative intensities of the five signals should be 1:(4 + 1):1:1.

These findings are in agreement with the hypothesis that two different COT rings are contained in **1**, one of them (A) "frozen" at −84° to a stable conformation with localized bonds and unequivalent protons (four signals having the same intensity), and the other (B) retaining the equivalence of all protons (unresolved signal at τ 4.91) due to valence tautomerism even at −84°.

Splitting of the sole nmr peak into four signals with lowering of the temperature was observed by the Winstein group[2] and by King[3] in $(COT)M(CO)_3$ complexes (M = Cr, Mo, or W). On the basis of nmr and X-ray studies,[2,4] $(COT)Mo(CO)_3$ contains in the "frozen" state a COT ring having three double bonds coordinated to Mo and one uncoordinated double bond. An analogous structure was attributed to the Cr and W complexes. The COT ring of $(COT)M(CO)_3$ complexes, where M = Fe or Ru, on the contrary, has two conjugated double bonds coordinated to the metal and two uncomplexed conjugated double bonds.[2,5–7] This structure is confirmed for $(COT)Fe(CO)_3$ by X-ray studies.[8] The two types of complexes greatly differ in the coalescence temperature: for the complexes containing a tricoordinated COT ring it is much higher than for those containing a bicoordinated COT ring, which freezes at −120° or even below. Admitting the presence of both types of COT rings in **1**, that frozen at −84° should hence be the tricoordinated.

The presence of one tricoordinated and of one bicoordinated COT ring in **1** is in agreement with the postulate of a rare gas configuration of the iron, as also suggested by ir evidence (Perkin-Elmer 125 spectrophotometer, mulls in Nujol and hexachlorobutadiene, 3100–2800- and 2000–400-cm^{-1} ranges). A C=C stretching band at 1662 cm^{-1} indicates one uncoordinated *cis*-double bond (A ring). A band at 1527 cm^{-1}, characterized by rather low intensity and strong lowering of the frequency compared with free COT, is attributable to stretching vibration of two uncomplexed conjugated double bonds (B ring), in analogy to $(COT)Fe(CO)_3$.[9] The bands at 1468 and 1437 cm^{-1} are attributed to C⩦C stretching of two coordinated conjugated double bonds (B ring). In the 600–900-cm^{-1} region some bands are associated with COT ring modes and others with out-of-plane deformations of the hydrogen atoms adjacent to the double bonds.

On the basis of our experimental evidence and considering the analogies with known COT–metal complexes, we propose for **1** in solution at −84° the structure given in Scheme I with a "frozen" tricoordinated (A) ring. The equivalence of all protons of the B ring between the coalescence temperature and −84° can be explained by postulating an intranuclear double-bond rearrangement. Scheme I illustrates schematically two of the eight possible equivalent conformations. The rearrangement of one of the eight configurations into another likely takes place, according to recent literature,[10] through 1,2 shift. It was not possible to carry out nmr measurements at lower temperatures at which the B ring also could be frozen with consequent splitting of the main signal too.

A correlation between the four nmr signals of the

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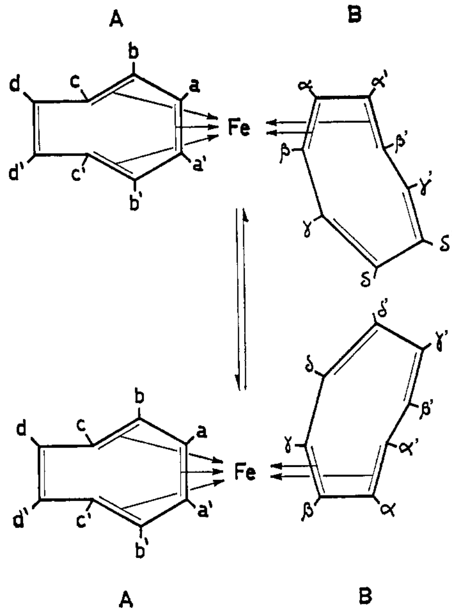
Scheme I



same intensity and the four pairs of protons of this ring can be made on the basis of the above spin-decoupling experiments. The decoupling of two pairs of protons observed when irradiating the signal at τ 5.02 suggests that this signal be attributed to the most coupled protons, *i.e.*, to $H_{b,b'}$. The signal at τ 5.42, which remains unchanged in this case, should be due to the protons having minimum interaction with $H_{b,b'}$, and hence to $H_{d,d'}$. With regard to the two signals at τ 4.60 and 5.50 the multiplet structure of the former induces us to attribute it to $H_{a,a'}$ and the latter to $H_{c,c'}$.

The uv spectrum of **1** (Unicam SP.800, room temperature, cyclohexane solution, 210–700-nm range) shows one broad absorption at 295 nm (log ϵ 3.2) and a flat one at 343 nm (log ϵ 3.1).

The assigned structure has been confirmed by the X-ray study of **1** carried out by Allegra, *et al.*, of the Politecnico of Milan in collaboration with our laboratory. Preliminary results are reported in this issue.[11] In the crystalline state the molecules in general position contain one COT ring that is tri- and one that is 1,3-bicoordinated to the iron. Unlike the situation in solution at −84°, the latter ring is also frozen, presenting localized bonds and fixed conformations.

A third situation is that existing in solution down to −35°. In this case, in addition to the cited intranuclear bond rearrangement in the B ring, the equivalence of all protons implies a steady internuclear rearrangement, which transforms the tricoordinated ring to a 1,3-bicoordinated one and *vice versa*, with consequent interconversion of the conformation of the two rings and interchange of all bonds.

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The Crystal Structure of Bis(cyclooctatetraene)iron

Sir:

In connection with the studies carried out in our laboratory on the structure of organometallic complexes containing transition metals and unsaturated ligands,[1-4] we performed the three-dimensional structural analysis of bis(cyclooctatetraene)iron(0).[5,6]

The complex crystallizes in the monoclinic system; the unit cell parameters are a = 25.13 ± 0.09, b = 10.68 ± 0.03, c = 13.98 ± 0.04 Å; β = 99.5 ± 0.2°. The density, calculated on the basis of 12 molecules per unit cell, is d 1.42 g/cm^3 (exptl, 1.38 g/cm^3); the space group is Cc or C2/c. Spectra were recorded using the equiinclination, multiple-film Weissenberg technique (Cu Kα radiation) on a crystal rotating around its b axis. Nine layers were collected at room temperature; 1003 nonzero independent intensities were visually estimated, out of 2380 reflections investigated. In order to prevent decomposition of the crystal, it was maintained in an inert atmosphere. A consistent array of Fe–Fe vectors was found in the three-dimensional Patterson synthesis, and this is in accord with the centrosymmetrical C2/c space group. Two crystallographically different Fe atoms were found in the unit cell: one in general position, and the other on the twofold axis. The structure was then elucidated by Fourier methods, assuming C2/c as the correct space group. The molecule containing the Fe atom in the twofold axis position was found to be strongly affected by structural disorder. On the basis of the assumption that the actual Fourier image of the molecule is due to the superposition of two molecules, the atomic coordinates were first derived by conformational considerations, the structure being then refined through 14 cycles of full-matrix least squares.

Figures 1 and 2 show the images of the two nonequivalent molecules; the differences between them are within the limits of experimental error. This conclusion and the fairly good degree of convergence found in the least-square refinement substantiate the correctness of the above assumption of structural disorder. Because of the limitations in the computer storage, either the ordered molecule (I, Figure 1) or that resulting from the splitting of the intertwined pair (molecule II, Figure 2) was maintained fixed in each least-square cycle. Anisotropic thermal parameters were assigned only to the Fe atoms; furthermore, in order to remove the indetermination in the refinement of the parameters, the B factors of the badly resolved C atoms of molecule II were maintained equal in corresponding pairs. The final R value ($=\Sigma|\Delta F|/\Sigma|F_o|$) is 0.148 for the reflections observed.

As might be expected, the two COT rings in each molecule differ in their geometrical conformation as well as in their mode of coordination to the central Fe

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