An Unexpected Skeletal Rearrangement of a Tricarbonyliron π-Complex; Crystal and Molecular Structure of Dicarbonyl-3-[π-(2-cyclohexadienyl)]-σ-propenoyliron

By P. JANSE-VAN VUUREN, R. J. FLETTERICK, J. MEINWALD, and R. E. HUGHES*
(*Department of Chemistry, Cornell University, Ithaca, New York* 14850)

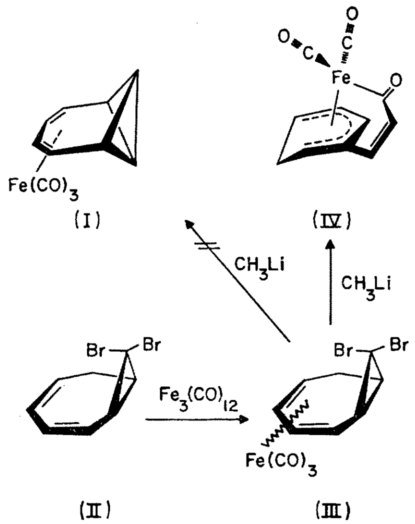
Summary An attempted carbene insertion reaction within a tricarbonyl iron π-complex gave an unexpected rearrangement product: X-ray structure analysis showed it to be an intramolecular "head-to-tail" bonded iron σ,π-complex exhibiting interesting bonding geometry.

IN an attempt to synthesize the theoretically interesting cyclo-octatetraene valence isomer tricyclo[5,1,0,0^{2,8}]octa-3,5-diene† as its stabilized π-complex (I), we obtained an isomeric product whose properties could not be reconciled with the desired structure.

8,8-Dibromobicyclo[5,1,0]octa-2,4-diene (II) was prepared by treating cycloheptatriene with bromoform and potassium t-butoxide in the usual way.[1]‡ Conversion of (II) into the corresponding tricarbonyliron π-complex (III) was accomplished by heating (II) under reflux in n-heptane for 6 h with tri-iron dodecacarbonyl. Dry-column chromatography, on Florisil, afforded a 15% yield of a yellow crystalline product, m.p. 101—103° (uncorr.); mass spectrum (50 ev, m/e) 404 [centre of mol. ion triplet, $FeC_8H_8Br_2(CO)_3^+$] and 104 (base peak). The physical and spectral data, including n.m.r. decoupling studies at 100 MHz, support structure (III) for the complex.

We hoped to produce (I) from (III) by an intramolecular carbene insertion reaction.[2] Treatment of an ethereal solution of (III) with MeLi (1 equiv.) at −90°, allowing the reaction mixture to warm up slowly, resulted in an exothermic reaction at −65° with a simultaneous rapid colour change from light-yellow to deep-red. The major product could be separated by dry-column chromatography on Florisil and purified by sublimation (80°, 0·1 mm Hg), affording a bright orange-yellow crystalline product, m.p. 99—102° (uncorr.); mass spectrum (50 ev, m/e) 244 [mol. ion, $FeC_8H_8(CO)_3^+$] and 56 (base peak). The lack of symmetry in the n.m.r. spectrum (virtually first-order with respect to each of the eight protons) and the strong i.r. absorption at 1620 cm^{-1} clearly indicated that the desired tricyclic π-complex (I) had not been obtained. Since it was not possible to make an unambiguous structural assignment on the basis of these data alone, a single-crystal X-ray structure analysis was undertaken; this analysis revealed that this new compound was dicarbonyl-3-[π-(2-cyclohexadienyl)]-σ-propenoyliron (IV).§

Preliminary photographic techniques uniquely indicated the space group $P2_1/c$. The unit-cell parameters, a = 10·740(3), b = 6·967(2), c = 13·514(4) Å and β = 97·64°(1), and the intensity data were measured with Zr-filtered Mo-K_α radiation on a Picker FACS-I automatic diffractometer. Of the 2280 independent reflections investigated, 1836 were statistically observable; L.p. corrections were applied but neither absorption nor extinction corrections were deemed necessary. The structure was solved from a Patterson analysis followed by successive Fourier syntheses.



Full-matrix least-squares analysis[4] was used to refine the non-hydrogen atoms with anisotropic thermal parameters; the eight hydrogen atoms, located from a difference Fourier, were included, but their parameters were not refined. Appropriate correction was made for anomalous scattering from the iron atom. The final value of the conventional R was 0·052, with estimated standard deviations of 0·005—0·007 Å for bond lengths and about 0·3—0·5° for bond angles. The final values of the bonding parameters are shown in the Figure.

The five conjugated atoms in the cyclohexadienyl ring are coplanar to within 0·01 Å although three of these atoms, C(1), C(2), and C(5), involve bonds that are seriously bent from the idealized sp^2 hybridization plane; nevertheless, the interior angles within this group are very nearly 120°. Moreover, the precise geometric coincidence of the cyclohexadienyl ring with that in the simpler complex,[5] $(C_6H_7)Mn(CO)_3$, is noteworthy. This structural integrity suggests that this is the characteristic geometry for the cyclohexadienyl ring in π-bonding complexes.

A conspicuous feature of the molecule is the propenoyl side-chain which is linked¶ to the iron atom through a σ-bond. The six atoms C(2), C(7), C(8), C(9), O(3), and Fe, lie within 0·02 Å of a plane which is nearly perpendicular (87·2°) to

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† For example, a series of symmetry allowed 1,5-sigmatropic shifts, would make all eight carbon atoms equivalent.

‡ Satisfactory i.r., u.v., n.m.r. and mass-spectral data were obtained for the dibromide.

§ An intramolecular carbonyl rearrangement of a different type, *via* alkyl migration in σ-Fe-alkyl complexes, is a well known and studied reaction.[3]

¶ One analogous cyclopentadienyl system involving an oxyvinyl side-chain, has been reported.[6]

the pentadienyl plane. The bond lengths of the enonyl group are normal, but the bond angles are moderately strained; a reflection of that strain appears in the 14·8° inclination angle of the C(2)–C(7) bond to the pentadienyl plane.

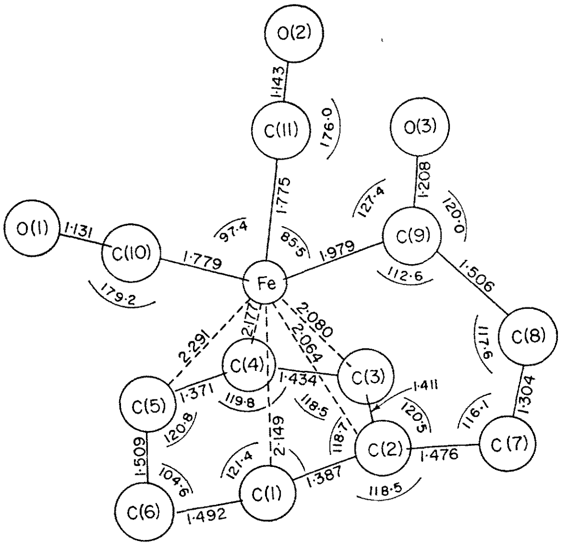

FIGURE. *A perspective drawing of the* $C_8H_8CO{\cdot}Fe(CO)_2$ *molecule* (IV) *showing the values of the molecular parameters. The iron atom is positioned* 1·659 Å *above the pentadienyl plane formed by atoms* C(1), C(2), C(3), C(4), *and* C(5).

As would be expected, the metal atom in the Mn-complex lies in a mirror plane which bisects the cyclohexadienyl ring.[5] In the present case, the enonyl group, unsymmetrically substituted on the ring, destroys this symmetry and distorts the π-bonding systems by displacing the iron atom towards C(2). The energies associated with this shift of 0·117 Å from the pseudo-mirror plane containing C(3) and C(6), and the resulting changes in the iron π-bonding distances, must be comparable to those involved in the strained enonyl system.

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