

MECHANISTIC DICHOTOMY IN CYCLOADDITIONS TO CYCLOOCTATETRAENEIRON TRICARBONYL.

X-RAY CRYSTAL STRUCTURE ANALYSIS OF THE TCNE AND CSI ADDUCTS

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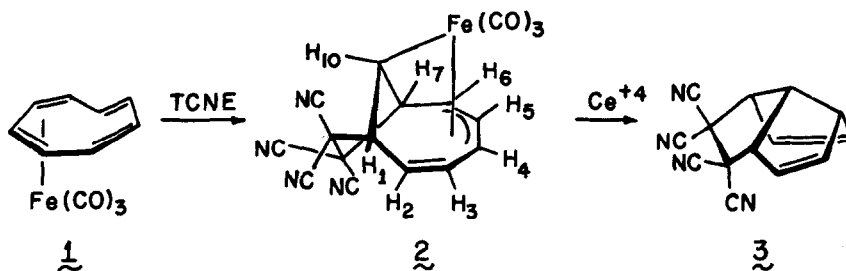
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Among several reasons for mechanistic interest in cycloaddition reactions of cyclooctatetraeneiron tricarbonyl (1) and related $M(CO)_3$ complexes is the expectancy that interesting modification of reactivity in the 'non-bonded' 1,3-diene moiety² might arise as a consequence of its conjugative proximity to the site of transition metal coordination. Moreover, the cycloadducts could serve as potentially important synthetic intermediates, particularly so if they are not available by direct reaction with the uncomplexed polyolefin.

Although there are now a number of reports describing the formal cycloaddition of several reactive dienophiles to 1, structural assignments to certain of these adducts have frequently been founded upon chemical intuition and unproven assumptions rather than detailed structural information. A case in point in the tetracyanoethylene (TCNE) adduct of 1 which has been variously considered to be a product of 1,4-³ 1,2-,⁴ and 1,3-bonding.⁵ No nmr data have been reported owing to the claim that the substance is too insoluble. The present study provides the first definitive structural data for this compound and its oxidation product, and contrasts the reactivity profile of TCNE with that of chlorosulfonyl isocyanate (CSI).

Admixture of equimolar quantities of 1 and TCNE in benzene solution at room temperature led to the rapid precipitation of 2 in high (96%) yield. Double resonance pmr experiments in DMSO- d_6 at 100 MHz established the presence of only five olefinic protons and permitted measurement of the following coupling constants: $J_{1,2} = 4.5$ Hz; $J_{1,3} = 2$ Hz; $J_{2,3} = 11$ Hz; $J_{3,4} = 9$ Hz; $J_{1,10} = 6.5$ Hz; and $J_{7,10} = 11.5$ Hz. The uncomplexed nature of H_2 and H_3 was evident from their downfield positions at δ 5.76 (dd) and 6.6 (ddd), respectively (compare with H_4 - H_6 at δ 4.4-4.68). The chemical shift of H_{10} (δ 1.56, dd) also suggested its attachment to a carbon atom σ bonded to iron.⁶

Confirmation of the 1,3-adduct formulation and establishment of the stereochemistry of 2 was achieved by X-ray analysis. Crystals of $C_{17}H_{14}N_4O_5Fe$ were of the triclinic space group $P\bar{1}$



with lattice dimensions $\underline{a} = 7.231(1)$, $\underline{b} = 10.052(3)$, $\underline{c} = 15.046(4)$ Å, $\alpha = 76.60(1)^\circ$, $\beta = 124.51(1)^\circ$, and $\gamma = 117.26(2)^\circ$. The observed density of 1.54 g/cc indicated two molecules in the unit cell ($\rho_{\text{calc}} = 1.54$ g/cc). All unique data with $\theta \leq 30^\circ$ were collected on a fully automated diffractometer using graphite monochromated Mo radiation (0.7107 Å). Of the 4504 measured reflections, 3151 were considered observed ($I \geq 3\sigma(I)$) after correction for Lorentz, polarization, and background effects. The structure was routinely solved by the heavy atom method and full-matrix least-squares refinements with anisotropic heavy atoms and isotropic hydrogens rapidly converged to a discrepancy index of 0.055 (Fig. 1).⁷

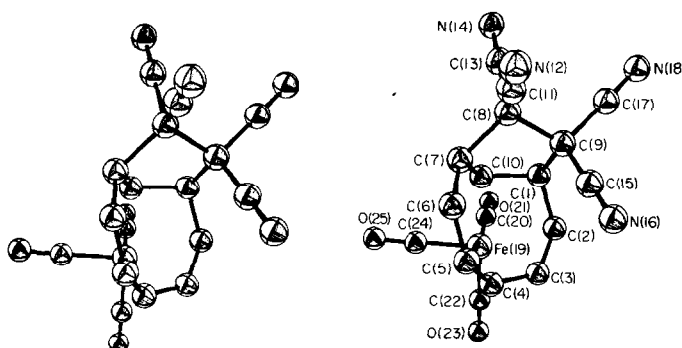
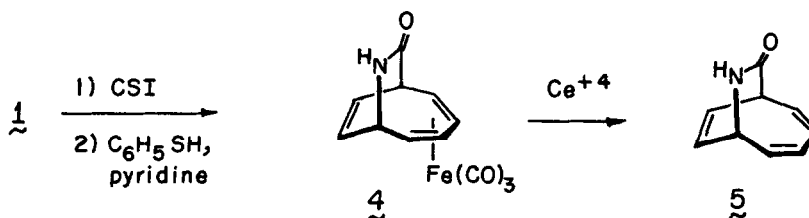


Figure 1. A Stereopair Drawing of $\text{C}_{17}\text{H}_8\text{N}_4\text{O}_3\text{Fe}$.

Oxidative degradation of $\underline{2}$ with ceric ammonium nitrate in 95% ethanol⁵ proceeded in 98% yield to give white crystals, mp 130-131 $^\circ$, which displayed cyano absorption in the ir at 2287 cm^{-1} and showed a simple nmr spectrum: doublets of area 2 at δ 6.22 ($J = 5.8$ Hz) and 5.75 ($J = 5.8$ Hz) and a narrow four-proton multiplet centered at 4.15. Confirmation of the dihydrotriquinacene structural assignment was again realized by X-ray analysis (monoclinic, $\underline{a} = 11.706$ (s), $\underline{b} = 8.470(4)$, $\underline{c} = 11.919(5)$ Å and $\beta = 96.59(2)^\circ$; $\text{CuK}\alpha$ radiation; 1308 observed reflections; space group $\text{P}2_1/\text{c}$. The structure was solved by a multiresolution tangent approach ($R = 0.063$)

which revealed the cyclopentene rings to be essentially planar and the cyclopentane ring to be in an envelope conformation with C₂ out of plane by 0.56 Å and the C₂-C₃ bond to be surprisingly long (1.599 Å).

In a further experiment, a solution of 1 in dry dichloromethane at 0° reacted readily with CSI to give after dechlorosulfonylation with thiophenol and pyridine in cold acetone⁵ a homogeneous adduct, mp 143.5-144.5°, in 80% yield. The yellow crystals exhibited ir carbonyl absorptions at 1675, 1990, and 2050 cm⁻¹ and a pmr spectrum showing an AA'XX' pattern at δ 5.55 and 3.62 typical of a Fe(CO)₃-complexed diene unit and multiplets characteristic of an isolated double bond (6.38), two bridgehead protons (4.0 and 3.3), and an amide hydrogen (6.9). The conclusion that structure 4 is uniquely compatible with these data is supported by ceric ion oxidation to 5 which was identical to the known substance.⁶



The formation of 4 is clearly stereospecific with the Fe(CO)₃ group taking up an orientation anti to the lactam bridge (Fig. 2). The

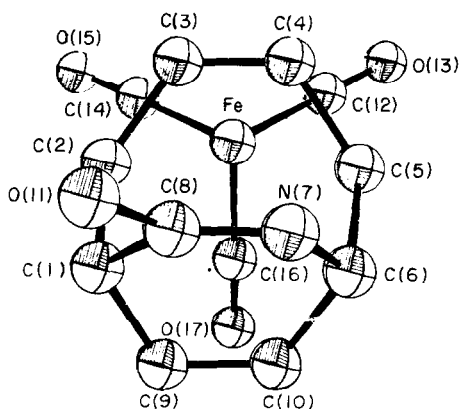


Figure 2. A Computer Generated Perspective Drawing of the Final X-ray Model of C₇H₁₁NO·Fe(CO)₃.

the heavy atom method and refined by full-matrix least-squares to a discrepancy index of 0.078 in space group P₁.⁷ Both independent molecules have the conformation shown in Fig. 2 and are

tation anti to the lactam bridge (Fig. 2). The lactam complex 4 crystallizes in the triclinic system with a reduced unit cell of dimensions $a = 14.317(7)$, $b = 14.428(6)$, $c = 6.701(5)$ Å, $\alpha = 95.64(3)^\circ$, $\beta = 91.62(2)^\circ$, and $\gamma = 114.89(2)^\circ$. A measured density of 1.62 g/cc indicated four molecules per unit cell ($\rho_{calc} = 1.60$ g/cc) or two molecules per asymmetric unit in the presumed space group P₁. Because of the small crystal size CuK α X-rays were used to measure all unique data with $\theta \leq 63^\circ$ (1181 reflections were judged observed). The structure was solved by

related approximately by a translation of $b/2$. A water of crystallization is between the two independent molecules and destroys the potential subcell symmetry.

In summary, TCNE and CSI have been shown to attack $\text{COT}\cdot\text{Fe}(\text{CO})_3$ stereospecifically from its less hindered surface to give, respectively, a 1,3- and 1,4-cycloadduct. The mechanistic factor(s) which leads to this phenomenologically interesting divergence in product formation constitutes a subject of continued study in this laboratory.¹⁰

FOOTNOTES AND REFERENCES

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10. We thank the National Science Foundation and the U.S. Atomic Energy Commission for financial support of this research.