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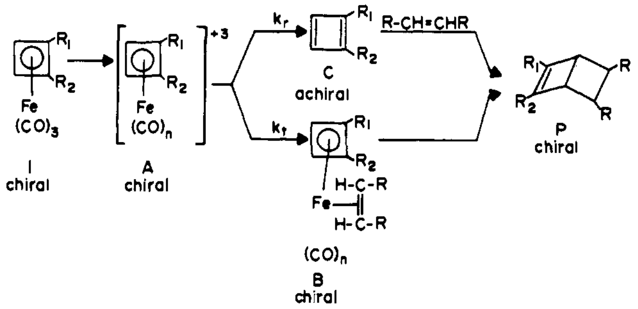
The Mechanism of the Oxidative Decomposition of Cyclobutadienyliron Tricarbonyl Complexes: Intramolecular Trapping

Sir:

Cyclobutadienyliron tricarbonyl produces cyclobutadienoid intermediates on oxidative decomposition. Pettit and his coworkers[1] have demonstrated that these intermediates can be trapped to yield a large number of interesting products. Although cyclobutadiene has been generated photochemically[2] and observed at low temperatures, these complexes remain the best synthetic source of cyclobutadiene. Earlier studies suggested that "free" cyclobutadiene is produced on oxidation of cyclobutadienyliron complexes.[3,4]

The possible schemes that were considered are:

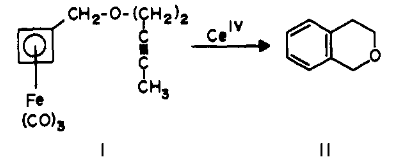


It was shown that if an optically active cyclobutadiene complex (I) was decomposed in the presence of a symmetrical dienophile the products (P) were racemic. Since the cyclobutadiene (C) was the only reasonable achiral intermediate, these results suggested that the cyclobutadiene was released before reaction; i.e., $k_r \gg k_t$, in an intermolecular reaction.

Rebek[5] applied the three phase test to this reaction. He demonstrated that cyclobutadiene was transferred through solution from a polymer containing the complex to another polymer containing a trapping agent. In this case k_t cannot be competitive with k_r.

We now have evidence that k_t is competitive with k_r under special conditions and that when the complexed intermediate is trapped, optically active products are produced. These results provide strong support for the results obtained earlier.[3,4]

Cyclobutadienyliron tricarbonyl complexes containing dangling dienophiles have been observed to produce intramolecular trapping products in high yield.[6]



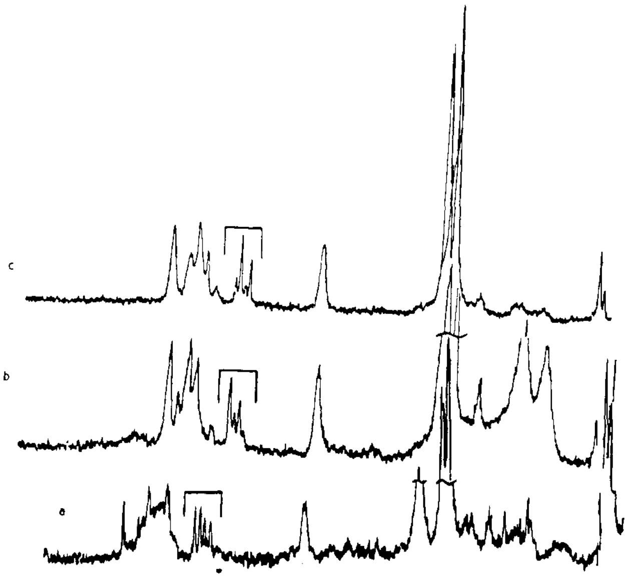
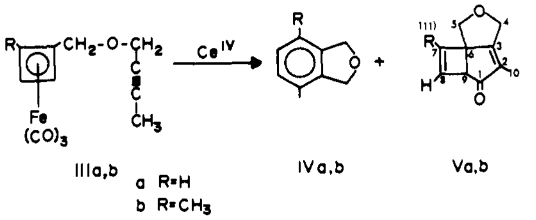
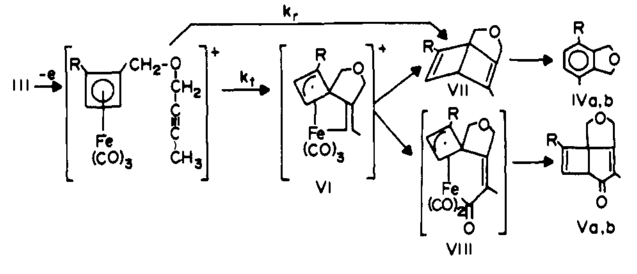


Figure 1. Optishifted spectra of Vb: (a) from racemic complex IIIb, (b) from (−) complex IIIb, (c) from (+) complex IIIb. The four peaks marked are produced from a doublet in the nonshifted spectra of IIIb.

When this reaction was carried out with the propargyl ether analogue (IIIa), two products were observed. The major product was the expected phthalan (80%) (IVa)[7] and a minor product (Va) (15%)[8] resulting from the insertion of carbon monoxide into the carbon framework of the ligand.



Past experience has shown that CO insertions only occur when a metal carbonyl is σ bound to a carbon. This suggested that in this case, k_t was competitive with k_r and the cyclobutadienoid was reacting while complexed to the metal. The products are best rationalized by the following scheme.



The intermediate VI is similar in structure to a series of neutral complexes prepared by Green and co-workers.[9] Since the chain linking diene and dienophile was short, the intramolecular trapping was competitive with the release of the ligand. However, once the intermediate (VI) was formed, reductive elimination to the Dewar benzene (VII) was inhibited due to the ring strain of the resulting system. Insertion of a carbon monoxide produced VIII and relieved sufficient strain for reductive elimination to occur to produce V.

To support this mechanism as well as to demonstrate that trapped cyclobutadienoid intermediates maintained chirality, IIIb was prepared and resolved. Oxidative decomposition (Ce^{IV}) of IIIb[10] produced the methylated analogues IVb (75%) and Vb (20%).[13,14] The experiment was repeated with optically active IIIb (32 ± 2% optically pure). The resulting Vb, isolated by column chromatography, showed a large optical rotation.[15] The optical purity of Va was determined by the use of chiral shift reagents.[16] Figure 1, shows the portion of the shifted spectrum resulting from *one* of the methylene protons adjacent to the ether oxygen. As can be seen (spectrum a) the doublet in the unshifted spectrum from this proton splits into four lines. When the opposite enantiomers of the complex were used different pairs of these lines decrease in intensity (spectra b, c). Although an exact integration was difficult, the optical purity (31 ± 2%) of the product appears to be the same as the starting complex.

Thus, the product Vb results from trapping of an intermediate cyclobutadienoid while it is still under the chiral influence of the metal. This suggests that in the earlier[3,4] intermolecular trapping experiments, optically active products would have resulted if the cyclobutadiene ligand was not free from the metal at the time of reaction.

References and Notes

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(7) Identified by NMR and molecular weight and comparison to analogous compounds.

(8) The spectral properties of compound Va are: ^{1}H NMR, δ (Me_4Si): 6.60 (doublet $J_{7,8}$ = 2.7 Hz, 1 H) (7), 6.33 (doublet of doublets, $J_{7,8}$ = 2.7, $J_{8,9}$ = 1.5 Hz, 1 H) (8), 4.47 (multiplet, 2 H) (4), 4.12 (doublet, J = 9 Hz, 1 H) (5), 3.72 (doublet, J = 9 Hz, 1 H) (5), 3.47 (doublet, $J_{8,9}$ = 1.5 Hz, 1 H), 1.70 (triplet, $J_{4,10}$ = 1.5 Hz, 3 H (10); ^{13}C: 191.7 (1), 171.1 (3), 145.3 (7), 136.0 (8), 131.6 (2), 69.0 (4), 64.6 (5), 62.5 (6), 56.4 (9), 9.45 (10); MS *m/e* 162.

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(10) Compound IIIb was prepared from 1,2-dicarbomethoxycyclobutadienyliron tricarbonyl (IX).[11] IX was converted to the half acid, reduced with BH_3/THF–$BF_3 \cdot Et_2O$ to 1-carbomethoxy-2-methylcyclobutadienyliron tricarbonyl and then with diisobutylaluminum hydride to 1-hydroxymethyl-2-methylcyclobutadieneiron tricarbonyl. The alcohol was converted to the bromide and resolved as before.[12]

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(13) The spectra of Vb are: ^{1}H NMR, δ (Me_4Si) 5.93 (multiplet, 1 H) (8), 4.47 (multiplet, 2 H) (4), 4.12 (doublet, J = 9 Hz, 1 H) (5), 3.72 (doublet, J = 9 Hz, 1 H) (5), 3.27 (multiplet, 1 H) (9), 1.80 (multiplet, 3 H) (11), 1.70 (triplet, $J_{4,10}$ = 1.5 Hz, 3 H) (10); ^{13}C: 201.7 (1), 171.9 (3), 155.3 (7), 131.3 (2), 126.5 (8), 67.5 (4), 64.4 (5), 63.1 (6), 52.8 (9), 13.6 (11), 9.3 (10); MS *m/e* 176.

(14) These yields were obtained when the reaction was carried out under 1 atm of carbon monoxide. Lower yields were obtained under nitrogen.

(15) Calculated $[\alpha]^{25}_{578}$ 280 ± 20° (0.015 g in ether).

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Stereospecific Synthesis of a Sulfenamide Cobalt(III) Complex Derived from (*R*)-Cysteine

Sir:

[$Co(en)_2$-(*R*)-cysteinato]$(ClO_4)_2 \cdot H_2O$ was prepared from (R,R)-cystine, ethylenediamine and cobalt(II) perchlorate and separated into two brown diastereoisomers (Ia, Ib). The proposed structure of one of these isomers (Ia, $[M]^{483}_{20}$ +9015 deg M^{-1} m^{-1}, 10^{-2} M $HClO_4$) is depicted in Figure 1. Two components are observed for the first ligand field band consistent with the C_{4v} symmetry of the bonding atoms (ϵ^{484}_{max} = 133, $\epsilon^{\sim 580}_{sh}$ 50 M^{-1} cm^{-1}, 10^{-2} M $HClO_4$) but a strong charge transfer absorption (ϵ^{281}_{max} 12 450) obscures the second ligand field band region ($\epsilon^{\sim 360}_{sh}$ 324). This spectral property is characteristic of S bound to Co(III).[1,2] For N,O amino acid chelates in general, both ligand field bands are observed (~485 and 345 nm). Comparison of the ^{1}H NMR and visible spectra of Ia with [$Co(en)_2S(CH_2)_2NH_2$]-$(ClO_4)_2$(ϵ^{481}_{max} 126, $\epsilon^{\sim 580}_{sh}$ 48, $\epsilon^{\sim 360}_{sh}$ 318, ϵ^{281}_{max} 13 400)[2] and [$Co(en)_2SCH_2OCO$]ClO_4 (ϵ^{514}_{max} 153, ϵ^{360}_{sh} 367, ϵ^{280}_{max} 11 300) eliminated the third possibility of S,O chelation. The other feature consistent with N,S bonding is the pK_a of the ionizable proton which is ~4, characteristic of a free carboxylic acid group in this type of complex.[3] Further, ion-exchange chromatography (pH 2 and 7) reflects the two possible cation charges, 2+ and +, and both mono- and diperchlorate salts of I have been isolated. Note that (uncoordinated) -NH_3^+ (pK_a ~ 9) or -SH (pK_a ~ 10) is expected to be significantly less acidic than -COOH.

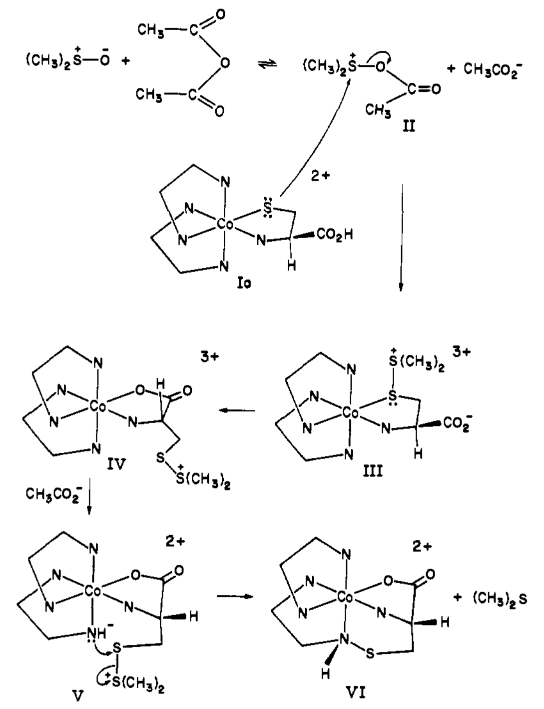

Figure 1. Mechanism for sulfenamide formation.

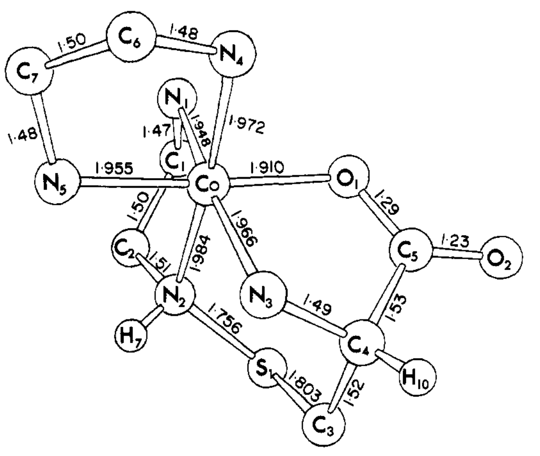

Figure 2. The crystal structure of Δ-(*S*)-(ethylenediamine-(*R*)-cysteinesulfenamide)(ethylenediamine)cobalt(III) tetrachlorozincate.

The cysteinato isomers show a capacity for oxidation at S by a variety of oxidizing agents. In particular, a dimethyl