Since the spectrum may be shifted to the longer wavelength region from that of flavone by the electronic effect of 3-hydroxy group, the triplet–triplet absorption band at 390–420 nm may be ascribed to the triplet state of 3-HF ($^3N^*$). The 2-methyltetrahydrofuran solution of 3-HF exhibits transient absorption spectra similar to those of the MP solution, though neither the $S_n \leftarrow S_1$ absorption spectrum of T* nor bleaching of the ground-state absorption could be observed because of a strong background from fluorescence due to T* and N*.

Transient absorption spectra of the aerated MP solution of 3-HC were observed at 380–400 and 400–450 nm. The decay times are ~90 and ~400 ns, respectively. By analogy to the spectra of 3-HF, the former and latter absorption bands may be ascribed to the triplet-triplet absorption of N* and the transient absorption of T, respectively. It is noteworthy that the decay time of T is significantly smaller in 3-HC than 3-HF. This means that the ground-state proton transfer from T to N occurs more rapidly in 3-HC than 3-HF. This fact suggests that the effect of phenyl group in 3-HF on the ground-state proton transfer is analogous to that observed for the excited-state process, as reported in the previous paper.

Acknowledgment. We are indebted to Dr. P. F. Barbara for supplying a copy of his paper[5] prior to publication.

Registry No. 3-HF, 577-85-5; 3-HC, 13400-26-5.

Sequential Mechanism in the Oxidative Demetalation of a Trimethylenemethane–Fe(CO)$_3$ Complex, Tricarbonyl[(1–3,6-η)-2-methylenecyclopentane-1,3-diyl]iron

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A crucial problem in the chemistry of transition metal–hydrocarbon complexes such as those of cyclobutadiene (CBD)[1] and trimethylenemethane (TMM)[2] concerns the extent and duration of the influence of the metal when the ligand is oxidatively[1,2a] or photochemically[2b] "liberated" and trapped by olefins or acetylenes. A general mechanism for such processes is shown in Scheme I, where O and G represent oxidizing and capture agents, respectively. The present paper uses the known properties[3–5] of 2-alkylidenecyclopentane-1,3-diyls as criteria by which to judge whether the metal influences the behavior of the TMM intermediate 2-methylenecyclopentane-1,3-diyl (1) generated from an iron complex. The results indicate a sequential mechanism and provide the first direct evidence of the liberation of a metal-free TMM in its ground triplet spin state in such reactions.

1

The title complex 2,[6] isolated in 3% yield as a yellow liquid by gas chromatography (GC), was prepared by heating cyclopent-1-enylmethyl chloride[7] and Fe$_2$(CO)$_9$ at reflux in degassed benzene under argon for 12 h.[8] Oxidation of 0.03 M 2 with carefully dried trimethylamine-*N*-oxide[9] (2–3 M) in benzene solution at 60 °C gave a 14% yield of a mixture of hydrocarbon products, at least ten of which were empirically dimers of 1. When the oxidation of 2 was carried out in the presence of a large excess of diethyl fumarate (DEF), two fused cycloadducts, 3[6] and 4,[6] designated tF$_1$ and tF$_2$ or vice versa according to their retention time on GC, and the trans-bridged adduct 5[6] were observed (Scheme II) in combined yields ranging from 9% to 19%.[10] The same three products were obtained from diazene 6 (96% yield) as was established by comparisons of GC retention times and spectroscopic properties of isolated materials.

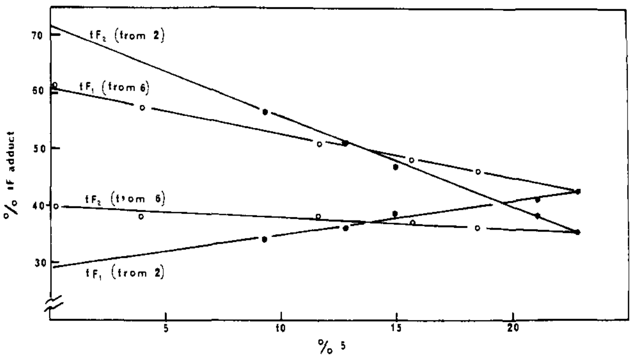
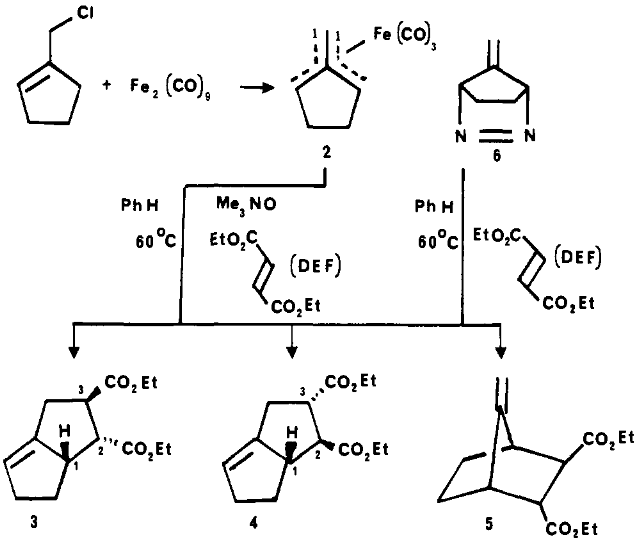


Figure 1. Least-squares fit to linear form of the percent of each trans-fused adduct (tF) as a function of trans-bridged adduct (5) in the thermal and oxidative decompositions of diazene 6 and complex 2, respectively, at 60 °C in benzene solution in varying concentrations of diethyl fumarate (DEF).

Scheme I

$$\begin{tikzcd}
& \text{organometallic complex} \arrow[dl, "k_1"', "O"] \arrow[dr, "O"', "k_2"] & \\
\text{oxidized metallic complex (M)} \arrow[rr, "k_3"] \arrow[d, "G"', "k_4"] & & \text{metal-free reactive ligand} \arrow[d, "G"', "k_5"] \\
\text{complex-derived adducts} & & \text{free-ligand-derived adducts}
\end{tikzcd}$$

Scheme II



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(9) Cf.: Shvo, Y.; Hazum, E. *J. Chem. Soc., Chem. Commun.* **1974**, 336.

(10) The yield of CO$_2$ was 0.22 mol/mol of 2. If only one CO ligand/mol of 2 is required to be oxidized to CO$_2$ to effect formation of the cycloadducts 3–5, the observed cycloadduct yield would correspond to 42–87%. Control experiments established that the product ratios were kinetically determined and did not change during prolonged reaction times.

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The product compositions from the TMM precursor diazene **6** depended on the concentration of the trapping agent. Such dilution effects have been observed previously[3-5,11] in alkylidenecyclopentane-1,3-diyl chemistry and signify a sequential cascade of capturable intermediates. In the reactions of the model 2-methylene diazene **6**, five concentrations of DEF in the range 0.0026-0.5 M were studied. The changes in product composition closely paralleled those observed[11] in the 2-isopropylidene analogue: the fused product dominated at high concentration, but dilution relatively favored the formation of bridged product. Plots of the yields of each fused adduct **3** or **4** vs. the yield of bridged adduct **5** ("product vs. product" plots) were linear, a finding that indicates a sequence of two (and only two) capturable intermediates.[11] Reference to a large body of experience[3-5,11,12] strongly suggests that these are a singlet and a triplet state of the biradical **1**.

Dilution effects also were observed in the oxidative decomposition of the TMM-$Fe(CO)_3$ complex **2**. Again, the "product vs. product" plots were linear, indicating two sequential intermediates. However, these plots differed sharply from those obtained in the diazene runs, as is graphically displayed in Figure 1. Whereas from diazene **6**, tF_1 is favored over tF_2 at the left extreme of the plot, a region in which singlet-derived products dominate,[3-5,11] this preference is *reversed* in the products from the iron complex **2**, where tF_2 is favored. Hence, the immediate precursor (designated M) of the products from iron complex **2** at high olefin concentration cannot be the singlet biradical.

The right-hand extreme of the percent **5** range corresponds to the low concentration limit, where triplet biradical-derived product prevails.[11] Figure 1 shows that in this domain, the product compositions from **2** and **6** are in exact agreement, which suggests that at low concentration the triplet biradical is the common immediate precursor of both sets of products.

By exclusion, the most likely candidate for the role of M is an unstable metallic complex. Scheme I shows a (perhaps oversimplified) way in which product could be formed by intermolecular capture of the species. It is not known whether the first oxidized metal complex and the product-forming metal complex are identical, but the present results demonstrate that the final demetalation step liberates free **1** triplet directly and does not pass through **1** singlet.

Previous experiments, employing optical activity[13-15] and three-phase traversal[16] criteria have shown convincingly that metal-free cyclobutadienoid species can be liberated from cyclobutadiene (CBD)-$Fe(CO)_3$ complexes. Although an *intramolecular* capture of a metal-bound CBD was observed,[15] no evidence was found for intermolecular capture. In terms of Scheme I, this would mean that $k_3 \gg k_4[G]$. It remains to be seen whether increasing the concentration or intrinsic reactivity of the trapping agent (G) may yet permit an intermolecular interception of a metal-bound CBD analogous to that of the metal-bound[17] TMM observed here.

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Registry No. 1, 60743-11-5; **2**, 85370-27-0; **3**, 85370-28-1; **4**, 85370-29-2; **5**, 85370-30-5; diethyl fumarate, 523-91-6.

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^{195}Pt NMR Investigation of the Head-to-Head to Head-to-Tail Isomerization of α-Pyridonate-Bridged Ethylenediamineplatinum(II) Dimer

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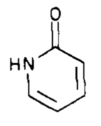
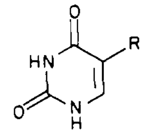
cis-Diamminedichloroplatinum(II) (*cis*-DDP) forms a variety of mononuclear and bridged polynuclear complexes with α-pyridone, including a crystalline platinum blue.[2] The range of structural types displayed by these complexes and their nucleobase (e.g., uracil, thymine) analogues[3] offers insight into the binding of the antitumor drug *cis*-DDP to its likely biological target, DNA. Little is known about the dynamic properties[4] of the large family of binuclear complexes bridged by the α-pyridonate ligand class.[5] Here we present results of ^{195}Pt NMR studies of α-pyridonate-bridged binuclear ethylenediamineplatinum(II) complexes, $[(en)Pt(C_5H_4NO)]_2^{2+}$, that clearly demonstrate the occurrence of a reversible, intramolecular, dissociatively activated stereochemical rearrangement from the head-to-head (HH) to head-to-tail (HT) isomer. This isomerization requires a relatively rapid off-rate for the Pt-N(heterocycle) bond in its approach to equilibrium. The proposed mechanism may be relevant to rearrangements of other binuclear complexes with asymmetric, bidentate bridging ligands,[3,6] and to the DNA binding properties of *cis*-bis(amine)platinum(II) antitumor drugs.



α-pyridone



uracil, R = H
thymine, R = CH_3

As expected from its known structure,[7] the ^{195}Pt NMR spectrum of a freshly prepared aqueous solution of the HH $[(en)Pt(C_5H_4NO)]_2^{2+}$ isomer consists of two resonances, Figure 1. The low- and high-field resonances are assigned to the N_2O_2- and N_4-coordinated platinum atoms, respectively, on the basis of established ^{195}Pt chemical shift trends.[2,8] As the solution is allowed to stand with time, a third resonance slowly appears at a chemical shift value midway between the other two resonances. The new signal results from the HT isomer, which is formed at the expense of the HH species. The appearance of the HT resonance and the disappearance of the HH resonances may be fit by a first-order approach to equilibrium (Figure 1) derived from the rate law given in eq 1. Specific rates obtained for HH loss and HT appearance

$$d[HT]/dt = -d[HH]/dt = k_f[HH] - k_r[HT] \qquad (1)$$

are in satisfactory agreement. Moreover, there is little or no dependence of the rate on pH (in the range 2.3-7.8), added free α-pyridone (up to a 5-fold excess at pH 6.5), added 6-methyl-α-pyridone (up to a 5-fold excess at pH 6.5), or added $[(en)Pt(H_2O)_2](NO_3)_2$ (up to a 5-fold excess at pH 2.3).

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