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Stepwise Photochemical CO Loss from $Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$ in Low-Temperature Matrices: Evidence for an Unsupported Fe–Fe Triple Bond

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The classic dinuclear organometallic complex $Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$ (**1**, Cp = η^5-C_5H_5) has exhibited an incredibly rich and varied photochemistry.[1] Early studies established the existence of two disparate photochemical channels for **1**, namely the cleavage into mononuclear radicals $CpFe(CO)_2$ (**2**)[2] and CO loss to give highly symmetric $Cp_2Fe_2(\mu\text{-}CO)_3$ (**3**).[3] More recent studies using matrix photochemistry,[4] fast[5] and ultrafast[6] spectroscopy, and slower solution IR studies[7] have allowed the evolution of a finely detailed mechanistic picture of the photochemistry of **1**. With respect to the CO-loss channel, these recent studies have led to the postulation of several isomers of **3** that are proposed intermediates in the photochemistry, including all-terminal $Cp_2Fe_2(CO)_3$, $Cp_2Fe_2(CO)(\mu\text{-}CO)_2$, and $Cp_2Fe_2(\mu\text{-}\eta^1,\eta^2\text{-}CO)(\mu\text{-}CO)_2$. These studies demonstrate that the photochemistry is extremely sensitive to the experimental conditions, the variability in the products formed illustrating the careful balance that exists between the many mechanistic channels. We report here new observations in the matrix photochemistry of **1** and the detection of a new CO-loss photoproduct that apparently has the first unsupported Fe–Fe triple bond.

We have been interested in addressing the formation of **3** from **1**,[8] a question that has interesting electronic as well as mechanistic considerations inasmuch as **3** has a triplet ground state.[9] Among the most intriguing questions is that of the apparent isomer specificity observed in the conversion of **1** to **3**. Previous matrix photochemistry studies of this process led to the conclusion that only *trans*-**1** loses CO to give the triply-bridged species.[3b,c] Wrighton *et al.* have proposed that a "least-motion pathway" may be operating, thereby suggesting that the larger amplitude motion necessary for the transformation of *cis*-**1** to **3** is prohibitive.[3b] Such an argument would seem to depend very strongly on the rigidity of the matrix that encases the molecule.

In the hope of placing molecules of **1** within more easily deformable matrix cavities, we chose 3-methylpentane (3-MP) as the glassing substrate. 3-MP provides a softer matrix than methylcyclohexane,[10] the predominant matrix material for earlier studies. UV irradiation of a matrix of 0.3 mM **1** in 3-MP at 98 K for ca. 1 min with an unfiltered medium-pressure Hg lamp led to preferential consumption of *trans*-**1** to give **3** (Figure 1a). Unlike in previous studies, we observe some consumption of *cis*-**1** as well. The consumption of the cis isomer does not provide incontrovertible proof that *cis*-**1** is converted photochemically to **3**; although the thermal interconversion of the two isomers is effectively "turned off" at this temperature,[11,12] photochemical cis–trans isomerization cannot be ruled out. Continued irradiation (4 min) leads to additional production of $Cp_2Fe_2(\mu\text{-}CO)_3$ and the appearance of a new absorbance at 1904 cm^{-1}. A total irradiation time of 15 min leads to continued growth of the peak at 1904 cm^{-1} and a decrease in the signal for $Cp_2Fe_2(\mu\text{-}CO)_3$. At this point in the irradiation, the cis–trans ratio of consumed **1** is essentially the same as the preirradiation value (Figure 1b).

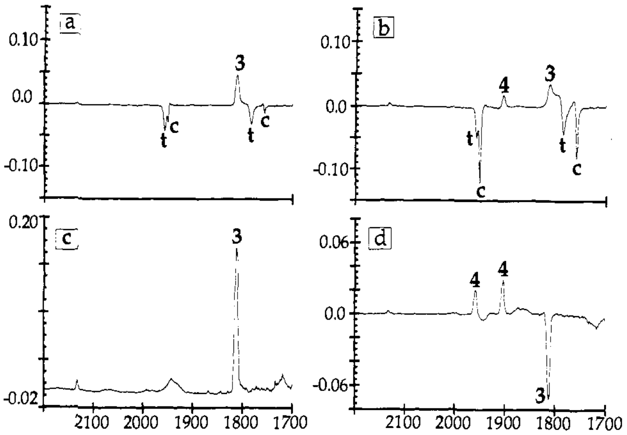

Figure 1. IR spectra of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$ (**1**) and photoproducts in 3-methylpentane at 98 K. All abscissae are in cm^{-1}. Spectra a, b, and d are difference spectra, and the ordinates are Δ(absorbance). The ordinate for spectrum c is absorbance. The peaks labeled "c" and "t" are due to the cis and trans isomers of **1**, respectively; numerical labels on peaks refer to species discussed in the text. (a) Difference between spectra obtained after 1 and 0 min of irradiation. (b) Difference between spectra obtained after 15 and 0 min of irradiation. The negative peaks in spectra a and b are due to consumed **1**. (c) Spectrum obtained after annealing the matrix to 160 K under continued irradiation. (d) Difference between the spectrum obtained after irradiation of the annealed matrix for 15 min and spectrum c.

In order to facilitate the complete conversion of **1**, the matrix was annealed by allowing it to warm gradually under continued irradiation. After 1 h, the temperature of the matrix had reached ca. 160 K, high enough to allow facile cis–trans interconversion. The matrix was then cooled back down to 98 K in the absence of light (ca. 10 min), and the IR spectrum was collected (Figure 1c). At this point, **1** has been completely consumed, and the predominant species present in the matrix is **3**. Broad features at ca. 1720 and 1940 cm^{-1} are also present. These bands are due to a different photoactive species, as will be discussed in a later publication.

Additional irradiation leads to consumption of **3** with the concomitant generation of free CO (2133 cm^{-1}) and the production of a species **4**, which has IR bands at 1904 and 1958 cm^{-1} (Figure 1d).[13] As noted above, the 1904 cm^{-1} band was observed after very short irradiation times. The 1958 cm^{-1} band, which grows in at the same rate as the 1904 cm^{-1} band, was masked by a band of unreacted **1** and therefore could not be observed prior to annealing the matrix. Longer irradiation times fail to increase

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[12] In order to test for cis–trans isomerization at 98 K, the nonequilibrium cis–trans mixture that follows irradiation was allowed to sit under "dark" conditions. The spectrum was unchanged after 5 min.

[13] Preliminary experiments indicate that the C_5Me_5 analog of **1** exhibits the same behavior, generating a species with CO stretching modes at 1875 and 1929 cm^{-1} (Husbands, Y. I., Kvietok, F. A., Bursten, B. E., unpublished results).

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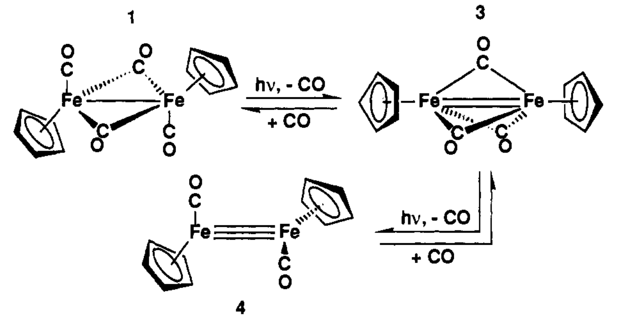
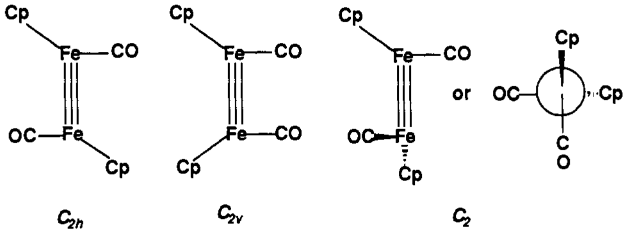
Scheme 1



the ratio of 4:3 beyond the value reached after 15 min. When the irradiation is discontinued, the peaks due to **4** decrease at the same rate, the peak for CO decreases, and the peak for **3** increases. Thus, **4** apparently undergoes a thermal back-reaction with CO to reform **3**, a reaction that is complete within 5 min at 98 K. By contrast, the thermal back-reaction that regenerates the bands at 1720 and 1940 cm^{-1} is considerably slower; 20 min after irradiation is discontinued, these bands are only slightly restored.

The facile back-reaction of **4** with CO to give **3** coupled with the presence of two IR absorbances in a range consistent with terminal carbonyls strongly suggests that **4** is the dinuclear complex $[CpFe(CO)]_2$ (Scheme 1). In the absence of any bridging ligands, the two CpFe(CO) fragments would necessarily be linked via an Fe–Fe bond. Two limiting structures might be suggested for all-terminal $Cp_2Fe_2(CO)_2$, namely the cis and trans configurations in which the two CO ligands are coplanar. Based on the structures of other dinuclear complexes with both Cp and CO ligands, it seems likely that the Fe–Fe–CO angles would be close to 90°. The trans configuration would exhibit only one IR-active CO stretching mode. The cis configuration should have two IR-active CO stretches; however, the symmetric (A_1) and antisymmetric (B_1) stretching modes should have very different intensities. The near equal intensities of the terminal CO stretches suggest instead a "nonplanar" C_2 structure in which the dihedral angle between the two Fe–Fe–CO planes is close to 90°. In this structure, both CO stretching modes are allowed and would be expected to have similar intensities due to the orthogonality of the changes in the dipole induced by the two modes.



Satisfaction of the 18-electron rule would dictate that the structure of **4** include an Fe–Fe triple bond. Because the matrix experiments do not allow us to gauge the extent of Fe–Fe bonding present in **4**, we have performed Fenske–Hall MO calculations[14] on the C_{2h}, C_{2v}, and C_2 structures shown above at an assumed Fe–Fe distance of 2.30 Å. These calculations, which are similar to those we have recently reported on other unsupported metal–metal multiple bonds in organometallics,[15] will be detailed in a subsequent publication. In the C_2 structure, the electron configuration for the 14 Fe-based electrons is $\sigma^2\pi^4\delta^4\delta^{*4}$, consistent with an Fe–Fe triple bond. In the C_{2h} and C_{2v} structures (which exhibit very similar electronic structures), the Fe–Fe bonding is less effective owing to extensive mixing between the nonbonding δ and antibonding π^* interactions, which comprise the nearly isoenergetic HOMO and LUMO of the complexes. Because we have been skeptical of some other recent reports of unsupported multiple metal–metal bonds,[15a] we are reluctant to place too much credence on MO calculations on a structurally uncharacterized complex. Nevertheless, in this case these calculations provide satisfying support for both the proposed C_2 structure of **4** and an Fe–Fe triple bond, as shown in Scheme 1.

The IR bands attributed to **4** seem unambiguously to indicate terminal carbonyl ligands and perforce an unsupported Fe–Fe bond. However, it strikes us as particularly unusual and unexpected that the carbonyls do not bridge the metal atoms as they do in the related complexes $Cp_2Co_2(\mu\text{-}CO)_2$ (**5**)[16] and $Cp_2Fe_2(\mu\text{-}NO)_2$ (**6**).[17] There are at least two possible explanations for this apparent anomaly. First, **4** contains two fewer electrons than either **5** or **6**. Previous electronic structure calculations on **5** and **6** indicate that the highest- and second-highest-occupied MOs are close in energy,[18] which could lead to an unstable situation for **4**, much as we observe for the C_{2h} and C_{2v} structures of **4**. Second, it is not inconceivable that the Fe–Fe interaction may be supported by agostic interactions[19] involving C–H bonds from the host matrix molecules.

The species **4** might be a precursor to the well-known tetrahedral cluster $Cp_4Fe_4(CO)_4$ (**7**), which is synthesized via prolonged (12 days) refluxing of **1** in xylene.[20] We will be exploring the possibility that the Fe–Fe triple bonds in **4** facilitate a 2 + 2 dimerization of **4** to **7**, a reaction that would be analogous to the perpendicular addition of alkynes to unsaturated metal–metal bonds.[21]

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