Theoretical and experimental studies of the unprecedented spin-dependent structures of [$Cp_2Fe_2(CO)_2$], the double-CO-loss product of [$Cp_2Fe_2(CO)_4$]

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Photochemically generated [(η-C_5R_5)$_2$$Fe_2(CO)_2$], which is a triplet molecule with terminal CO ligands, undergoes thermal relaxation to the singlet ground state of the molecule, which has bridging CO ligands.

Dinuclear organometallic complexes (DOCs) demonstrate remarkably rich and diverse photochemistry.[1] This paper focuses on new aspects of the photochemistry of one of the best studied DOCs, namely the diiron complex [$Cp_2Fe_2(CO)_4$] (**1**, Cp = η^5-C_5H_5), and its half-methylated and permethylated derivatives [Cp(Cp*)$Fe_2(CO)_4$] (**1′**, Cp* = η^5-C_5Me_5) and [Cp*$_2Fe_2(CO)_4$] **1***.[2] We report evidence here for a remarkable and unprecedented spin-dependent structural change in an organometallic photoproduct.

In 1983, Rest and coworkers[3] and Wrighton and coworkers[4] demonstrated that irradiation of **1** in frozen hydrocarbon matrices leads to CO loss and the formation of [$Cp_2Fe_2(\mu$-$CO)_3$] **2**, which has a formal Fe–Fe double bond and three symmetrically bridging CO ligands (ν_{CO} = 1812 cm^{-1}). Complex **2** is unusual inasmuch as it has a triplet ground state owing to its high, pseudo-D_{3h} symmetry.[5] We demonstrated that irradiation of **1** in softer hydrocarbon matrices leads to subsequent loss of CO from **2**, yielding the double-CO-loss product [$Cp_2Fe_2(CO)_2$] **3**:[6]

$$\underset{\mathbf{1}}{[\{CpFe(CO)\}_2(\mu\text{-}CO)_2]} \xrightarrow{h\nu,\ -CO} \underset{\mathbf{2}}{[(CpFe)_2(\mu\text{-}CO)_3]} \xrightarrow{h\nu,\ -CO} \underset{\mathbf{3}}{[\{CpFe(CO)\}_2]} \quad (1)$$

Based on the positions and near-equal intensities of its IR bands in the CO-stretching region (1904, 1958 cm^{-1}), we proposed that **3** has a C_2 structure in which two equivalent CpFe(CO) fragments are bonded together *via* an unsupported Fe–Fe triple bond, with a dihedral angle of *ca.* 90° between the two CO ligands.[6] Compounds **1′** and **1*** exhibit wholly analogous matrix photochemistry, with methylation of the Cp ligands leading to the expected red-shift of the CO-stretching bands in the IR.†

The presence of terminal CO ligands in **3**, **3′** and **3*** is highly unusual. Other [{CpM(EO)}$_2$] complexes of first-row transition elements, such as [{CpCo(CO)}$_2$], contain bridging EO ligands.[7] [{CpPt(CO)}$_2$] does have terminal CO ligands, but it seems likely that the Pt–Pt single bond in the latter is too long to support bridging CO ligands.[8]

In order to add insight into the unusual structure of **3**, we have performed electronic structure calculations of **3** using density functional theory.‡ We and others have used this methodology to predict the structures of metal carbonyl complexes with good success.[9] The calculated lowest-energy structure of **3** has C_{2v} symmetry with two symmetric bridging CO ligands [Fig. 1(*a*)], corresponding to a $^1A_1$ closed-shell electron configuration. The calculated dihedral angle between the two Fe–C(O)–Fe planes is 125°; it can therefore be viewed as structurally analogous to **2** with the removal of one of the μ-CO ligands.

We were initially puzzled by the apparent disagreement between this calculated structure of **3** and the one indicated by experiment. However, **3** is produced by a triplet precursor (**2**), and **3** readily back-reacts to form **2**, even in frozen matrices at < 90 K. These observations suggest that the conversion **3** + CO → **2** is a spin-allowed reaction, which would require that **3** be a triplet molecule. Our calculations on excited triplet states of **3** indicate that a low-lying ^3B state has a C_2 structure in perfect accord with that proposed from the matrix experiments, *viz.* terminal CO ligands and a dihedral angle of 86° [Fig. 1(*b*)].§ These calculations provide support for the notion that the double-CO-loss products **3**, **3′** and **3*** are produced as excited triplet molecules.

Our calculated Fe–Fe bond lengths for *trans*-**1** (2.548 Å) and **2** (2.274 Å)[10] are in good agreement with the crystallographic Fe–Fe bond lengths in *trans*-**1** (2.534 Å)[11] and **2** (2.265 Å).[5] These results give us confidence in the reliability of our calculated Fe–Fe bond lengths in the singlet and triplet forms of **3**, which are 2.116 Å and 2.189 Å, respectively. Both of these are significantly shorter than the Fe–Fe bond length in **2**, consistent with an increase in the formal Fe–Fe bond order from two in **2** to three in **3**.

The gross structural change predicted between the ground-state bridging-CO singlet form of **3** (denoted ^{1}**3**) and the terminal-CO triplet form of **3** (^{3}**3**) is unprecedented and suggests that ^{3}**3** is the kinetically favored product of the irradiation of **2**.

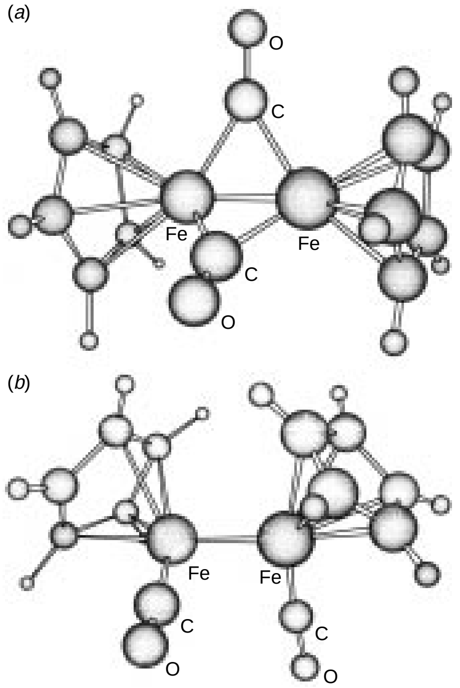


Fig. 1 (*a*) Calculated structure of the singlet ground-state structure of [$Cp_2Fe_2(CO)_2$] **3**. Selected calculated metric parameters: Fe–Fe 2.116 Å, Fe–C(CO) 1.926 Å, Fe–(Cp centroid) 1.773 Å, Fe–Fe–(Cp centroid) 174°, dihedral angle between Fe–C(CO)–Fe planes 125°. (*b*) Calculated structure of the unbridged ^3B excited state of **3**. Selected calculated metric parameters: Fe–Fe 2.189 Å, Fe–C(CO) 1.778 A, Fe–(Cp centroid) = 1.850 A, Fe–Fe–(Cp centroid) 141°, dihedral angle between Fe–Fe–C(CO) planes 86°.

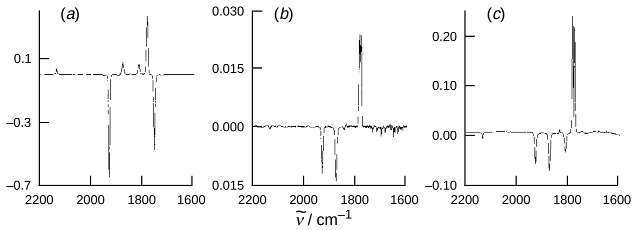
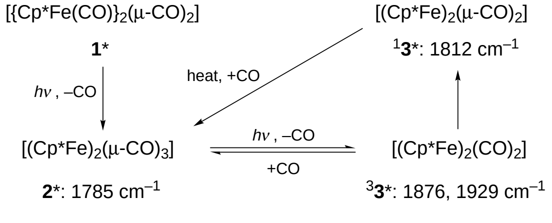


Fig. 2 Difference IR spectra of the CO-stretching region of a frozen solution of **1*** in 3-methylpentane at 98 K. (*a*) Difference spectrum obtained by subtracting the initial spectrum prior to irradiation from the spectrum obtained after 150 min irradiation. (*b*) Difference spectrum obtained by subtracting the spectrum immediately following 150 min irradiation from the spectrum obtained after 150 min irradiation followed by 5 min of thermal (dark) reaction at 98 K. (*c*) Difference spectrum obtained by subtracting the spectrum immediately following 150 min irradiation from the spectrum obtained after 150 min irradiation followed by dark warming of the matrix to 163 K and cooling back to 98 K.

It also suggests that, under appropriate conditions, ^{3}**3** should relax to form ground-state ^{1}**3**. We now believe that we have observed ^{1}**3*** in new matrix photochemical experiments.

When a frozen solution of **1*** (1 mM) in neat 3-methylpentane is irradiated for 150 min, we observe IR bands for free CO (2132 cm^{-1}), **2*** (1785 cm^{-1}), and ^{3}**3*** (1876 cm^{-1}; the 1929 cm^{-1} band of ^{3}**3*** is obscured by a band of **1***). We also observe a new bridging-CO band at 1812 cm^{-1} [Fig. 2(*a*)]. Observation at short irradiation times (< 5 min) indicates that the species that causes the band at 1812 cm^{-1} is formed only after ^{3}**3*** is formed. If the irradiation is discontinued and the matrix maintained at 98 K, we observe, *via* difference IR spectroscopy, only the thermal back-reaction ^{3}**3*** + CO → **2***, as was the case in the original report of **3** [Fig. 2(*b*)].[6] The band at 1812 cm^{-1} does not disappear on standing at 98 K. However, if the dark matrix is warmed to 163 K, we observe that free CO, ^{3}**3***, and the species at 1812 cm^{-1} are consumed as **2*** is produced [Fig. 2(*c*)]. We see analogous results upon prolonged irradiation of a matrix of **1′**, with the new band blue-shifted to 1833 cm^{-1}.

These new experimental data are consistent with the slow thermal or photochemical formation of ^{1}**3*** and ^{1}**3′** from ^{3}**3*** and ^{3}**3′**, respectively, and the slower (higher activation energy) back-reactions of ^{1}**3*** and ^{1}**3′** with CO to reform **2*** and **2′**. The slowness of these conversions is expected given that they are spin-forbidden. If our calculated structure of ^{1}**3** is correct, then the 1812 and 1833 cm^{-1} bands are likely the antisymmetric (B_1 under C_{2v} symmetry) stretching mode of the bridging CO ligands in ^{1}**3*** and ^{1}**3′**, respectively. The symmetric A_1 mode for each molecule should be at higher energy and, assuming the dipole moment changes are similar, will be only about half as intense as the B_1 mode. We have not yet observed the A_1 band for either ^{1}**3*** or ^{1}**3**. Our proposed series of transformations in the matrix photochemistry of **1*** is summarized in Scheme 1.



Scheme 1 Summary of proposed matrix photochemistry of **1*** in frozen 3-methylpentane

Direct kinetic access to the triplet double-CO-loss photoproducts such as **3** is a consequence of the symmetry-driven triplet ground state of the single-CO-loss photoproduct **2**. Lowering the symmetry of the initial precursor should favor the formation of singlet rather than triplet products. We believe that we have observed such an effect in the photochemistry of the lower-symmetry precursor [{Cp*Fe(CO)}$_2$(μ-CO)(μ-CH$_2$)], which forms a double-CO-loss product with a bridging or semi-bridging CO ligand.[12] We will continue to explore this interplay between spin state and structure in the photochemistry of other DOCs.

We thank Timothy Barckholtz for helpful discussions. We gratefully acknowledge the National Science Foundation (Grant CHE-9528568) and the Ohio Supercomputer Center for support of this research. M. E. A. is thankful for support as a GAANN Fellow, granted by the US Department of Education and administered by The Ohio State University.

Footnotes and References

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† IR data in the CO-stretching region for relevant species in frozen 3-methylpentane at 90–100 K: **2′**, 1797 cm^{-1}; **2***, 1785 cm^{-1}; **3′**, 1886, 1942 cm^{-1}; **3***, 1876, 1929 cm^{-1}.

‡ *Computational details*: density functional calculations were carried out using the Amsterdam Density Functional (ADF) package, Version 2.1 (Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands). The calculations employed the local density functional of Vosko, Wilk, and Nusair (S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200). Non-local corrections to the exchange and correlation used the methods of Becke (A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098) and Perdew (J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822), respectively. The atomic basis sets used were triple-ζ for the Fe atoms, double-ζ plus polarization for the CO ligands, and double-ζ for the Cp ligands. Geometries were fully optimized using gradient techniques under the constraint of C_2 symmetry.

§ The ^{3}B state is not the lowest energy triplet state of **3**. The lowest-energy triplet state, $^{3}B_1$, which we calculate to be *ca.* 20 kcal mol^{-1} (1 cal = 4.184 J) lower than the ^{3}B state, corresponds to a doubly bridged C_{2v} structure, like the ground state. We propose that the irradiation of **2*** produces both ^{3}B unbridged and $^{3}B_1$ bridged **3***. We further propose that the latter state, which we do not observe experimentally, undergoes a rapid, essentially barrier-free back-reaction with CO to reform **2***. A complete analysis of the excited states will be provided in a separate publication.

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Received in Bloomington, IN, USA, 28th August 1997; 7/06303B