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Inorganica Chimica Acta 334 (2002) 371–375

Inorganica Chimica Acta

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Observation of the photogenerated CO-loss intermediate from $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ via time-resolved IR spectroscopy

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Received 4 December 2001; accepted 21 January 2002

With thanks to Professor Andrew Wojcicki, our colleague, our mentor, and, most of all, our friend

Abstract

Nanosecond time-resolved IR (TRIR) measurements were performed for both $[CpFe(CO)(\mu\text{-}CO)]_2$ (**1**) and $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (**4**). The results obtained for **1** are consistent with those previously reported. The TRIR spectrum of **4** in cyclohexane at room temperature ($\lambda_{exc} = 355$ nm) both under argon and in CO atmosphere is consistent with the formation of the triply-bridged intermediate $[CpFe]_2(\mu\text{-}CO)_2(\mu\text{-}CHCH_3)$ (**5**) that results from loss of CO. The IR absorption peaks observed at 1840 and 1808 cm^{-1} in the TRIR spectrum of **5** are similar to those previously reported in matrix isolation experiments and the lifetimes are consistent with published time-resolved data in the visible region. In addition, DFT calculations result in the calculated frequencies of 1842 and 1810 cm^{-1} for the predicted $^3B_2$ ground state of the structurally related $[CpFe]_2(\mu\text{-}CO)_2(\mu\text{-}CH_2)$ complex. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Organometallic photochemistry; Dinuclear complexes; Time-resolved IR spectroscopy; Density functional theory

1. Introduction

$[CpFe(CO)(\mu\text{-}CO)]_2$ (**1**; $Cp = \eta^5\text{-}C_5H_5$), which exists as *cis* and *trans* isomers, has been one of the most studied organometallic compounds since it was first reported in 1956 [1,2]. As first elucidated by Caspar and Meyer [3], **1** exhibits rich photochemistry in fluid solution that is dominated by two distinct processes, namely homolysis to the mononuclear radical $CpFe(CO)_2$ (**2**) and ligand loss to form the unsaturated dinuclear product $Cp_2Fe_2(\mu\text{-}CO)_3$ (**3**) (Scheme 1) [4]. These photochemical products have also been detected using resonance Raman spectroscopy in solution [5] and in matrix-isolation experiments in solid CH_4 or PVC films at 20 K and in hydrocarbon glasses at 77 K. Experiments by Wrighton et al. [6] and by Rest et al. [7] suggested that, in rigid hydrocarbon matrices, **3** is formed specifically from *trans*-**1** whereas *cis*-**1** does not exhibit CO-loss photochemistry. More recently, we have shown that in softer hydrocarbon matrices, **3** is formed from both *cis*-**1** and *trans*-**1**, and that **3** can undergo a second photochemical CO loss to form $Cp_2Fe_2(CO)_2$ [8]. Compound **3** is unusual inasmuch as it has a triplet ground state, which results from the high pseudo-D_{3h} symmetry of this photoproduct [9].

The room temperature solution photochemistry of **1** has been recently investigated with time-resolved infrared spectroscopy (TRIR) on the microsecond [10], nanosecond [11], picosecond [12], and femtosecond [13] time scales. These studies show that 308 nm photolysis of **1** in a CO atmosphere generates both the short-lived radical **2** (1935 and 2006 cm^{-1}, $\tau > 10$ μs) and the longer-lived CO-loss intermediate **3** (1824 cm^{-1}, $\tau = 1.25$ ms).[10] The absorption frequencies of **2** and **3** observed in the TRIR spectrum were similar to those reported in the matrix isolation experiments [6], and the kinetics of the formation and decay of the transients were consistent with those from the existing transient absorption data [3]. In contrast, irradiation of **1** with visible light (510 nm) was shown to only result in the cleavage of the Fe–Fe bond to form the mononuclear radical, **2** [11].

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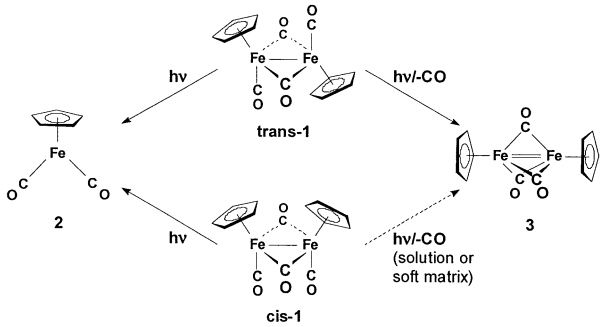
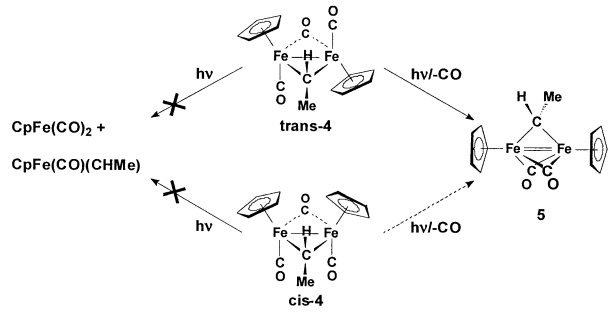
PII: S0020-1693(02)00766-1



Scheme 1. Photochemical channels for $[CpFe(CO)(\mu\text{-}CO)]_2$.



Scheme 2. Photochemical channels for $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CHMe)$.

The specific factors that determine how excited-state **1**, **1***, partitions into its two distinct photochemical channels are still poorly understood. One approach to understanding the relationship between the electronic structure of these complexes and their photochemical reactivity has been to replace one of the bridging carbonyl ligands with alternative ligands that provide an electronic perturbation of the reactant and photoproducts. In particular, derivatives of **1** with bridging alkyl and alkylidene groups, which are readily synthesized and allow variable substituents, have the potential to provide deeper insight into the overall reactivity patterns of dinuclear organometallic complexes.

Although there have been several studies concerning the synthesis, thermal reactivity, and electronic structure of the alkyl and alkylidene complexes [14], very little is known about their photochemistry. We have previously reported some of the solution photochemistry of $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (**4**) [15], a compound that is structurally analogous to **1** and also exists as *cis* and *trans* isomers. The electronic spectrum of **4** is virtually identical to that of **1**, which indicates that the electronic structures of **4** and **1** are very similar. However, alkylidene ligands do not undergo the facile bridging-to-terminal conversion that CO ligands do, so we anticipated different photochemistry for **4** than was observed for **1**. Indeed, bulk irradiation experiments showed that compound **4** does not undergo fragment crossover when irradiated with $Mn_2(CO)_{10}$, $[Cp'Fe(CO)(\mu\text{-}CO)]_2$ ($Cp' = C_5H_4Me$), or $[Cp^*Fe(CO)(\mu\text{-}CO)]_2$ ($Cp^* = C_5Me_5$), which is strong evidence that the metal–metal bond homolysis channel has been shut down by the presence of the bridging alkylidene ligand. Time-resolved UV–Vis laser flash photolysis of **4** led to a single long-lived photoproduct, which was assigned as the triply-bridged CO-loss intermediate $[CpFe]_2(\mu\text{-}CO)_2(\mu\text{-}CHCH_3)$ (**5**). Matrix photochemical studies of **4** [16] and of $[Cp^*Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ [17] also provide unequivocal evidence for single-CO loss to form species with two bridging CO ligands, consistent with the formation of triply-bridged intermediates. The photochemistry of **4** is summarized in Scheme 2.

The electronic structure of triply-bridged species such as $[CpFe]_2(\mu\text{-}CO)_2(\mu\text{-}CHCH_3)$ is of interest in understanding the relationships between the photochemical reactivity of alkylidene-bridged derivatives of **1** and that of **1** itself. As noted earlier, the CO-loss product of **1**, $Cp_2Fe_2(\mu\text{-}CO)_3$ (**3**), has a triplet ground state.[9] Due to the pseudo-D_{3h} symmetry of **3**, the HOMO is an e″ orbital that is half-occupied by two electrons. The replacement of one bridging CO in **3** with a CHR ligand, as in **5**, reduces the symmetry to C_{2v}, and, therefore, lifts the degeneracy of the e″ orbital. If the splitting is small enough, **5** might also favor a triplet ground state and, therefore, be electronically similar to **3**. In fact, the reactivity of **5** exhibits both similarities and differences to that of **3**, so further studies are warranted to elucidate the spectroscopy and electronic structure of **5**.

In this paper we report the direct observation of the formation and decay of the triply-bridged CO loss intermediate **5** in fluid solution at room temperature. These studies utilize TRIR spectroscopy on the nanosecond timescale in conjunction with density functional theory (DFT) calculations of the vibrational frequencies of the triply-bridged CO-loss photoproduct. These calculations provide excellent corroboration of the spectroscopic results and predict that, in spite of its lower symmetry, **5** has a triplet ground state similar to that of **3**.

2. Experimental

2.1. Materials

$[CpFe(CO)(\mu\text{-}CO)]_2$ (**1**) was purchased from Strem and recrystallized from hexane. $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (**4**) was prepared by methods previously reported and was crystallized twice from hexane [14d]. Hexane was purchased from Mallinckrodt and used without further purification. Cyclohexane was purchased from Aldrich and dried for several days over molecular sieves (Fisher) before use.

2.2. Time-resolved infrared experiments

TRIR experiments were conducted on a JASCO TRIR-1000 dispersive-type IR spectrometer with 6 cm^{-1} resolution as previously described [18], utilizing 355 nm pulses of the Nd:YAG laser (95 Hz repetition rate, 0.6–0.7 mJ per pulse, FWHM ~8 ns) as the excitation source. A reservoir of sample solution (10–15 ml of 0.8 mM $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ or 1.8 mM $[CpFe(CO)(\mu\text{-}CO)]_2$ in cyclohexane) was continuously circulated between two calcium fluoride plates with 0.5 mm path length. Samples were bubbled with argon for at least 15 min immediately prior to the start of each experiment and were kept under slight positive argon pressure throughout the experiment. A similar procedure was followed for the experiments conducted under CO.

2.3. Density functional theory calculations

The DFT calculations were performed using the AMSTERDAM DENSITY FUNCTIONAL (ADF) program, version 2000.01, developed by Baerends and coworkers [19] and vectorized by Ravenek [20], with the numerical integration scheme reported by te Velde and Baerends [21]. The geometry optimization was based on the method of Versluis and Ziegler [22], and the frequency calculations were performed using the method of Fan and Ziegler [23]. For iron, ADF Basis Set IV was used, consisting of a triple-zeta basis. For carbon, hydrogen, and oxygen, ADF Basis Set III was used, consisting of a double-zeta basis augmented with a polarization function. All inner shells were treated with the frozen core approximation, up to 2p for iron and 1s for carbon and oxygen. All calculations utilized the local exchange-correlation potential of Vosko and coworkers [24], corrected by the nonlocal exchange-correlation potential of Perdew and Wang (PW91) [25].

All calculations were performed under C_{2v} symmetry and an integration parameter of eight was used in both geometry and frequency calculations. The self-consistent field was held to a convergence criterion of 10^{-9} au, and a gradient accuracy of 10^{-5} au $Å^{-1}$ for all geometry optimizations. The frequencies were calculated utilizing double-sided displacements.

3. Results and discussion

3.1. Time-resolved IR experiments

The TRIR spectrum of $[CpFe(CO)(\mu\text{-}CO)]_2$ **(1)** recorded by us in cyclohexane at room temperature collected under argon (1 atm) is consistent with those previously reported [9–12]. Both *cis*-**1** and *trans*-**1** exist in equilibrium in this solution, although the *trans* isomer undergoes more facile CO loss to form **3**. Bleaching of the ground state signals from the normal modes of vibration associated with the terminal and bridging carbonyls of *trans*-**1** was observed at 1960 and 1792 cm^{-1}, respectively, which can be fit to a second order decay with $t_{1/2} = 4$ ms. The expected ground state bleaching at 2008 cm^{-1} arising from the terminal CO ligands of *cis*-**1** appears as a weak shorter-lived ($t_{1/2} = 8$ μs) positive signal previously assigned to a superimposed transient arising from the mononuclear product $CpFe(CO)_2$ formed upon Fe–Fe bond homolysis [10]. The growth and decay of the $CpFe(CO)_2$ radical, **2**, with absorption at 1930 cm^{-1} ($t_{1/2} = 7.6$ μs) was observed, as well as a signal at 1824 cm^{-1} assigned to the CO-loss product $Cp_2Fe_2(\mu\text{-}CO)_3$, **3**, with $\tau = 4$ ms. The observed half-lives and peak positions are consistent with those reported previously in cyclohexane under argon.

The ground state and TRIR spectra of $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ **(4)** under an argon atmosphere are shown in Fig. 1. The bleaching of the ground state signal following the laser pulse is observed at 1984 cm^{-1} (*cis*-**4**), 1944 cm^{-1} (*trans*-**4**), and 1796 cm^{-1} (*cis*- and *trans*-**4**). It is evident from the relative intensities of the bleaching signals in the terminal CO region at 1980 and 1944 cm^{-1} that the *cis* isomer is significantly less photoreactive than *trans*-**4**, as is the case for **1**. The signals from a new photogenerated species appear at 1840 and 1808 cm^{-1}. Previous work in a low temperature matrix with **4** resulted in a photogenerated intermediate with IR absorptions at 1832 and 1795 cm^{-1}, assigned to the C_{2v} CO-loss product $[CpFe]_2(\mu\text{-}CO)_2(\mu\text{-}CHCH_3)$ **(5)** [16]. These peaks are readily assigned to the symmetric (A_1) and antisymmetric (B_2) stretching modes of **5**, respectively. Both the bleaching of *trans*-**4** and the positive absorption signals can be fit to a second order decay, and return to the baseline with $t_{1/2} = 400$ μs under argon. These results

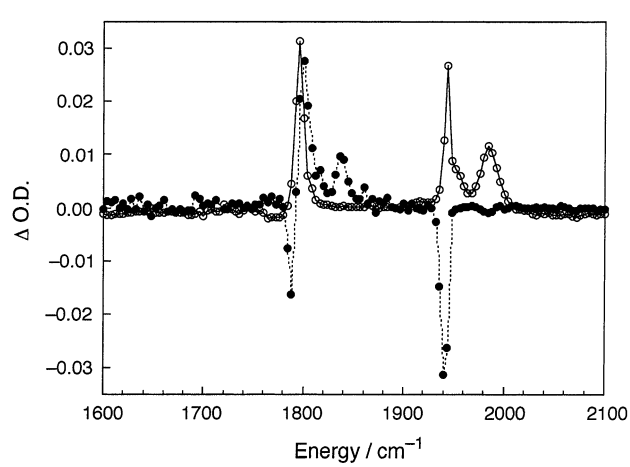


Fig. 1. Ground state (–○–) and time-resolved (–●–) IR spectra of $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ **(4)** in cyclohexane ($\lambda_{exc} = 355$ nm) collected 10 μs following excitation.

indicate that on the microsecond time scale only one intermediate is formed upon excitation, and that it regenerates the ground state of the molecule.

These results are consistent with the published time-resolved absorption spectrum of this compound in the UV–Vis region, which shows evidence for only one intermediate with an absorption maximum at 485 nm [15]. The lifetime reported here for the TRIR signal from **5** under argon is significantly longer than that reported previously by McKee for the transient absorption experiments in the UV–Vis region under a CO atmosphere. However, McKee's experiments are in agreement with the monoexponential decays observed here following bubbling of the solution with CO, with $\tau =$ 100 μs. The lack of evidence for the formation of mononuclear radicals resulting from the homolytic cleavage of the iron–iron bond is also consistent with the transient absorption experiments.

The close agreement between our experiments and those previously reported suggests that the species observed in the r.t. TRIR experiments is the same as that which was trapped in the low-temperature matrix. The lack of a signal in the terminal CO region, as well as the presence of a peak consistent with free CO in the matrix experiments, and the lifetime dependence on CO concentration indicates that the observed intermediate is the triply-bridged CO loss product $[CpFe]_2(\mu\text{-}CO)_2(\mu\text{-}CHCH_3)$ **(5)**. The proposed identity of the transient as **5** is further supported by the DFT calculations discussed below.

3.2. DFT calculations on $[CpFe]_2(\mu\text{-}CO)_2(\mu\text{-}CH_2)$

An intriguing aspect of the comparative photochemistry of **1** and it alkylidene-bridged congener **4** relates to the electronic structures of the resultant unsaturated CO-loss products **3** and **5** (Schemes 1 and 2). As noted earlier, **3** is an unusual example of a paramagnetic 18-electron organometallic complex. The triplet ground state of **3** is a consequence of the D_{3h} $Fe_2(\mu\text{-}CO)_3$ core of the molecule. The HOMO of the molecule is a doubly degenerate e″ orbital that consists of the Fe–Fe π* orbitals stabilized by backbonding to the 2π orbitals of the bridging CO ligands. When one of the CO ligands is replaced with an alkylidene ligand, which we can consider to be neutral, the degeneracy of the Fe–Fe π* orbitals is lifted. Since the vacant π orbital of a neutral bridging CHR ligand is lower in energy and more localized than the 2π orbital of a bridging CO ligand, we anticipate that the Fe–Fe π* orbital that points at the CHR ligand (the 'vertical' π* orbital, π^*_v, with b_1 symmetry) is stabilized more than the π* orbital that can interact only with the bridging CO ligands (the 'horizontal' π* orbital, π^*_h, with a_2 symmetry). Depending on the magnitude of the splitting, **5** could have a singlet ground state ($^1A_1$), corresponding to a $(\pi^*_v)^2(\pi^*_h)^0$ electron configuration, or a triplet ground state ($^3B_2$) resulting from a $(\pi^*_v)^1(\pi^*_h)^1$ configuration. These results will have significance in determining whether the CO-loss photochemistry of **4** follows the same spin potential surface as that of **1**.

We have used DFT calculations on the model C_{2v} complex $[CpFe]_2(\mu\text{-}CO)_2(\mu\text{-}CH_2)$ (**6**) to explore these bonding questions. Optimized structures of both singlet and triplet **6** were determined using methodology that we have used with success previously on photogenerated unsaturated dinuclear organometallic complexes [26]. As anticipated above, the replacement of a bridging CO with a bridging CH_2 ligand leads to a stabilization of the Fe–Fe π^*_v MO relative to the π^*_h MO. The splitting of these MOs is only 0.26 eV, which is small enough to favor a triplet ground state for **6** (Fig. 2). The closed-shell singlet state, in which the π^*_v MO is completely filled, lies only 0.289 eV above the triplet ground state. The predicted Fe–Fe bond length in the triplet ground state of **6**, 2.242 Å, is comparable to that observed experimentally for $[Cp^*Fe]_2(\mu\text{-}CO)_3$ (2.265 Å) [9] and is consistent with an Fe–Fe double bond in **6**.

We have used calculated CO-stretching frequencies as an important diagnostic of the correctness of calculated structures for unsaturated dinuclear organometallic complexes [27]. We were hopeful that calculated CO-stretching frequencies for **6** would provide support for the predicted triplet ground state of the molecule. The calculated CO-stretching frequencies of triplet **6** are 1842 and 1810 cm^{-1} for the A_1 and B_1 modes, respectively. These calculated frequencies are in superb agreement with the observed frequencies of 1840 and 1808 cm^{-1} for **5** from the TRIR experiments. Somewhat surprisingly, the calculated frequencies of singlet **6**, 1842 and 1814 cm^{-1}, are very close to those of the triplet and perforce are also in good agreement with the experimental results. We, therefore, cannot use these calculated frequencies to provide support for the triplet ground state; nevertheless, it is clear that the calculated frequencies provide strong support for the triply-bridged C_{2v} structure of **6** and related intermediates.

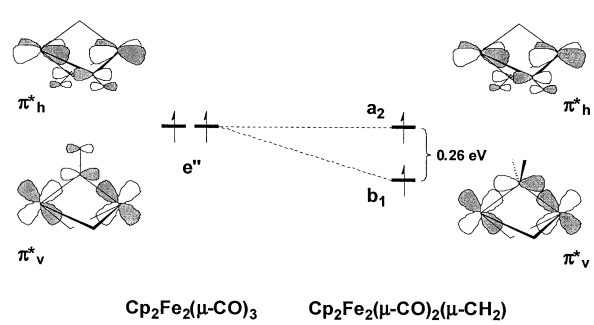


Fig. 2. Energy-level diagram showing the highest filled MOs of $Cp_2Fe_2(\mu\text{-}CO)_3$ (**3**) and $Cp_2Fe_2(\mu\text{-}CO)_2(\mu\text{-}CH_2)$ (**6**).

4. Conclusions

Nanosecond TRIR measurements were performed for both $[CpFe(CO)(\mu\text{-}CO)]_2$ (**1**) and $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (**4**). The results obtained for **1** are consistent with those previously reported. The TRIR spectra of **4** in cyclohexane at r.t. ($\lambda_{exc} = 355$ nm) both under argon and under a CO atmosphere are consistent with the formation of the triply-bridged intermediate $[CpFe]_2(\mu\text{-}CO)_2(\mu\text{-}CHCH_3)$ (**5**) that results from photoinduced loss of CO. The IR absorption peaks observed at 1840 and 1808 cm^{-1} in the TRIR spectrum are similar to those previously reported in matrix isolation experiments and the lifetimes are consistent with published time-resolved data in the visible region. In addition, DFT calculations result in the calculated frequencies of 1842 and 1810 cm^{-1} for the predicted $^3B_2$ ground state of the $[CpFe]_2(\mu\text{-}CO)_2(\mu\text{-}CH_2)$ model complex.

Acknowledgements

C. Turro thanks the partial support for this work from The National Science Foundation (CHE-9733000), National Institutes of Health (RO1 GM64040-01), and The Arnold and Mabel Beckman Foundation Young Investigator Award. Bruce E. Bursten thanks the Ohio Supercomputer Center for a generous grant of computer time.

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