Table I. Unimolecular Losses of Ethene and Hydrogen from RCN/Fe^+ Complexes[a]

	precursor[b]			
	5a	**5b**	**5c**	**5d**
C_2H_4	61	61	68	
$C_2H_2D_2$	39	39		60
C_2D_4			32	40
H_2	73	63	79	
HD	27	37		69
D_2			21	31

[a] Data are expressed in %$\sum$neutral = 100% for each class of species formed. [b] $CH_3CD_2(CH_2)_2CH(CN)C_4H_9$ (**5a**); $CD_3(CH_2)_3CH(CN)C_4H_9$ (**5b**); $CD_3CD_2(CH_2)_2CH(CN)C_4H_9$ (**5c**); $CD_3CD_2(CH_2)_2CH(CN)(CH_2)_3CD_3$ (**5d**).

averaged by using the VG 250/11 data system. All nitriles were synthesized by standard laboratory conditions, purified by GC, and fully characterized by spectroscopic means.

Results and Discussion

The metastable ion (MI) mass spectrum of the Fe^+ complex of 5-cyanononane (**5**–Fe^+) contains only signals due to the losses of H_2, C_2H_4, and CH_4 (Scheme II).[9]

The organization of the discussion of the data, given in Table I for the isotopomers **5a–d** of 5-cyanononane, is such that we will first describe the loss of ethylene.

The identical ratio of the losses of C_2H_4 and $C_2H_2D_2$ from both **5a** and **5b** proves already that the oxidative addition of the terminal $CH_3(CD_3)$ group[10] to the metal ion (Scheme I = step I) is *not* rate-limiting. If this would be the case, one should observe a primary kinetic isotope effect, discriminating against D transfer in **5b**–Fe^+,[11] thus increasing the ratio for loss of $C_2H_4/C_2H_2D_2$ from **5d**–Fe^+ in comparison to **5a**–Fe^+. This is not the case. A kinetic isotope effect is, however, operative in the elimination of $C_2H_{4-x}D_x$ (step III). Loss of C_2H_4 is favored over that of $C_2H_2D_2$ (C_2D_4) by factors of 1.56 in **5a** and **5b** and 2.13 in **5c**, and $C_2H_2D_2$ and C_2D_4 are competitively eliminated in a ratio of 1.50 (**5d**–Fe^+). Slightly smaller secondary isotope effects were observed for the Fe^+-induced eliminations of $C_2H_{4-x}D_x$ from Fe(4-octyne)$^+$ complexes.[4b,c,12] We note that both ethylene and hydrogen eliminations occur without any scrambling.

The hydrogen molecule liberated from **5**–Fe^+ originates exclusively from the ω and $(\omega - 1)$ positions of the alkyl chain, and the neutral is formed in a formal 1,2-elimination. This is convincingly evidenced by the data shown in Table I. As to the rate-limiting step for the generation of hydrogen, we know already from the analysis of the $C_2H_{4-x}D_x$ losses that the insertion step I is *not* rate-determining. This information together with the data for loss of $H_{2-x}D_x$ (x = 0, 1, 2) permit us to solve in an unambiguous way the algebraic equations for step IV (k_H/k_D) and step V (reductive eliminations of H_2/HD and HD/D_2, i.e., k_{H_2}/k_{HD} and k_{HD}/k_{D_2}, respectively). The following kinetic isotope effects are obtained, which demonstrate that both the β-hydrogen transfer *and* the reductive elmination of hydrogen are crucial for the product distribution: (i) step IV, $k_H/k_D = 1.59$; (ii) step V, $k_{H_2}/k_{HD} = 1.70$[13] and $k_{HD}/k_{D_2} = 1.44$.

In conclusion the present data provide the missing link in the understanding of the highly remarkable remote functionalization of saturated nitriles by bare Fe^+ in the gas phase.

Acknowledgment. The generous support of our work by the Deutsche Forschungsgemeinschaft, Fonds der Chemischen Ind., and Stiftung Volkswagenwerk is gratefully acknowledged. We are indebted to Dr. Carlito B. Lebrilla and Karsten Eller for many stimulating discussions and Dr. Thomas Weiske for technical assistance.

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[9] In this article we refrain from discussing the mechanistic aspects of CH_4 loss from **5**–Fe^+. This reaction will be discussed in another context: Czekay, G.; Drewello, T.; Eller, K.; Zummack, W.; Schwarz, H. *Organometallics*, in press.

[10] Insertion of Fe^+ into a *methylene* CH bond as a reaction-initiating step can be excluded as this would result in the generation not of C_2H_4 but rather of higher alkenes.[2d] These products are, however, not observed for **5**–Fe^+.

[11] Kinetic isotope effects $2 \leq k_H/k_D \leq 6$ (depending on the excess energy of the chemically activated organometallic compounds) were reported for β-hydrogen (deuterium) transfer by: Bomse, D. S.; Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 5503.

[12] Schulze, C.; Weiske, T.; Schwarz, H. *Organometallics* **1988**, *7*, 898.

[13] A similar isotope effect was recently reported[12] for the Cr^+- and Mn^+-induced dehydrogeneration of 4-octyne in the gas phase.

Picosecond Infrared Probing of Metal Carbonyl Photodissociation Products

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Abstract: Picosecond time-resolved infrared spectroscopy has been used for the first time to study the spectra and kinetics of the primary products obtained on visible photolysis of $[CpFe(CO)_2]_2$ (Cp = cyclopentadienyl) in cyclohexane. Observations in the terminal CO stretch region show an initially diffuse spectrum that develops with a rise time of 50 ps into two bands at 1933 and 1926 cm^{-1}. No further spectral changes occur within 4 ns. These observations can be interpreted as the production of a structure with Fe–CO bridge bonds broken, but the formation of $CpFe(CO)_2$ is not the primary process; alternative interpretations are discussed.

The photochemistry of transition-metal carbonyls has been studied extensively, often because of its relevance to the understanding of the role such systems play in homogeneous catalysis.[1-3] The aim of such studies is the characterization of both the structures and reactivities of the species produced following photolysis, thereby allowing complete reaction mechanisms to be determined. Several approaches to this problem have been adopted.

The use of low-temperature techniques, including matrix isolation, has allowed the characterization of numerous unstable species since their lifetimes are considerably extended under such

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[1] Wrighton, M. S. *Chem. Rev.* **1974**, *74*, 401.

[2] Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1978.

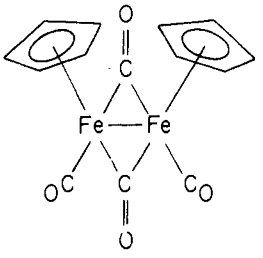
[3] Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187.

0002-7863/89/1511-4563$01.50/0

conditions.[4-6] This allows conventional spectroscopic methods to be used. An alternative approach is that of time-resolved spectroscopy at ambient temperatures. Transient species have been studied routinely by using UV-visible absorption spectroscopy, with time resolution extending into the picosecond regime.[7-11] . However, the broad optical spectra reveal little structural information. Time-resolved vibrational spectra are able to provide this.

Time-resolved Raman spectroscopy, now a well-developed technique that has been used into the ultrafast regime,[12-15] has found little use in the study of metal carbonyls, in part because of their high photosensitivity. In contrast, time-resolved IR methods have been developed specifically for their study in the CO stretch region (2150-1750 cm^{-1}) and have already allowed the characterization of several transient species.[16] The time resolution available with such IR methods is limited by the detectors employed and is typically in the 0.1-1.0-μs regime. To observe the primary event in the photophysics and photochemistry, an IR technique with faster time resolution is required. We have recently reported such a technique[17] and have applied it with picosecond resolution[17-19] to the study of carboxy-heme proteins and hemes. The time resolution is attained by sum-frequency mixing an IR probe beam with a pulse of visible radiation and hence is limited only by the pulse widths attainable from visible wavelength lasers. Indeed, the time resolution of the technique has now been extended to the femtosecond regime.[20] Such a technique offers an opportunity to observe the primary events in organometallic photochemistry.

We report here the first IR study of organometallic photochemistry with picosecond time resolution. The system studied is $[CpFe(CO)_2]_2$ (Cp = cyclopentadienyl) which exists as a mixture of cis (I) and trans (II) isomers in cyclohexane solution.



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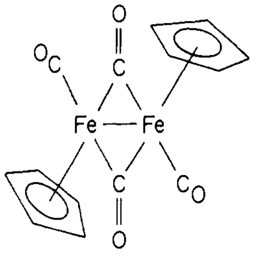

II

This molecule is an important example of a metal-metal bonded dimer and has already been studied extensively by using the methods listed above.[3] This study details the changes occurring on the picosecond time scale in the terminal CO stretch region by measurement of both spectra and kinetics and demonstrates the necessity of ultrafast IR spectroscopy to observe the primary events occurring on photolysis.

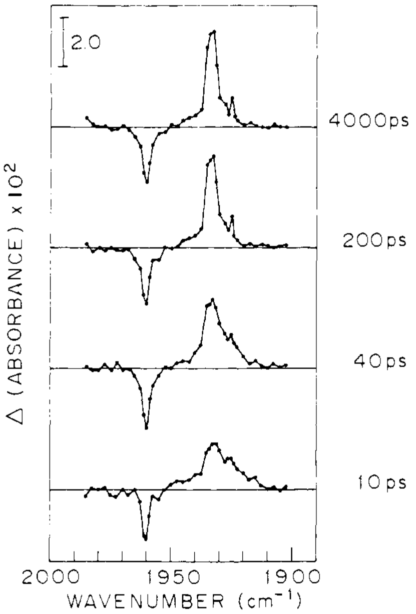

Figure 1. Time-resolved IR spectra of $[CpFe(CO)_2]_2$ in cyclohexane solution taken at the given time delays. The horizontal lines correspond to zero change in absorbance at each time delay, and the actual data points are given as dots.

Experimental Section

The experimental apparatus has been described in detail previously.[17,18] Briefly, the IR probe in the experiment is the output of a tunable diode laser (Spectra Physics, Laser Analytics Division, Bedford, MA) which is passed through the sample collinearly with the photolyzing beam. The photolyzing pulse (558 nm, 25 ps, 5 μJ) is selected at a repetition rate of ca. 700 Hz from the pulse train of a dye laser which is synchronously pumped by the frequency-doubled output of a mode locked, Q-switched Nd:YAG laser. The changes induced in the intensity of the transmitted IR as a result of the optical pumping are monitored by sum-frequency mixing the IR in $LiIO_3$ with a pulse from a second dye laser (560 nm, 20 ps, 1 μJ) synchronously pumped by the same source as the photolyzing laser. The up-converted signal, which is in the visible wavelengths region, is separated from the dye laser beam by a custom-built bandpass filter and then detected with a photomultiplier tube and lock-in amplifier.

The particular diode laser used is continously tunable over the range 1900-1995 cm^{-1}. The diode laser is temperature tuned by varying the temperature of the laser cold head or varying the current across the diode. Thus, current vs frequency tuning curves may be constructed for different cold-head temperatures. We construct such curves by monitoring the wavelength of the up-converted radiation obtained from the IR and a known dye laser wavelength, using a double monochromator. The transient infrared spectra are obtained by incrementally tuning the diode laser through several overlapping temperature/current regions corresponding to different frequency ranges of the diode to span the available region of interest (1900-1985 cm^{-1}). The up-converted signal intensity is monitored both with the photolysis beam incident upon the sample and with it blocked to obtain the change in absorbance. The spectra and tuning curves are calibrated against the known band positions of a ground-state absorption of the trans isomer of $[CpFe(CO)_2]_2$ and of toluene.

Kinetic traces are obtained for a fixed frequency of the diode laser by varying the relative delay between photolysis and up-converting pulses by an optical delay line. All kinetic traces, as well as spectra, were recorded with the relative orientation of the polarizations of the photolysis and IR probe beams at the "magic angle", 54.7°, to avoid effects due to rotational reorientation.

The $[CpFe(CO)_2]_2$ was dissolved to ca. 3×10^{-3} M in deaerated spectral grade cyclohexane (both Aldrich). Both solvent and dimer were used without further purification. Sample solutions were contained in a closed circulating system previously used for handling other air-sensitive systems[18,19] under 1 atm of CO (Airco) and flowed at a rate sufficient to ensure a fresh sample volume for each laser shot. A pathlength of 250 μm was used. Conventional continuous-wave (CW) IR spectra were

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(4) Burdett, J. K.; Poliakoff, M.; Turner, J. J.; Dubrost, H. *Adv. Infrared Raman Spectrosc.* **1976**, *2*, 1.

(5) Burdett, J. K. *Coord. Chem. Rev.* **1978**, *27*, 1.

(6) Hitam, R. B.; Mahmound, K. A.; Rest, A. J. *Coord. Chem. Rev.* **1984**, *55*, 1.

(7) Welch, J. A.; Peters, K. S.; Vaida, V. *J. Phys. Chem.* **1982**, *86*, 1941.

(8) Rothberg, L. J.; Cooper, N. J.; Peters, K. S.; Vaida, V. *J. Am. Chem. Soc.* **1982**, *104*, 3536.

(9) Simon, J. D.; Peters, K. S. *Chem. Phys. Lett.* **1983**, *98*, 53.

(10) Simon, J. D.; Xie, X. *J. Phys. Chem.* **1986**, *90*, 6751.

(11) Simon, J. D.; Xie, X. *J. Phys. Chem.* **1987**, *91*, 5538.

(12) Terner, J.; Stoug, J. D.; Spiro, T. G.; Nagumo, M.; Nicol, M. F.; El-Sayed, M. A. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 1313.

(13) Gustafson, T. L.; Roberts, D. M.; Chernoff, D. A. *J. Chem. Phys.* **1983**, *79*, 1559.

(14) Johnson, C. K.; Dalickas, G. A.; Payne, S. A.; Hochstrasser, R. M. *Pure Appl. Chem.* **1985**, *57*, 195.

(15) Petrich, J. W.; Martin, J. L.; Hovda, D.; Poyart, C.; Orszag, A. *Biochemistry* **1987**, *26*, 7914.

(16) Poliakoff, M.; Weitz, E. *Adv. Organomet. Chem.* **1986**, *25*, 277.

(17) Moore, J. N.; Hansen, P. A.; Hochstrasser, R. M. *Chem. Phys. Lett.* **1987**, *138*, 110.

(18) Moore, J. N.; Hansen, P. A.; Hochstrasser, R. M. *Proc. Natl. Acad. Sci. U.S.A.* **1988**, *85*, 5062.

(19) Hansen, P. A.; Moore, J. N.; Hochstrasser, R. M. *Chem. Phys.*, in press.

(20) Anfinrud, P.; Han, C.; Hansen, P. A.; Moore, J. N.; Hochstrasser, R. M. In *Ultrafast Phenomena VI*; Springer: Berlin, in press.

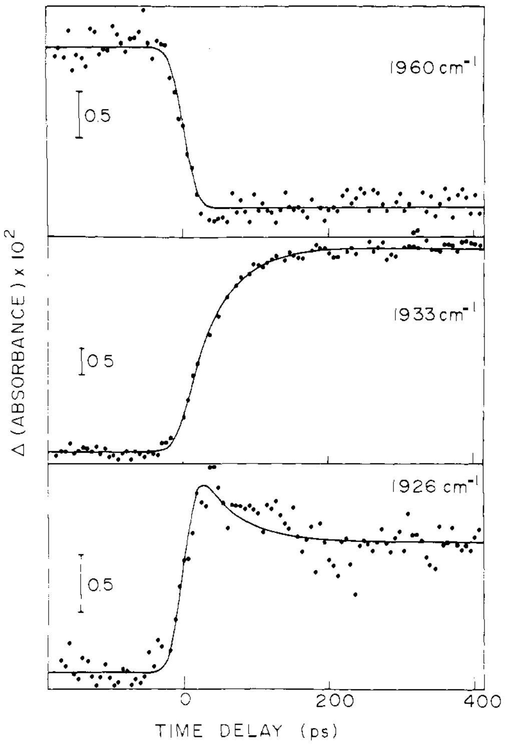

Figure 2. Time dependence of the change in IR absorbance at 1960, 1933, and 1926 cm^{-1}. The actual data points are given as dots. Solid lines show fits to the data: rise time corresponding to the instrument response function with no decay (1960 cm^{-1}); rise time corresponding to the instrument response function convoluted with a single-exponential rise time of 50 ps, again with no decay (1933 cm^{-1}); instrument-limited rise time with a single-exponential decay of 50 ps (1926 cm^{-1}).

recorded on a double-beam instrument (Perkin-Elmer Model 1430) before and after data collection to ensure the integrity of the sample.

Results

The central frequencies (and corresponding half-widths) of the CO stretch bands were obtained from CW IR spectra as 2004 (7), 1960 (9), and 1792 (10) cm^{-1}. Band positions were calibrated against those of polystyrene film and are in agreement with those in the literature.

The transient IR spectra obtained at 10 ps, 40 ps, 200 ps, and 4 ns after optical pumping are displayed in Figure 1. The negative peak centered at 1960 cm^{-1} corresponds to the bleach of the ground-state absorption band of the trans isomer of the starting material. At earliest times, the growth of a broad new absorption peaked at ca. 1933 cm^{-1} is seen. An absorption feature at 1925 cm^{-1}, which is just discernible in the spectrum at 40 ps, is clearly apparent in the spectra at later times. The absorption at 1933 cm^{-1} is seen to sharpen and grow in during the period between 10 and 200 ps following the photolysis pulse. The spectrum reamins essentially unchanged over the time interval 200 ps–4 ns.

The ratios of the integrated intensities of the bleach to new absorption are 4:12 and 5:14 for the 10- and 40-ps spectra, respectively. The integrated intensities of the principal features at 1960, 1933, and 1925 cm^{-1} fall roughly in the order 5:11:1 in both the 200-ps and 4-ns spectra. These values correspond to a ratio of new absorbance to bleach of 3.0 (10 ps), 2.8 (40 ps), and 2.4 (200 ps).

Kinetic traces were obtained at diode laser frequencies of 1960, 1933, and 1926 cm^{-1}. These data are presented in Figure 2 along with the best-fit curves, which were obtained as follows. The change in absorbance at 1960 cm^{-1} was fit well by a Gaussian corresponding to the cross correlation of the dye laser pulses with no recovery of the bleach. This Gaussian was therefore taken as the instrument response function and convoluted with an appropriate sum of exponential functions to generate, by a nonlinear least-squares fitting procedure, the best fit to the experimental data obtained at 1933 cm^{-1}. The change in absorbance at 1933 cm^{-1} exhibits an exponential rise time of approximately 50 ps. An examination of the spectra shows a time dependence in the absorption change at 1926 cm^{-1}. The kinetic trace obtained at this frequency has poorer S/N but clearly displays a pulse-width-limited rise and a decay on a similar time scale to the rise of the absorption at 1933 cm^{-1}.

Discussion

The principal findings of this study are as follows:

(i) The ground state of the trans form of $[CpFe(CO)_2]_2$ is bleached by pulses at 558 nm as is evidenced by the disappearance of the IR absorption at 1960 cm^{-1} corresponding to the terminal CO stretch of the trans isomer.[21]

(ii) No recovery of this bleaching and hence no geminate rebinding of any fragments occurs on the time scale 10 ps–4 ns.

(iii) A diffuse new absorption in the range 1910–1950 cm^{-1} is created concomitantly with the bleaching.

(iv) A more sharply defined spectrum consisting of a line at 1933 cm^{-1} (fwhm 8 cm^{-1}) and a weaker sharper line at 1925 cm^{-1} (fwhm 3 cm^{-1}), superimposed on a background, is formed with a time constant of 50 ps concomitant with the decay of the diffuse spectrum (iii).

(v) No spectral changes occur from 200 ps to 4 ns in the region 1905–1985 cm^{-1}.

(vi) The strongest generated band is at 1933 cm^{-1}, shifted from one at 1938 cm^{-1} reported[22-24] to be present at 5 μs.

(vii) The total integrated intensity of the new features in the spectrum is 2.7 ± 0.3 compared with 1.0 for the bleached terminal CO absorption at 1960 cm^{-1}.

Evidently there are picosecond primary photochemical steps occurring in the photolysis that the previous microsecond work did not expose. At 5 μs the radical $[CpFe(CO)_2]^\bullet$ was identified[22] through its IR band at 1938 cm^{-1}. The triply bridged product $[CpFe(\mu\text{-}CO)_3FeCp]$ (ν_{CO} = 1823 cm^{-1}), previously characterized in low-temperature matrices[25,26] was also identified.[22]

The 558-nm photolysis pulse used in this work is absorbed by both the cis and trans isomers with the extinction coefficient for both isomers approximately (3–4) × 10^2 M^{-1} cm^{-1}.[27] This pulse excites the molecule to $(d\pi)\sigma^*$ type configurations, although detailed assignments are not available.[28,29] If the photoreaction is a one-photon process, the photon energy of 51 kcal mol^{-1} would be barely adequate to break a terminal FeCO bond of ca. 55 kcal mol^{-1}, as found in $Fe(CO)_5$,[30,31] but easily enough to sever bridging Fe–CO–Fe bonds, which are expected to have lower bond energies, even if some vibrational and electronic relaxation were to occur prior to the photodissociation. This proposition is supported by the observation of a CO-loss product only on UV photolysis, while the homolytic cleavage product is observed on both UV and visible wavelength photolysis.[24]

The IR spectrum of $[CpFe(CO)_2]_2$ in cyclohexane has bands at 2004, 1960, and 1792 cm^{-1}. The 2004-cm^{-1} band corresponds to the symmetric stretch of the terminal CO groups of the cis isomer and that at 1960 cm^{-1} to the asymmetric CO stretch of the trans isomer.[21] The solution in cyclohexane at ambient tem-

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(21) Manning, A. R. *J. Chem. Soc. A* **1968**, 1319.

(22) Moore, B. D.; Simpson, M. B.; Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* **1984**, 972.

(23) Dixon, A. J.; Healy, M. A.; Poliakoff, M.; turner, J. J. *J. Chem. Soc., Chem. Commun.* **1986**, 994.

(24) Dixon, A. J.; Healy, M. A.; Hodges, P. M.; Moore, B. D.; Poliakoff, M.; Simpson, M. B.; Turner, J. J.; West, M. A. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 2083.

(25) Hooker, R. H.; Mahmoud, K. A.; Rest, A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1022.

(26) Hepp, A. F.; Blaha, J. P.; Lewis, C.; Wrighton, M. S. *Organometallics* **1984**, *3*, 174.

(27) Abrahamson, H. B.; Palazzotto, M. C.; Reichel, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1971**, *101*, 4123.

(28) Benard, M. *Inorg. Chem.* **1979**, *18*, 2782.

(29) Jemmis, E. D.; Pinhas, A. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2576.

(30) Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1979**, *101*, 5569.

(31) Seder, T. A.; Ouderkirk, A. J.; Weitz, E. *J. Chem. Phys.* **1986**, *85*, 1977.

perature has a trans-to-cis ratio of ca. 1.8.[21] The 1792-cm^{-1} band corresponds to the stretch of the bridged CO's. The trans symmetry (C_{2h}) is such that the symmetric CO stretch of the terminal CO's is IR inactive. There is experimental evidence[32] for the existence of a very small amount (ca. 0.5%) of nonbridged isomer in solution, an amount completely negligible under our experimental conditions. The radical $[\mathrm{CpFe(CO)_2}]^\bullet$ is reported to have a band at 1938 cm^{-1}.[22,24] The 5-cm^{-1} difference between 1938 cm^{-1} and our observed strong band at 1933 cm^{-1} is significant: We observe no band at 1938 cm^{-1} so that if this indeed corresponds to the radical $[\mathrm{CpFe(CO)_2}]^\bullet$ we should conclude that the production of this radical is not a primary process. However, the discrepancy may lie in the accuracy of the reported wavelength measurements or be a result of spectral shifts on the time scale nanoseconds to microseconds.

The increase in IR absorption in the terminal CO stretch region following photolysis indicates clearly that the number of terminal CO groups after photolysis exceeds the two that occur in the trans isomer. The occurrence of two resolved bands in this region indicates that there are at least two types of terminal CO created by the photolysis. Such a situation would arise if the primary photoprocess involved the energetically favorable breaking of just one or both bridged Fe–CO bonds, thereby creating three or four terminal CO units in both the trans and cis isomers. In that case the bleach absorption measures the number of photolyzed trans molecules each with two terminal CO's and the new absorption derives from both cis and trans photolysis products. If one bridge were opened, the ratio of photogenerated to bleached signal, assuming equal IR absorption coefficients and photochemical yields for both cis and trans isomers, would be less than $3 \times 1.8/2 = 2.7$. If two were opened, the ratio would be approximately 3.0 dependent on the angles between CO groups in the radical. Both these estimates are actually quite close to the observed ratio. Of course the CO infrared absorption coefficients will not be independent of structure as assumed in these zero-order arguments. This structure dependence of the IR absorption coefficient could be the cause of the time dependence in the integrated absorption strength as the system composition evolves during and immediately following photolysis.

The early time evolutions shown in Figure 2 can be understood in terms of the dynamics of a structure where first one Fe–CO bridge bond and then the other is broken. The 50-ps narrowing of the spectrum could correspond to the rearrangements of an initially nonhomogeneous distribution of product–solvent structures from photodissociation of cis and trans dimers. The product would be expected to have a polarity different from either the nonpolar trans or polar cis forms, so that significant structural and solvent reorganization would have to occur after photolysis. It could be expected that the configuration of ligands around the iron would be required to change significantly after the FeCO bonds were severed and that solvent molecules could perhaps become coordinated into the structure. There is precedent for metal–cyclohexane coordination.[7,9,10,32,33] The early evolution of the spectrum could incorporate the breaking of the second bridge bond with the present time resolution being too slow to expose distinct spectral features.

There are other possible interpretations of the picosecond spectra and dynamics. The initial spectrum may be due to an excited electronic state with a lifetime of 10–50 ps. The IR spectral evidence for symmetry lowering (i.e., broadening and multiple lines) argues against this interpretation but does not eliminate it. However, the strong band at 1933 cm^{-1} most likely corresponds to the radical $[\mathrm{CpFe(CO)_2}]^\bullet$ with an absorption shifted by ca. 5 cm^{-1} from that previously reported[22,24] at 5 μs and with further dynamics obviously occurring during the period from 4 ns to 5 μs following photolysis. Then the unresolved early time transitions could correspond to the singly bridged short-lived species as previously described. Further work using the methods described here should allow clarification of these issues. Additional ultrafast IR studies of cis bleaching (if any) and the bridging CO region will also help complete the picture. In the present experiments the diode used had too narrow a frequency range to study these regions, but these other experiments could be accomplished with current technology. The structural rearrangements proposed here to account for the $\sim$50 ps growth of the final spectrum could be further evaluated by varying the solvent viscosity.

It is apparent from this study that processes are occurring on the sub-10-ps time scale. Our recent demonstration that IR spectra can be recorded at 100-fs time resolution[20] will allow the study of this system during the evolution of the primary photoproduct and faster than the solvent molecules can coordinate to the exposed metal.

Note Added in Proof. Recent IR spectroscopic investigations by P. Anfinrud and C. Han in this laboratory with 300-fs time resolution have revealed two new transient absorptions at $\sim$1945 and $\sim$1985 cm^{-1}. These features disappear with a time constant of less than 10 ps to yield the spectra observed in the current work. Evidently the earliest time spectrum in Figure 1 is an average over the pulse width of an evolving spectrum. The cis and bridging CO regions of the dicarbonylcyclopentadienyliron dimer have also been examined now. The cis absorption exhibited bleaching which was rapidly ($\sim$2 ps) overwhelmed by an absorption centered at $\sim$2004 cm^{-1}. No evidence was found for a triply bridged carbonyl near 1824 cm^{-1} when using 580-nm excitation. These results indicate, in agreement with the present work, that both bridging bands are probably broken by $\sim$10 ps. These preliminary results will be expanded in a future publication.[35]

The methods introduced here can provide a new dimension to the understanding of photoreactions of organometallic and inorganic coordination compounds.

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(32) Noack, K. *J. Organomet. Chem.* **1967**, *7*, 151.

(33) Bonneau, R.; Kelly, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 1220.

(34) Kelly, J. M.; Long, C.; Bonneau, R. *J. Phys. Chem.* **1983**, *87*, 3344.

(35) Anfinrud, P.; Han, C.; Hochstrasser, R. M. Femtosecond Study of Iron Carbonyls in Solution. In press.