the accuracy of such measurements and enables activation barriers to be identified. In addition, a correlation of the appearance and disappearance of different products permits gross features of the potential energy surfaces to be ascertained.

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Registry No. V^{3+}, 22541-77-1; ethane, 74-84-0; ethene, 74-85-1; ethyne, 74-86-2.

Fast Time-Resolved IR Spectroscopy: The Photolysis of *trans*-[η-$C_5Me_5Fe(CO)_2$]$_2$, the Detection of *cis*-[η-$C_5Me_5Fe(CO)_2$]$_2$, and the Activation Energy for Cis to Trans Isomerization

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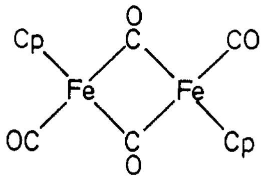
Abstract: Fast (μs) time-resolved IR spectroscopy is used to follow the UV flash photolysis of *trans*-[$Cp^*Fe(CO)_2$]$_2$ (Cp^* = ηC_5Me_5) in cyclohexane solution at room temperature. The primary photoproducts observed on this time scale are $Cp^*Fe(CO)_2\cdot$ (major product) and $Cp^*Fe(\mu\text{-}CO)_3FeCp^*$ (minor product). The $Cp^*Fe(CO)_2\cdot$ radicals dimerize to reform both the cis and trans isomers of [$Cp^*Fe(CO)_2$]$_2$. The previously unknown cis isomer, **2a**, decays into the thermodynamically more stable trans isomer, **1a**, by a first-order process with activation energy 68 ± 5 kJ mol^{-1}.

Although the first organometallic applications of time-resolved IR spectroscopy have only recently been reported, the technique has already led to significant results.[1] The experiments are similar to conventional microsecond UV flash photolysis but the reactive intermediates are detected by IR rather than UV–vis spectroscopy. This has a number of distinct advantages for organometallic systems. (1) The UV–vis absorption bands of organometallic intermediates are generally broad and structurally uninformative, while IR spectra, particularly ν(CO) bands of metal carbonyls, contain considerable structural information. (2) IR bands, even in the gas phase, are relatively narrow so that it is often possible to distinguish several different intermediates by scanning quite a restricted wavenumber region of the spectrum. (3) Matrix isolation experiments[2] have provided a large body of highly diagnostic IR data for organometallic intermediates and these data can often be used directly to identify transient species in time-resolved IR experiments.

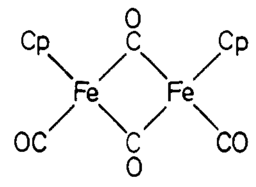
Time-resolved IR is particularly fruitful in the elucidation of the photochemistry of dinuclear transition-metal carbonyls. While matrix isolation only supplies structural information about CO-loss products (radicals are not observed because the "cage effect" promotes recombination), time-resolved IR allows study of all the primary photoproducts. One can obtain a valuable insight into the relative importance of CO loss and metal–metal bond homolysis in each system,[3-6] and furthermore, the well-separated ν(CO) IR bands can be used to monitor the thermal reactions of the various photoproducts. We are currently exploring the reactivity of 17e$^-$ species, such as (ηC_5H_5)$Fe(CO)_2\cdot$, toward various ligands.[6]

In this paper, we concentrate on a different aspect of dinuclear carbonyls, intramolecular isomerization. In particular, we contrast the behavior of [$Cp^*Fe(CO)_2$]$_2$, Cp^* = ηC_5Me_5, and its hydrogen analogue [(η-C_5H_5)$Fe(CO)_2$]$_2$. In room temperature solution only the trans isomer of [$Cp^*Fe(CO)_2$]$_2$ (**1a**) is stable,[7] while [(η-C_5H_5)$Fe(CO)_2$]$_2$ exists as a mixture of both cis and trans isomers,[8] **2b** and **1b**. The interconversion of these two isomers, **2b** $\rightleftarrows$ **1b**, has been extensively studied by ^1H and ^{13}C NMR[8,9] and is one of the classic examples of fluxional behavior.



trans

1



cis

2

a Cp = ηC_5Me_5

b Cp = ηC_5H_5

Here, we use time-resolved IR spectroscopy to show that the predominant photolytic process for *trans*-[$Cp^*Fe(CO)_2$]$_2$ (**1a**) is formation of radicals $Cp^*Fe(CO)_2\cdot$ and that both the cis and trans isomers **2a** and **1a** are formed when these radicals recombine. The

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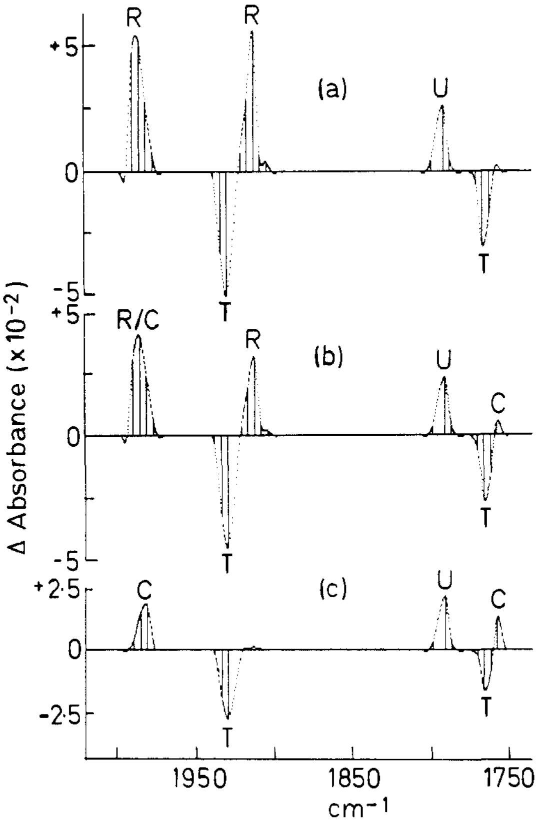

Figure 1. Time-resolved IR spectra of $[Cp^*Fe(CO)_2]_2$ (2×10^{-4} M) in cyclohexane solution. The spectra correspond to the following delay times after the UV flash: (a) 10 μs, (b) 25 μs, and (c) 500 μs. Bands are labeled T (*trans*-$[Cp^*Fe(CO)_2]_2$), R (the radical $CpFe(CO)_2\cdot$), U (the unsaturated complex $Cp^*Fe(\mu\text{-}CO)_3FeCp^*$), and C (*cis*-$[Cp^*Fe(CO)_2]_2$). (Details of how the "point-by-point" spectra were obtained are given in the Experimental Section.)

previously unknown cis isomer, **2a**, rapidly reverts to the trans, **1a**, and we have obtained the activation energy for this process, **2a** → **1a**, by measuring the rate of isomerization at different temperatures.

Experimental Section

Apparatus. The general problems of building time-resolved IR spectrometers have been discussed in detail elsewhere.[1] Our own apparatus uses a UV flash lamp (Noblelight/Applied Photophysics 100J, 8 μs fwhm) as a photolysis source and a CO laser (Edinburgh Instruments PL3, with low temperature cooling[10]) as the IR monitoring beam. The apparatus has been described previously[5] but has since been somewhat modified. We now use a different HgCdTe IR detector (Infrared Associations Inc., HCT-100) with a home built preamplifier (1 MHz-5 Hz bandwidth) and a redesigned optical system which gives much improved S/N. Most measurements can now be made on single shot (i.e., an absorbance change of only 2×10^{-3} can be measured with an S/N ratio of 5).

Presentation of Spectra. For each flash of the UV lamp, the IR transmission is measured at *one* IR wavelength. A full spectrum has to be built up point-by-point, in our case, using IR lines ~4 cm^{-1} apart. The resulting spectrum therefore has a "resolution" of ~8 cm^{-1}. However, because each trace also provides kinetic data about the decay of the species, it is often easier to unravel overlapping absorptions in a time-resolved spectrum than in a similar conventional spectrum. Since our detector is ac-coupled, the "point-by-point" spectrum only registers *changes* in IR transmission; species destroyed by the UV flash appear as negative peaks, while photoproducts appear as positive absorptions. In Figure 1, the *measured* IR signals are shown as solid lines and these have been interpolated by using a "cubic spline" to produce more recognizable spectra.

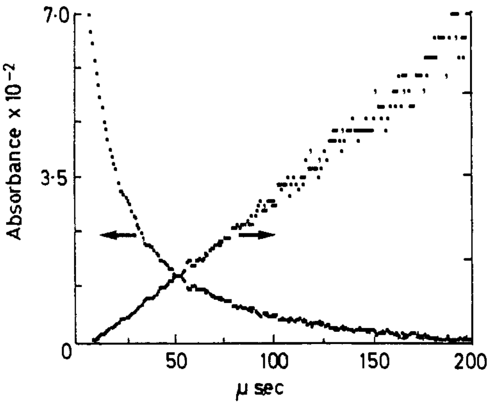

Figure 2. Traces showing the IR signal, 1916 cm^{-1}, due to the decay of the radical $Cp^*Fe(CO)_2\cdot$ and the fitting of this decay to second-order kinetics. (Note that the scatter of points at the upper right hand side is digitization noise of the transient digitizer.)

Table I. Wavenumbers[a] (cm^{-1}) of $[(\eta\text{-}C_5Me_5)Fe(CO)_2]_2$, $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$, and Their Photoproducts in Cyclohexane Solution at 25 °C

	Cp = η-C_5Me_5[b]	Cp = η-C_5H_5[c]
trans-$[CpFe(CO)_2]_2$	1928 1765	1960 1792
$CpFe(\mu\text{-}CO)_3FeCp$	1790[d]	1823
$CpFe(CO)_2\cdot$	1984 1915	2004 1938
cis-$[CpFe(CO)_2]_2$	1981 1756	2004 1792[e]

[a] Band positions ±2 cm^{-1}. [b] This work. [c] Reference 5. [d] 1785 cm^{-1}, methylcyclohexane, low temperature. Reference 13. [e] Coincident with ν(CO) bridging of trans isomer.

Kinetic Measurements. All kinetic measurements were made on the average of four UV flashes with the IR signal digitized on a Datalab DL902 8-bit transient digitizer. The evacuable IR cell, 4 mm path length, was heated when necessary with heating tape and the temperature was measured with a Comark electronic thermometer, type 1605 Cr/Al. In the Arrhenius experiment, the largest source of error was uncertainty in the temperature of the solution.

Chemicals. $[Cp^*Fe(CO)_2]_2$ (Strem Chemicals) and cyclohexane (BDH "Aristar" grade) were used without further purification. Solutions (2–6 $\times 10^{-4}$ M) were degassed under vacuum. All experiments were carried out under an Ar atmosphere (Messer Griesheim).

Results

Primary Photoprocesses. Figure 1a shows a "point-by-point" IR spectrum corresponding to a time 10 μs after the UV flash photolysis of $[Cp^*Fe(CO)_2]_2$. There are two strong negative peaks (labeled T) due to isomer **1a** of $[Cp^*Fe(CO)_2]_2$ which is destroyed by the flash and three strong positive bands due to primary photoproducts. The lowest frequency of these product bands (labeled U) can be unequivocally assigned to $Cp^*Fe(\mu\text{-}CO)_3FeCp^*$, a CO-loss product[11,12] which has recently been isolated and characterized by X-ray crystallography.[13] The other two bands (marked R) can be reasonably assigned to the 17e$^-$ radical, $Cp^*Fe(CO)_2\cdot$, for the following reasons. (1) The two bands belong to the same short-lived species and decay at the same rate, by good second-order kinetics (see Figure 2). (2) The rate of decay is unaffected by added pressures of CO.[14] (3) Two IR ν(CO) bands are predicted for $Cp^*Fe(CO)_2\cdot$ and the observed wavenumbers are close to those which would be expected by analogy with $(\eta\text{-}C_5H_5)Fe(CO)_2\cdot$,[5] since all ν(CO) bands for η-

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(14) There is some evidence that $Cp^*Fe(CO)_2\cdot$ can undergo very rapid CO exchange with free CO dissolved in the solution but the overall decay rate is unaffected (see ref 6).

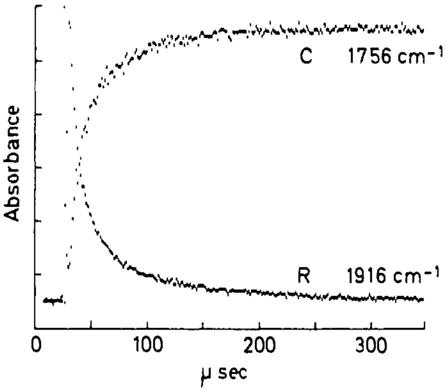

Figure 3. Kinetic traces showing the simultaneous decay of the radical $Cp^*Fe(CO)_2\cdot$ (R) and the generation of the cis isomer of $[Cp^*Fe(CO)_2]_2$ (C). Note that the traces have been normalized to the same absorbance. The IR wavenumbers used to monitor these processes are marked on the traces.

C_5Me_5 species are generally 20–30 cm^{-1} lower than those of the corresponding η-C_5H_5 compounds (see Table I).

Thus, like $[(\eta C_5H_5)Fe(CO)_2]_2$,[5] there are two primary photochemical pathways for $[Cp^*Fe(CO)_2]_2$.

$$[Cp^*Fe(CO)_2]_2 \xrightarrow{UV} 2Cp^*Fe(CO)_2\cdot$$
$$\xrightarrow[UV]{} Cp^*Fe(\mu\text{-}CO)_3FeCp^* + CO$$

For $[Cp^*Fe(CO)_2]_2$, however, formation of $Cp^*Fe(CO)_2\cdot$ radicals is the predominant pathway, while for $[(\eta$-$C_5H_5)Fe(CO)_2]_2$ bond homolysis and CO loss occur with a similar probability. Thus, matrix isolation, which was invaluable in understanding the CO-loss process,[11,12] clearly did not provide a complete picture of the overall photolysis.

Formation of *cis*-$[Cp^*Fe(CO)_2]_2$ (2a). It is difficult to translate the kinetic data in Figure 2 into a second-order rate constant because the extinction coefficients of the IR bands of $Cp^*Fe(CO)_2\cdot$ are not known. However, a reasonable estimate of the IR molar extraction coefficients would lie in the range 5×10^3 to 5×10^4 M^{-1} cm^{-1}, which would give rate constants for the decay of $Cp^*Fe(CO)_2\cdot$ in the range 5×10^8 to 5×10^9 M^{-1} s^{-1}, close to the diffusion-controlled limit.

It can be seen from Figure 2 that almost half of the $Cp^*Fe(CO)_2\cdot$ radicals produced by the UV flash have decayed after 25 μs. After 500 μs virtually all of the radicals have disappeared. Two more IR spectra corresponding to 25 and 500 μs after the flash are shown in Figure 1, b and c. Several points are immediately clear from the changes in the three spectra of Figure 1. (i) The negative peaks, T, become smaller, indicating some regeneration of the trans isomer, **1a**, of $[Cp^*Fe(CO)_2]_2$. (ii) The band U, due to $Cp^*Fe(\mu$-$CO)_3FeCp^*$, is little changed in intensity because, in the absence of added CO, the compound decays very slowly. (iii) A new band, marked C, appears in the bridging ν(CO) region at the low wavenumber end of the spectrum. Less immediately apparent from the spectra is the growth of a new terminal ν(CO) absorption (labeled C), which overlaps the higher frequency band, R, of $Cp^*Fe(CO)_2$. We see, however, that after 500 μs the lower band of R at 1915 cm^{-1} has completely gone, while the almost coincident band (C) remains. What is the origin of these C bands?

Figure 3 shows that the low-frequency C band, 1756 cm^{-1}, grows in at the same rate as the radical $Cp^*Fe(CO)_2\cdot$ decays. (The high-frequency C band overlaps the absorption of the radical too extensively for a good correlation of growth and decay.) Both bands of C decay at the same rate and are clearly due to the same species. The decay follows first-order kinetics and exactly mirrors the growth of the trans isomer, **1a**, of $[Cp^*Fe(CO)_2]_2$ (see Figure 4). The rate of decay of C is unaffected by added CO nor does it depend on the initial concentration of $[Cp^*Fe(CO)_2]_2$. Thus, to summarize:

$$2Cp^*Fe(CO)_2 \xrightarrow{\text{2nd order}} C \xrightarrow{\text{1st order}} [Cp^*Fe(CO)_2]_2$$

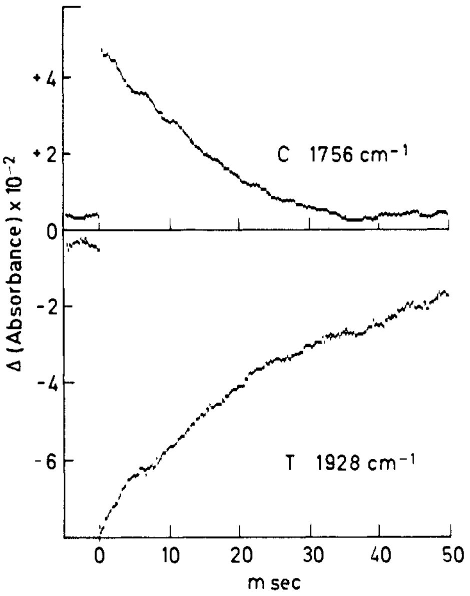

Figure 4. Kinetic traces showing the simultaneous decay of *cis*-$[Cp^*Fe(CO)_2]_2$ and the regeneration of the trans isomer (T). Note that the time scale is much longer than in Figure 3. Note also that the regeneration of the trans isomer (T) is not complete (i.e., the trace does not return to zero) because the decay of the CO-loss photoproduct, $Cp^*Fe(\mu$-$CO)_3FeCp^*$, is slow and thus the photolysis of *trans*-$[Cp^*Fe(CO)_2]_2$ is not totally reversible on the time scale of these measurements.

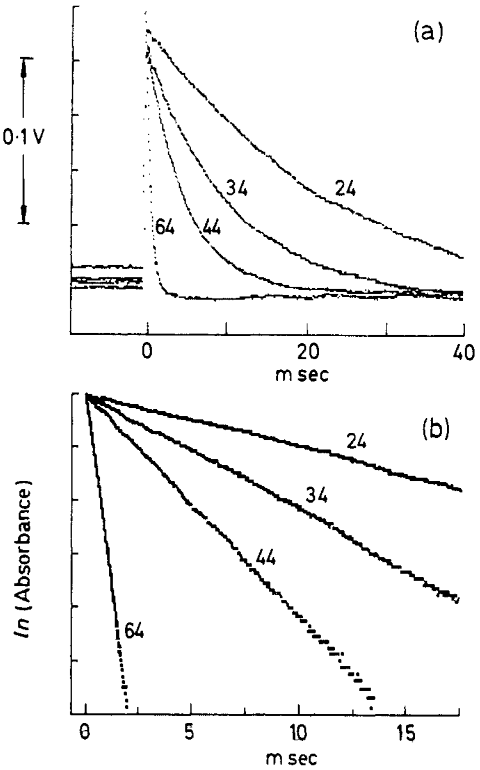

Figure 5. (a) IR detector signals, 1981 cm^{-1}, corresponding to the decay of *cis*-$[Cp^*Fe(CO)_2]_2$ at various temperatures (°C). Unlike the other traces in this paper, signals have not been converted to absorbance and show the raw data as recorded. (b) First-order kinetic traces corresponding to the signals in part a. Note that the time scales in the two parts of the figure are different.

All of the evidence suggests that C is the cis isomer, **2a**, of $[Cp^*Fe(CO)_2]_2$. Furthermore, the IR bands of C are ~30 cm^{-1} lower in frequency than the ν(CO) bands of the cis isomer of $[(\eta$-$C_5H_5)Fe(CO)_2]_2$, a shift similar to that observed for the trans isomers **1a** and **1b** (see Table I).

Cis → Trans Isomerization of $[Cp^*Fe(CO)_2]_2$. The rate of decay of the cis isomer, **2a**, shows a substantial temperature dependence,

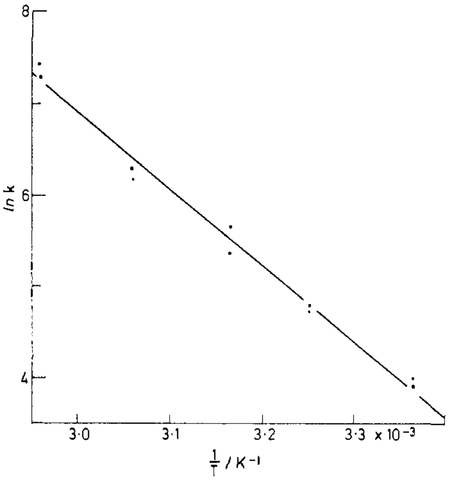

Figure 6. Arrhenius plot for the first-order rate constant of the cis → trans isomerization of $[Cp^*Fe(CO)_2]_2$, over the temperature range 24–65 °C.

over the range 24 to 65 °C (see Figure 5). This has enabled us to obtain the activation parameters from the Arrhenius plot illustrated in Figure 6. We find an activation energy of 68 ± 5 kJ mol^{-1} and a preexponential factor, $5 \times 10^{13\pm1}$ s^{-1}, close to the value anticipated for a unimolecular isomerization.

For the cis → trans isomerization of $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$, **1b** → **2b**, the activation energy has been estimated to be 54 ± 8 kJ mol^{-1} from measurements of ^{1}H NMR line shapes. As might have been anticipated, our value for $[Cp^*Fe(CO)_2]_2$, 68 ± 5 kJ M^{-1}, is significantly higher but it is not yet clear whether this higher activation barrier is due to electronic or steric factors. However, steric factors do not seem to be very important in the dimerization of $Cp^*Fe(CO)_2$, since approximately equal amounts of the cis and trans isomers, **1a** and **2a**, of the dimer are formed.

$$2Cp^*Fe(CO)_2\cdot \rightarrow \tfrac{1}{2}\mathbf{1a} + \tfrac{1}{2}\mathbf{2a}$$

Our activation parameters allow us to estimate the lifetimes of *cis*-$[Cp^*Fe(CO)_2]_2$ at low temperatures. At −67 °C the half-life is 40 min and at −100 °C it is ~50 days! These long lifetimes suggested that the cis isomer may have already been observed, but not identified, in low temperature solution photolysis experiments. Thus, in methylcyclohexane solution, two unassigned IR bands at 1979 and 1753 cm^{-1} have been observed[15] during the photolysis of $Cp^*Fe(CO)_2H$ (at −67 °C) and of $[Cp^*Fe(CO)_2]_2$ in the presence of H_2 (at −78 °C). Although these bands could be due to hydrogen-containing species, they are extremely close in frequency to the IR bands of *cis*-$[Cp^*Fe(CO)_2]_2$ (**2a**), observed by us at room temperature. We are therefore encouraged to suggest that it may be possible to devise a low-temperature preparation of *cis*-$[Cp^*Fe(CO)_2]_2$ and to isolate it as a crystalline solid.

Conclusions

The results described here have a double significance. First, they demonstrate that there is little or no *kinetic* barrier to the formation of *cis*-$[Cp^*Fe(CO)_2]_2$ (**2a**). Only the trans isomer, **1a**, is observed under normal conditions, because **1a** is *thermodynamically* more stable than **2a**. Second, using time-resolved IR spectroscopy, one can make measurements which would be almost impossible with conventional flash photolysis because, by analogy with $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$, the two isomers, **1a** and **2a**, of $[Cp^*Fe(CO)_2]_2$ would be indistinguishable by UV–vis spectroscopy.

We are now applying time-resolved spectroscopy to the reaction of dinuclear carbonyls with reactive substrates, e.g., CH_3CN, $P(OMe)_3$, etc., where the ability to identify intermediates and measure activation parameters should prove particularly powerful tools in unravelling the complex photochemistry.

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Registry No. 1a, 100813-29-4; **2a**, 100896-53-5.

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