Mechanisms of *cis/trans* Isomerization of (η^5-C_5H_5)$_2$Fe$_2$(CO)$_2$(μ-SR)$_2$, Where R = Methyl or *tert*-Butyl, Under Photochemical and Thermal Conditions

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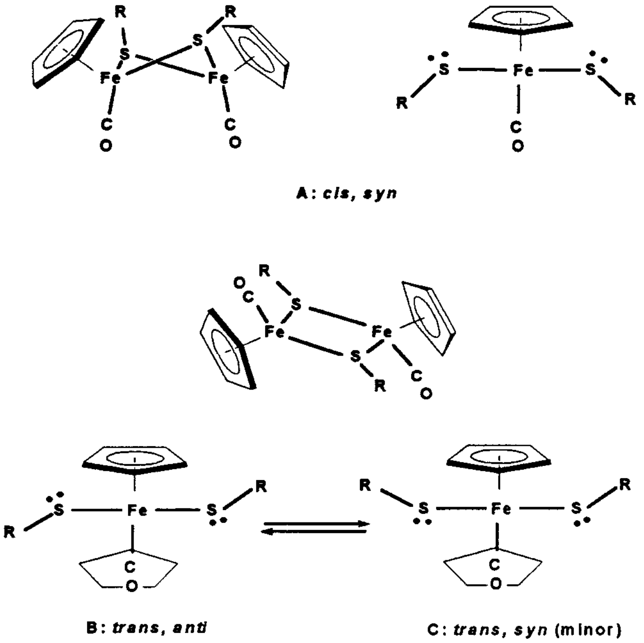
Photolysis of *cis,syn*-(η^5-C_5H_5)$_2$Fe$_2$(CO)$_2$(μ-SMe)$_2$ and mixtures enriched in the *trans,anti* isomer in frozen Nujol matrixes at ca. 90 K has revealed a complex set of wavelength-dependent photoproducts. These photoproducts include three species with bridging carbonyl groups that appear to be a set of conformers differing in the relative orientation of the S−Me groups, a dicarbonyl species that may be a conformer of the *trans,anti* isomer, and two species that appear to have a single terminal carbonyl group. Evidence is also presented for the formation of an IR-silent intermediate, (η^5-C_5H_5)$_2$Fe$_2$(μ-SMe)$_2$. Solution studies have demonstrated that the bridging carbonyl species are sufficiently stable to be observed at room temperature. These bridging isomers readily react with CO to mostly form the *trans,anti* isomer, providing one mechanism for *cis* to *trans* interchange. Photolysis of *cis,syn*-(η^5-C_5H_5)$_2$Fe$_2$(CO)$_2$(μ-SMe)$_2$ in petroleum ether under ^{13}CO at room temperature results in formation of both labeled and unlabeled *trans,anti* isomer, suggesting both a CO-loss and an internal non CO-loss pathway for isomer interconversion. Consistent with this, thermal reequilibration of *trans,anti*-enriched mixtures in petroleum ether under ^{13}CO results in formation of labeled *trans,anti* isomer, labeled (η^5-C_5H_5)Fe(CO)$_2$(SMe), and mostly unlabeled *cis,syn* isomer. Photolysis of *cis,syn*-(η^5-C_5H_5)$_2$Fe$_2$(CO)$_2$(μ-S-t-Bu)$_2$ in frozen Nujol yields a bridging carbonyl photoproduct and the *trans,anti* isomer. Photolysis of the *tert*-butyl derivative in petroleum ether at 0 °C results in formation of the *trans,anti* isomer.

Introduction

Current work in this and other laboratories is directed toward an understanding of the photochemistry of dimetallatetrahedrane compounds having a M_2E_2 core.[1,2] These compounds are expected to form novel CO-loss photofragments and have unique photophysical properties involving orbitals of the tetrahedrane core. Compounds of the general formula (η^5-C_5H_5)$_2$Fe$_2$(CO)$_2$(μ-SR)$_2$ are unusual members of the family of iron/sulfur tetrahedranes in that bonding models predict the HOMO to be Fe−Fe antibonding.[3]

Five conformers might be expected on the basis of the relative orientations of Cp and CO ligands and on the orientations of the S−R groups; however only three of these, Figure 1, have been observed experimentally. Early solution IR and NMR studies[4] established the identities of the *cis,syn* and *trans,anti* isomers, and recent work by Talarmin and co-workers[5] have identified the *trans,syn* isomer as a minor component in equilibrium with the *trans,anti* isomer. A number of



A: *cis, syn*

B: *trans, anti*

C: *trans, syn* (minor)

Figure 1. Observed conformers of (η^5-C_5H_5)$_2$Fe$_2$(CO)$_2$(μ-SR)$_2$.

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molecular structures of derivatives of these compounds have been reported, and in every case the structures correspond to the thermodynamically more stable *cis*,*syn* isomer.[6] In this text we shall use the shorthand of *cis* and *trans* to refer to the *cis*,*syn* and *trans*,*anti* isomers, respectively.

Photolysis of solutions of most derivatives result in the transformation of the *cis* isomer to the *trans* isomer, and in many cases the *trans* isomer is sufficiently stable to be isolated chromatographically. The *tert*-butyl derivative has been observed only in the *cis* isomeric form, and it is assumed that steric considerations destabilize the *trans* isomer. The *trans* isomer of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-SPh})_2$ re-equilibrates to the *cis* isomer by simple first-order kinetics.[7] Activation energies were calculated to be 30.68 ± 0.60 kcal/mol in THF and 31.84 ± 0.54 kcal/mol in CS_2. Although the re-equilibration was somewhat faster in THF, the entropies of activation were found to be sufficiently similar (21.66 ± 0.2 and 24.67 ± 0.3 cal K^{-1} mol^{-1}, respectively) to rule out a THF-containing intermediate.

One report suggests that the *cis*/*trans* ratio in THF and benzene is sensitive to the presence of CO and demonstrates that $(\eta^5\text{-}C_5H_5)Fe(CO)_2(SR)$ can be formed by these compounds under an atmosphere of CO.[8] Treichel and Rublein[9] have found that reaction of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-SMe})_2$ with PPh_3 in hot toluene or refluxing benzene yields $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(SMe)$, indicating that Fe−S bond dissociation can occur under these conditions.

Several examples are known in which photochemical loss of carbonyl ligands from bimetallic compounds having only terminal carbonyl groups results in the formation of photointermediates having bridging or semibridging carbonyl ligands.[10] For the $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-SR})_2$ compounds such a photointermediate would be predicted to have an exact electron count and be stabilized by Fe−Fe, or 3-centered Fe−μ-CO−Fe, bonding.

We are interested in the mechanisms of photochemical processes, particularly those that result in significant molecular rearrangements; thus we believed that application of frozen Nujol matrix photochemistry to this problem might yield evidence for intermediates in these transformations. A subsequent series of solution photochemical and thermal (dark) studies under ^{13}CO have revealed further aspects of these transformations that point to a more complex set of processes than we initially imagined.

Results

Matrix Studies. Photochemical studies were carried out using a liquid nitrogen cooled cryostat designed by Dr. Antony Rest of the University of Southampton. Typical sample preparation and experimental procedures have been reported previously.[11] Photolysis was conducted using a 350 W high-pressure mercury lamp with the irradiation wavelength ranges controlled using band-pass or cutoff optical filters. Band-pass filters typically have a peak transmittance of about 63% and a half-height transmittance (30%) about ±30 nm of the band center. In the text these band-pass filters are listed with their nominal bandwidth of ±70 nm even though relatively little light is transmitted between ±30 and ±70 nm.

Matrix photochemical experiments typically involve the recording of a spectrum of the unphotolyzed sample followed by a 30 min photolysis at a specified wavelength. “Walk-up” experiments, e.g., Exp 1, involve a series of photolyses in which the incident light energy is increased in a series of steps. These experiments make it possible to establish the appearance and disappearance of reactants and photoproducts as a function of light energy. Annealing experiments, e.g., Exps 1, 2, and 6, involve the controlled warming of a sample, typically from 90 K to about 133 K, to allow the Nujol matrix to soften slightly, allowing CO recapture and other rearrangements. Back-photolyses, e.g., Exps 3, 4, and 5, involve the irradiation of a sample previously photolyzed at high energy with relatively low-energy light (550−600 nm). While the photophysics of back photolysis is not well understood, it is known that CO recapture and rearrangement of high-energy species to lower energy species can be triggered by low-energy light. Annealing and back-photolysis experiments are particularly useful in the assignment of bands to photoproducts and to establishing relationships between pairs of photochemically linked species. Because of the complexity of the bands observed in these experiments, all experiments were repeated at least twice and in some cases four times to confirm the presence of small bands. Values of spectral positions indicated in the text are averages of several photochemical runs; the values in the figures may shift 1−2 cm^{-1}. Spectra were recorded at a 4 cm^{-1} resolution.

$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-SMe})_2$[12] and $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-S-t-Bu})_2$[6c] were prepared by standard literature methods. UV−visible spectra were recorded on *cis*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-SMe})_2$ in petroleum ether with bands found at 600 nm ($\epsilon = 142$), 450 nm ($\epsilon = 1500$), and 318 nm ($\epsilon = 11\,100$). King and Bisnette have reported bands at 218 nm ($\epsilon = 48\,100$) and 321 nm ($\epsilon = 15\,500$) in cyclohexane. Photolysis of a sample of the *cis* isomer at 0 °C was found by IR to have resulted in about 60% conversion to the *trans* isomer. A UV−visible spectrum of this *trans*-enriched sample found a new shoulder at 360 nm and a new band maximum at 292 nm that are attributable to the *trans* isomer.

UV−visible spectra of *cis*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-SMe})_2$ were recorded in petroleum ether, benzene, THF, CH_2Cl_2, and acetone. No significant changes in band

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Table 1. Summary of Photolysis Experiments for *cis*- and *trans*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}SMe)_2$[a]

Exp #	λ_{irr} (nm)	A	B	C	D	E	F	G	H
		1957, 1926	1942, 1932	1978, 1951	1777	1784	1793	1972	1964
	Cis photolysis								
1a	600 ± 70	NC							
1b	550 ± 70	↓	↑		↑			↑(w)	
1c	400 ± 70	↓	↑		↓	↑		↑	
1d	350 < 410	↓	↓	↑			↑	↑	↑(sh)
1e	280 ± 10 or 250 to 400	↓	↓	↑		↓	↑	↑	↑(sh)
1f	anneal (ca. 133 K)		↑	↓		↑	↑	↑	
2a	550 ± 70	↓	↑		↑			↑(w)	
2b	anneal (ca. 133 K)	NC	NC		NC			NC	
3a	550 ± 70	↓	↑		↑			↑(w)	
3b	> 600	↑(w)	↑		↓			NC	
4a	400 ± 70	↓	↑	↑	↑	↑		↑	
4b	> 600	↑	↑	↓	↓	↓		↑	
5a	350 to 410	↓		↑	↑	↑	↑	↑	
5b	> 550		↑	↓	↓	↑	↓	↑	
	Cis/Trans mixture photolysis								
6a	550 ± 70	↓	↓		↑	↑		↑	↑(sh)
6b	350 to 400	↓	↓	↑	↓		↑	↑	↑(sh)
6c	anneal		↑	↓		↑	↑	↑	↑(sh)

[a] Free CO bands at 2131 cm^{-1} are observed whenever **A** or **B** bands are found to decrease (w = weak, sh = shoulder).

positions were observed, although the relative intensity of the band at 600 nm appears to be dependent upon solvent polarity and is particularly pronounced in CH_2Cl_2.

The overall appearance of the electronic spectrum of the *cis* isomer is very similar to that of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$.[13] In the case of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ the high-energy transition at 346 nm has been assigned to a $\sigma \rightarrow \sigma^*$ transition, although the actual nature of this transition is more complex than this assignment might suggest.[14] In the case of *cis*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}SMe)_2$, which formally has two more electrons than $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$, the Fe−Fe σ^* (designated b_{3u} by Hoffman et al.)[3] is occupied. This raises the interesting possibility that excitations from the σ^* level may result in an excited state with increased Fe−Fe bonding. Exactly this effect has been observed in studies of the mono- and dications of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}SR)_2$ compounds.[15,5] The lower energy absorptions in the spectrum of the *cis* isomer are probably attributable to $\pi d \rightarrow$ LUMO transitions.

The results of Exps 1−6 and spectral band positions for the various species are summarized in Table 1, and difference spectra for Exps 1b, 1c, and 1f are illustrated in Figure 2. Photolysis of frozen Nujol solutions of *cis*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}SMe)_2$, **A**, at ca. 90 K at $\lambda_{irr} > 600$ nm, Exp 1a, does not result in any changes in the IR spectra of the sample, as established by difference spectral analysis. Increasing the photolysis energy, Exps 1b−e, results in the appearance of bands associated with *trans*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}SMe)_2$, **B**, new bands in the bridging carbonyl region (1777, **D**, 1784, **E**, and 1793 cm^{-1}, **F**), and new bands in the terminal carbonyl region (1972, **G**, and 1964 cm^{-1}, **H**). The band at 1964 cm^{-1} appears as a shoulder in the subtraction spectra in Exp 1, while a more clearly defined band at this position is observed in Exp 6. Exp 6, vide infra, involves a sample that had been photolyzed to convert **A** to **B**; thus the overlap between the band of **H** and the band of **A** being subtracted is less severe in Exp 6.

Annealing samples that had been photolyzed at high energy ($\lambda_{irr} < 410$ nm), Exps 1f and 6c, were characterized by the decrease of a pair of bands at 1978 and 1951 cm^{-1}. Although the relative intensities of these two bands did vary somewhat between experiments, they always decreased together, prompting us to assign them to a single, dicarbonyl species, **C**.

Experiments 2 and 3 examined in detail the relationships among the species formed at the lowest energy, $\lambda_{irr} = 550 \pm 70$ nm, for which photolysis was observed. At this energy, **B** is formed along with one of the bridging carbonyl species, **D**. A trace of **G** is also formed at this energy. Annealing these samples resulted in no apparent change in the bands of these species, but a back-photolysis, Exp 3, $\lambda_{irr} > 600$ nm, revealed that at this very low energy **D** is converted to **B** and a small amount of **A** is re-formed.

Repeated attempts to obtain isomerically pure *trans*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}SMe)_2$ were unsuccessful; thus solutions containing a mixture of the *cis* and *trans* isomers were prepared by photolysis of the *cis* isomer in petroleum ether at −20 °C. A trickle of carbon monoxide eliminated decomposition during photolysis, but did result in the formation of a trace of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(SMe)$. A *cis*:*trans* ratio of about 1:4 was obtained by this method, and these mixtures were used in subsequent studies of the photochemistry of the *trans* isomer.

Perhaps the most significant features of the photolysis of the *cis*/*trans* mixture are observed upon photolysis at $\lambda_{irr} = 550 \pm 70$ nm. Under these conditions both **A** and **B** decrease, while **D**, **E**, **G**, and **H** grow in. Comparing the products of this experiment, Exp 5a, with those of Exps 1b, 2a, and 3a allows us to make a connection between the *cis* isomer, **A**, and the photoproducts **D** and **G**, while the *trans* isomer, **B**, appears related to photoproducts **E** and **H**. Higher energy photolyses of the *cis*/*trans* mixture yield results that are essentially identical to those of the *cis* isomer alone. This is probably due to the fact that photolysis of the *cis* isomer produces the *trans* isomer; thus over the course of the reaction a photoequilibrium between **A**, **B**, and their various photoproducts will be established.

Finally, we note that species **C** and **F** appear to be related in that they both appear upon high-energy photolysis ($\lambda_{irr} < 400$ nm), Exps 1d, 5a, and 6b, and **F** grows in when **C** decreases upon annealing, Exps 1f and 6c. Both **F** and **C** decrease upon back-photolysis, Exp 5b.

In contrast to the complex set of photoproducts found for the methylthiol compounds, the photochemistry of the *tert*-butylthiol compound is simple. These data are summarized in Table 2. Photolysis at $\lambda_{irr} > 550$ nm, Exp

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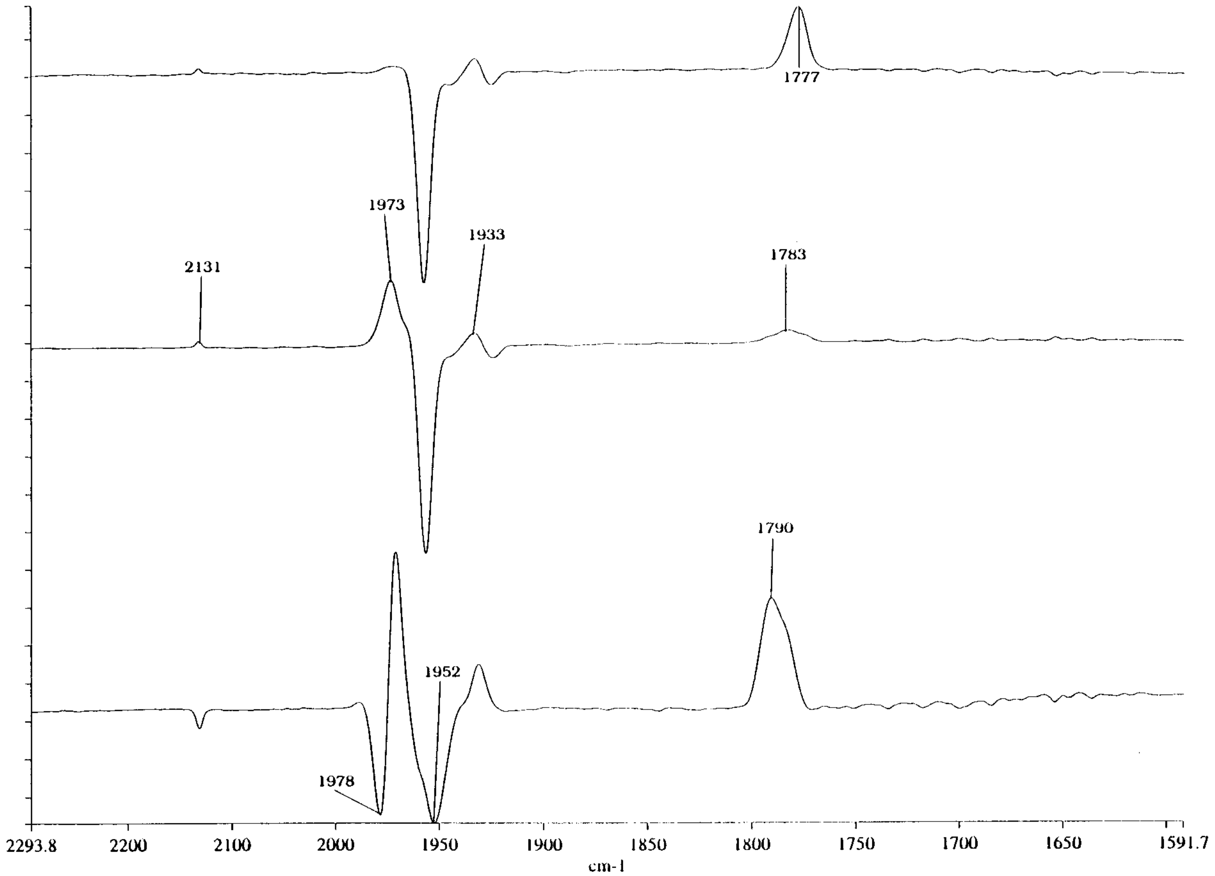

Figure 2. Photolysis of *cis*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}SMe)_2$ in Nujol at ca. 90 K. (a) $\lambda_{irr} = 550 \pm 70$ nm; (b) $\lambda_{irr} = 400 \pm 70$ nm; (c) 250 nm $< \lambda_{irr} <$ 400 photolysis follwed by 10 min anneal (ca. 130 K).

Table 2. Summary of Photolysis Experiments for *cis*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}S\text{-}t\text{-}Bu)_2$

Exp #	λ_{irr} (nm)	1950, 1920	1930	1777
7a	> 500	NC		
7b	550 ± 70	↓ (w)		↑ (w)
7c	450 ± 70	↓	↑	↑

7a, was found to have no observed effect. Photolysis at $\lambda_{irr} = 500$ nm $\pm$ 70 nm, Exp 7b, gives rise to a decrease of the starting material bands at 1950 and 1920 cm^{-1} and appearance of a band at 1777 cm^{-1}, although these changes were only barely above the noise level. Shifting the photolysis window to $\lambda_{irr} = 450$ nm $\pm$ 70 nm, Exp 7c, results in the clear decrease of the bands of the starting material and growth of bands at 2131, 1930, and 1777 cm^{-1}. Further irradiation at higher energies gave no new bands.

Solution Studies. It has been observed by several groups that photolysis of *cis*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}SR)_2$ samples results in formation of the *trans* isomer that reequilibrates to the *cis* isomer upon standing. It appeared to us that two mechanisms might be at work in these processes, so we undertook an examination of these two routes using ^{13}CO as a tag for CO-loss or electron-deficient intermediates.

A petroleum ether solution of *cis*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}SMe)_2$, containing a trace of the *trans* isomer, under 1 atm of ^{13}CO was allowed to stand at room temperature in the dark for 1 h, during which time no significant ^{13}CO was incorporated into the sample. Photolysis of this sample using a 300 W tungsten lamp was followed at 20 min intervals over 1 h. During this time bands associated with *trans*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}SMe)_2$ (1946 and 1934 cm^{-1}) and its ^{13}CO derivative (1902 and 1889 cm^{-1}) were found to grow in along with a trace of the ^{13}CO derivative of the *cis* isomer (1914 cm^{-1}), Figure 3. Integration showed the unlabeled-to-labeled ratio to be about 1:2. After removal of the ^{13}CO gas, the sample was protected from light and allowed to thermally reequilibrate, during which time bands associated with the ^{13}CO-labeled *cis* isomer grew while bands of the *trans* isomer decreased. It is likely that the labeled *cis* isomer observed during photolysis resulted from the thermal equilibration of the labeled *trans* isomer.

A second sample of *cis*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}SMe)_2$ was photolyzed in petroleum ether until approximately a 1:5 *cis*/*trans* ratio was produced. In addition to bands of the *trans* isomer, a small band was observed at 1763 cm^{-1}. This band is reproducible and is not found in solutions containing CO. The sample was wrapped with foil, one atm of ^{13}CO was introduced, and the sample was allowed to stand overnight at room temperature. IR analysis of the solution, Figure 4, established that bands associated with the *trans* isomer and the band at 1763 cm^{-1} declined while new bands assigned to ^{13}CO-labeled *trans* isomer and bands associated with ^{13}CO-labeled $(\eta^5\text{-}C_5H_5)Fe(CO)_2(SMe)$ (1941 and 1880 cm^{-1}) grew. Although bands of unlabeled *cis* isomer (1958 cm^{-1}) grew, there was only a trace of labeled *cis* isomer (1913 cm^{-1}) formed during the re-equilibration process.

A solution of *cis*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}SMe)_2$ was photolyzed ($\lambda_{irr} >$ 400 nm) in petroleum ether at −15

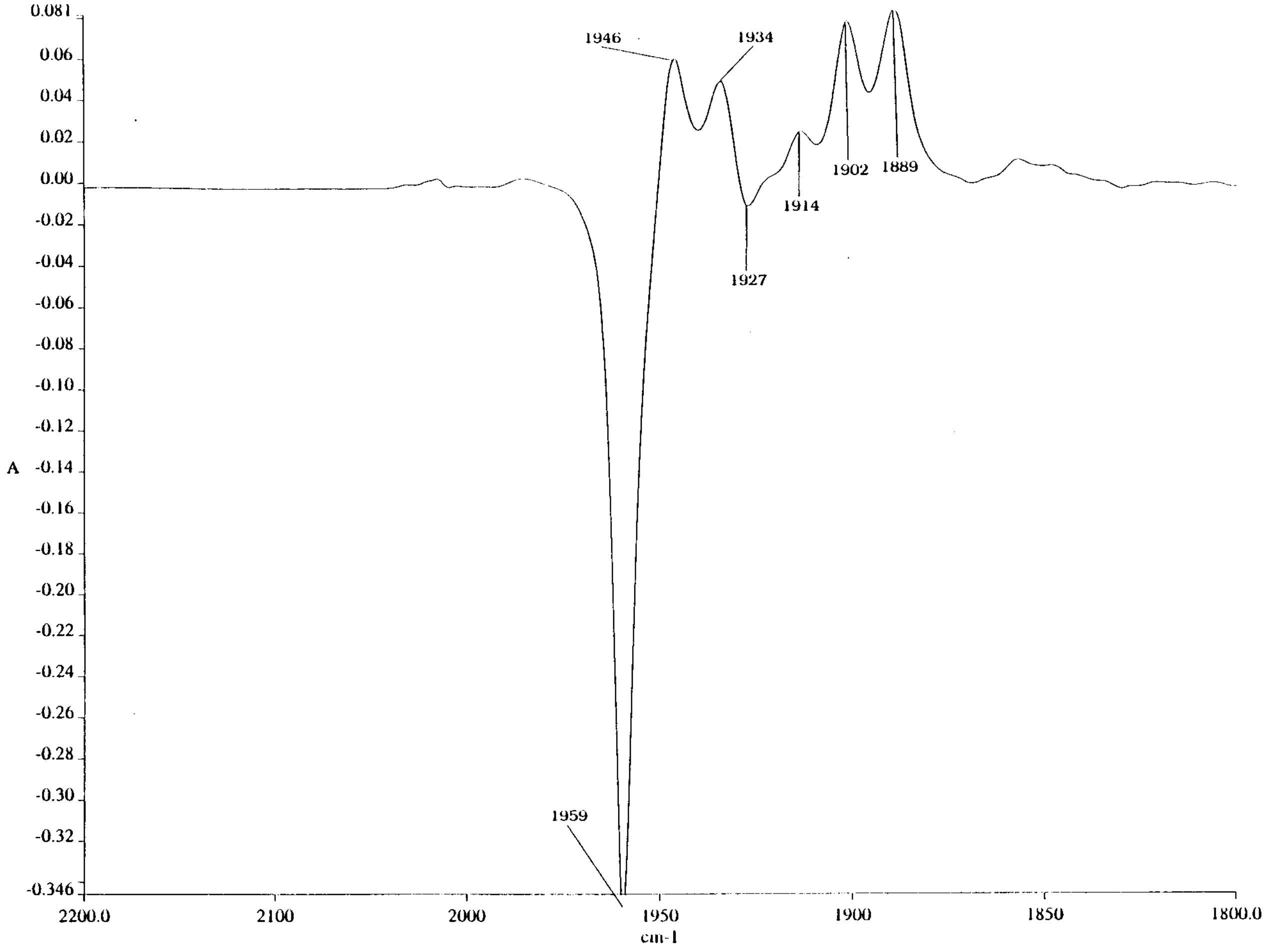

Figure 3. Broad band visible photolysis of *cis*-(η^5-C_5H_5)$_2$$Fe_2(CO)_2$($\mu$-SMe)$_2$ in petroleum ether under 1 atm of ^{13}CO at room temperature.

°C with vigorous sparging by nitrogen until approximately a 1:5 *cis*/*trans* ratio was produced. As before, a small band at 1763 cm^{-1} was observed. After bubbling CO through this solution for 3 min difference IR spectra established that bands at 1791, 1784, and 1763 cm^{-1} decreased while bands for (η^5-C_5H_5)Fe(CO)$_2$(SMe) and *cis*- and *trans*-(η^5-C_5H_5)$_2$$Fe_2(CO)_2$($\mu$-SMe)$_2$ grew, with the *trans* isomer being the dominant product.

Broad band visible photolysis of *cis*-(η^5-C_5H_5)$_2$$Fe_2(CO)_2$($\mu$-S-t-Bu)$_2$ in petroleum ether at 0 °C results in a decrease in bands of the *cis* compound and appearance of bands at 1939 and 1932 cm^{-1} attributable to the *trans* isomer.

Discussion

Matrix Photolysis. Average band positions of the several experiments are presented in Table 1. Low-energy photolysis ($\lambda_{irr} = 550 \pm 70$ nm) into the πd → LUMO transition of the *cis* and *trans* isomers of the methylthiol derivative results in loss of CO and formation of species characterized by bridging carbonyl bands at 1777 and 1783 cm^{-1}, respectively. These two species, **D** and **E**, must differ only in the relative orientations of the S−R groups, Figure 5, and it is possible that they may photochemically interconvert. These species do not recapture CO or undergo rearrangement upon annealing to 133 K, although they do so in solution at low temperature (vide infra).

Low-energy ($\lambda_{irr} > 600$ nm) back-photolysis of a sample containing **D** results in CO capture and formation of **B** as well as a small amount of **A**. It is likely that the **B** that arises from photolysis of **A** at $\lambda_{irr} = 550 \pm 70$ nm is actually produced by the secondary photolysis of **D**. The photochemical sequence **A** → **D** → **B** thus constitutes one mechanism for photochemical *cis* to *trans* interconversion.

Species **G** is observed as a trace product in the photolysis of **A** at $\lambda_{irr} = 550 \pm 70$ nm and grows with increasing incident light energy. Unfortunately the number of species present preclude an analysis of the direct precursor to **G**, or for that matter any of the other species observed upon higher energy photolysis.

Very high energy photolysis and annealing steps reveal the presence of additional species, and it is appropriate to note that **A** and **B** yield almost identical spectra at high energy. A pair of bands at 1978 and 1952 cm^{-1} decrease in all annealing experiments accompanied by the loss of bands associated with “free” CO and the growth of bands at 1972, **G**, 1964, **H**, 1932, **B**, 1793, **F**, and 1784 cm^{-1}, **E**. The decrease in small bands at 1978 and 1951 cm^{-1} was also observed in photoreversal experiments. The differences in relative intensities of these bands in various annealing experiments are probably subtraction artifacts arising from a slightly different ratio of photoproducts depending upon whether the experiment begins with the pure *cis* isomer or a

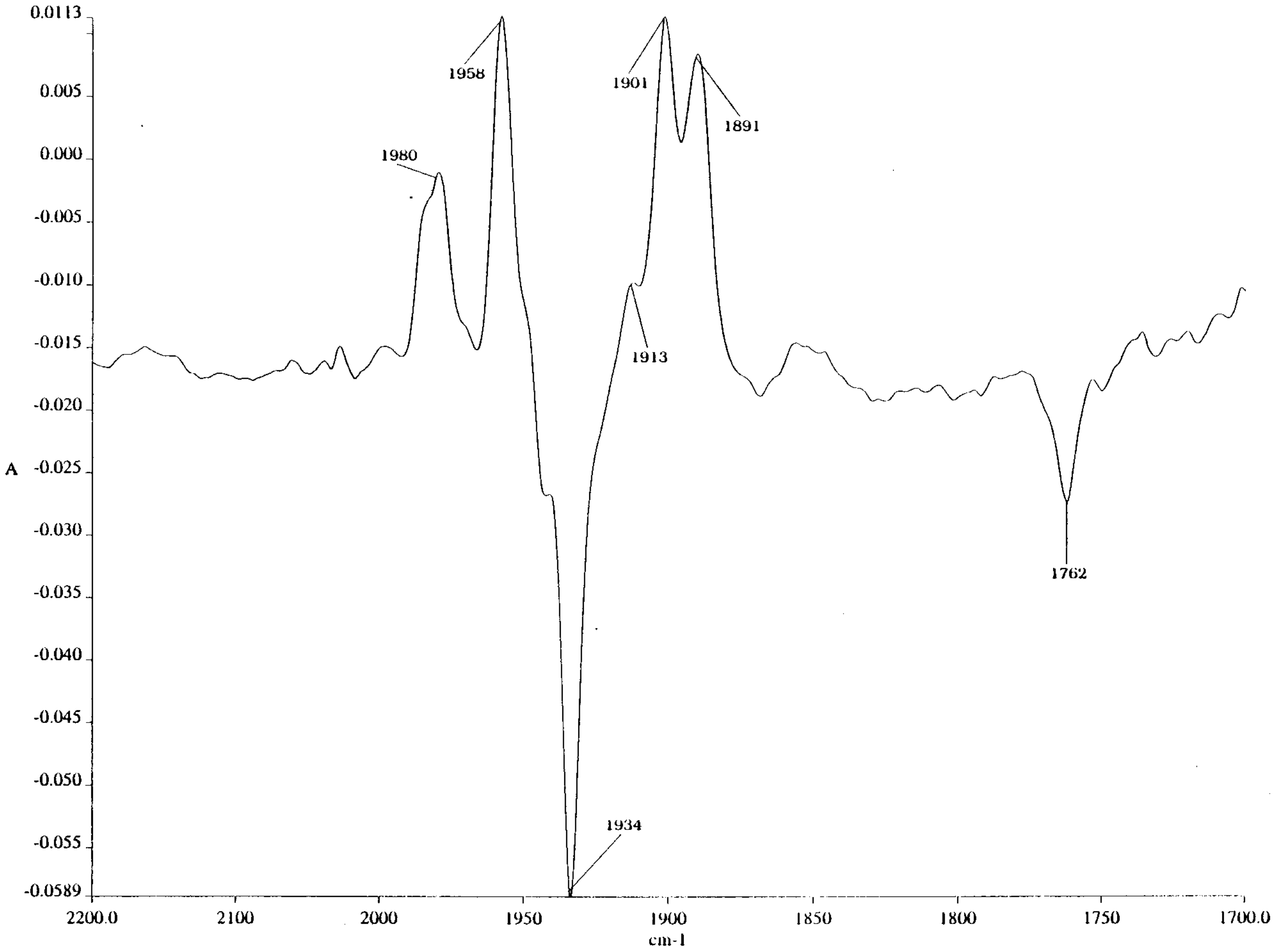

Figure 4. Thermal re-equilibration of a 1:5 *cis*:*trans* sample in petroleum ether under 1 atm ^{13}CO and protected from light at room temperature.

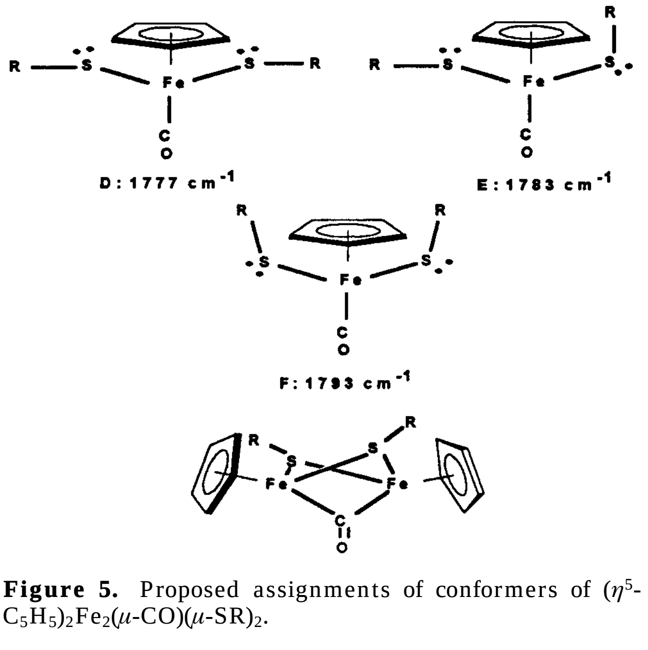

Figure 5. Proposed assignments of conformers of (η^5-C_5H_5)$_2$Fe$_2$(μ-CO)(μ-SR)$_2$.

trans-enriched sample. The band at 1951 cm^{-1} is observed to grow in upon high-energy photolysis, while the related band at 1978 cm^{-1} is occasionally masked by the stronger 1973 cm^{-1} band.

Perhaps the most important feature of the annealing spectra is the disappearance of free CO and the appearance of bands associated with monocarbonyl species, **G**, **H**, **F**, and **E**. Since the only carbonyl-containing species that decreases upon annealing seems to be a dicarbonyl complex, we suggest that an IR-silent species, (η^5-C_5H_5)$_2$Fe$_2$(μ-SMe)$_2$, is also formed on high-energy photolysis and that it is the recapture of CO by this species that is responsible for the appearance of the mono-terminal and bridging carbonyl species. Indeed, (η^5-C_5Me_5)$_2$Ru$_2$(SR)$_2$ compounds are known,[16] and reaction of the R = t-Bu derivative with CO yields *cis*-(η^5-C_5Me_5)$_2$Ru$_2$(CO)$_2$(S-t-Bu)$_2$.[17] Our preliminary matrix photochemical studies on (η^5-C_5H_5)$_2$Ru$_2$(SMe)$_2$ have established that this compound undergoes CO loss to form a bridging carbonyl species at $\lambda_{\mathrm{irr}} = 400 \pm 70$ nm;[18] thus it is likely that both the iron and ruthenium compounds have a sequential photochemistry and thermal chemistry with a set of products, Cp$_2$M$_2$(CO)$_n$(S−R)$_2$, where $n = 0$, 1, or 2.

C may be a thermally unstable, but photochemically accessible isomer of **B**, such as the *trans*,*syn* isomer that

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has been observed in solution, Figure 1, accounting for the formation of **B** upon annealing. We further note that the appearance or disappearance of **C** is always accompanied by the formation of the third bridging carbonyl isomer, **F**.

The three bridging carbonyl species appear to constitute a set of conformers differing only in the relative orientation of the S−R units, Figure 5. If we may assume that the S−R orientation of the parent *cis,syn* and *trans,anti* species is retained in the bridging carbonyl derivatives, **D** and **E**, respectively, then it seems likely that the third isomer must be *syn*, but in the opposite sense of **D**. Again, assuming that the conformation of the bridging derivative reflects the conformation of its dicarbonyl parent, then this provides further support for an assignment of *trans,syn* for **C**.

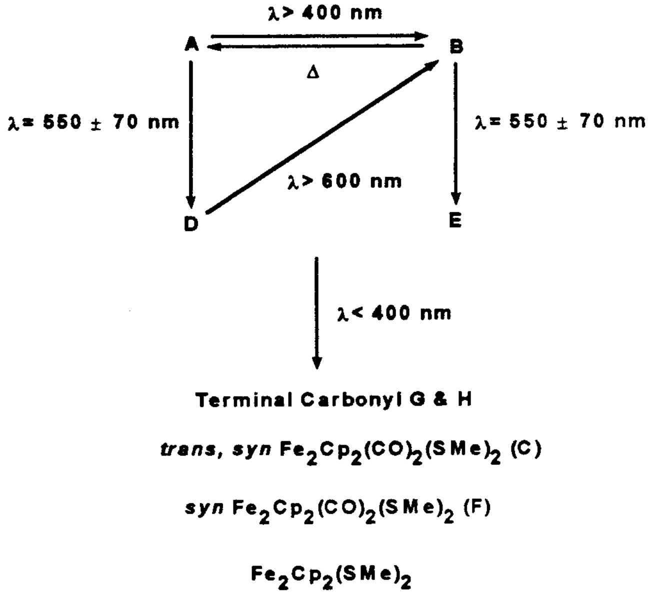
The monocarbonyl species **G** and **H** are particularly unusual for CO-loss fragments in that their stretching frequencies are *above* those of either **A** or **B**. In typical cases, loss of a CO with its strong π-acid properties results in greater electron density being distributed among the remaining carbonyl ligands, and hence a shift to lower frequencies is expected. In the current case, loss of a CO from one iron atom may be compensated for by either a transfer of electron density from the bridging sulfur atoms or even by formation of a dative bond between the iron atoms. The reorganization of bonding upon loss of a carbonyl ligand in these compounds would result in a net loss of electron density by the iron bearing the remaining carbonyl group and would result in a shift of the carbonyl frequency to higher values.

It has been reported that the *tert*-butylthiol derivative exists only in the *cis* form, and all attempts to generate the *trans* form have been unsuccessful. Photolysis of this compound resulting in CO-loss requires somewhat higher energy than for the methylthiol derivative and yields a bridging carbonyl band at 1777 cm^{-1}. A band at 1930 cm^{-1} is very consistent with the formation of the *trans* isomer. There was no evidence to suggest that a terminal carbonyl photoproduct was formed at any energy in the photolysis of the *tert*-butylthiol compound.

An overall mechanism that seems to be consistent with the matrix photochemical data is presented in Scheme 1. While the identities and conformations of the dicarbonyl and bridging carbonyl species discussed above appear to be reasonable, there is no clear assignment possible for the terminal-monocarbonyl species or for the putative IR-silent, and presumed non-carbonyl, species revealed by annealing experiments.

Interchange of the *cis* and *trans* forms certainly occurs in the matrix as a low-energy, two-step, and hence two-photon process via a bridging carbonyl species, but we cannot rule out additional higher energy processes. The very low energies necessary for loss of the first CO from these compounds suggests that the traces of *trans* isomer generally found to accompany the dominant *cis* isomer in synthesis may well arise from photolysis from ambient laboratory light. The failure to observe the *trans*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-S-t-Bu})_2$ at room temperature is probably due to steric considerations that favor the thermal *trans* to *cis* relaxation, and, indeed, we have established that the *trans* species can be observed in solution at 0 °C.

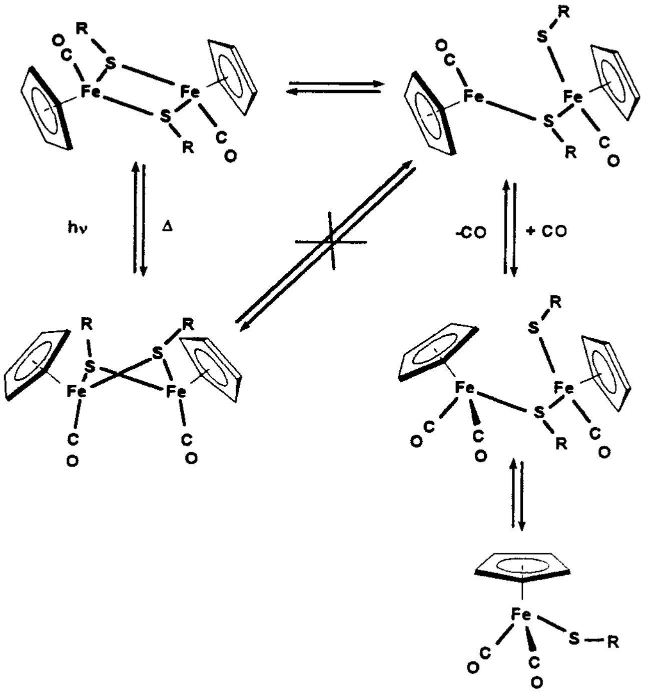
Scheme 1. Photochemical Transformations of $(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-CO})(\mu\text{-SR})_2$ with Increasing Energy



Solution Photolysis Studies. Photolysis of a petroleum ether solution of *cis*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-SMe})_2$ under ^{13}CO established that *trans*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-SMe})_2$ and its ^{13}CO-labeled derivative were formed in about a 1:2 ratio. A trace of ^{13}CO-labeled *cis* isomer was also observed, although it is not clear whether this forms directly by photolysis of the *cis* isomer or by thermal equilibration by the labeled *trans* isomer. The relatively large amount of unlabeled *trans* isomer formed in this experiment requires comment. In these experiments the mole ratio of metal complex to ^{13}CO is about 1:10, and one would expect a similar ratio of unlabeled to labeled product upon photolysis. Although the disparity between the observed and predicted ratios of products may simply reflect an unusually efficient recapture of CO by the photointermediate, there is also the possibility that a direct photochemical interchange between *cis* and *trans* isomers *not involving CO-loss* may be occurring.

Re-equilibration under ^{13}CO of a solution that had been photochemically enriched in *trans* isomer is particularly informative. The bands associated with unlabeled *trans* isomer decrease over time, while bands of labeled *trans*, labeled $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\mu\text{-SPh})$, and *unlabeled cis* isomer grow in. Only a trace of the labeled *cis* isomer is observed. Clearly there are two pathways for reaction of the *trans* isomer, one involving uptake of ^{13}CO, leading to exchange and disruption of the bimetallic species, and a second pathway leading directly to the *cis* isomer without opening up a site for possible exchange. In fact, it seems likely that the small amount of labeled *cis* isomer observed to form comes from *trans* species that had already exchanged by the first pathway. The CO exchange route may involve breaking an Fe−S bond as shown in Scheme 2, while the latter route involves a torsional motion that reverses the relative orientations of the iron fragments. This torsional pathway is entirely consistent with the reported first-order kinetics of this process. While not previously recognized for this class of compounds, similar rotations have been observed under photochemical and thermal conditions

Scheme 2. Proposed Thermal Transformation Pathways for *trans*-$(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)(\mu\text{-}SR)_2$



by Vollhardt, Weidman, and their co-workers[19] for $Ru_2(CO)_4(\eta^5,\eta^5\text{-}C_5H_4C_5H_4)$, Zhou and co-workers[20] for $Fe_2(CO)_4[\eta^5,\eta^5\text{-}C_5H_4\text{-}E_2(CH_3)_2C_5H_4]$, where E = Si and Ge, and ourselves[21] for $Ru_2(CO)_4[\eta^5,\eta^5\text{-}C_5H_4Si(CH_3)_2\text{-}C_5H_4]$. The fulvalene example is particularly relevant since in this case the molecule undergoes a torsional transformation photochemically and relaxes back thermally. In each of the above examples, a ligand σ bond lies close to the M−M bond. Since the HOMO in the $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}SR)_2$ series is Fe−Fe antibonding, excitation of an electron from this orbital, like oxidation, would have the effect of strengthening the Fe−Fe bond, possibly leading to the observed transformation.

In addition to forming the *trans* isomer, tungsten lamp photolysis of *cis*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}SMe)_2$ in the absence of CO gives rise to a small band at 1763 cm^{-1}, which declines when the solution is exposed to CO, and is not observed when solutions containing CO are photolyzed. When this experiment was repeated at −15 °C using a high-pressure mercury lamp and $\lambda_{irr} >$ 400 nm, addition of CO resulted in the decline of bands at 1791, 1784, and 1763 cm^{-1}. Although there is a 14 cm^{-1} difference between the lowest of these bands and species **D** observed in Nujol, the other bands are readily assigned to species **F** and **E**, respectively. Why the band of one of this set of compounds would be shifted and not the other two is not clear.

Finally, we note that contrary to earlier literature reports *trans*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}S\text{-}t\text{-}Bu)_2$ can be formed in solution by broad band photolysis of a 0 °C solution.

Conclusions

The number and variety of possible pathways for the thermal and photochemical reactions of the *cis* and *trans* isomers of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}SR)_2$ were wholly unexpected. Although we have identified a number of photointermediates, additional work remains to be done on examining the lifetimes of these species in solution, the relative importance of CO-loss and torsional transformations in the photochemistry, and the wavelength dependence of the solution processes. Similarly, the torsional process associated with the thermal *trans* to *cis* conversion of these compounds and others that have been reported would greatly benefit by a modern theoretical analysis.

Considering the ease with which the μ-CO species form, it is surprising that they have not yet been isolated. We are currently pursuing this goal as well as investigating the photochemical substitution chemistry of these compounds.

Experimental Section

Apparatus and procedures for Nujol matrix photochemistry have been previously reported.[11] $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}SMe)_2$[12] and $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}S\text{-}t\text{-}Bu)_2$[6c] were prepared by standard literature methods. ^{13}CO was purchased from Cambridge Isotopes. Solutions were prepared under standard Schlenk conditions using dry, air-free solvents. IR spectra were recorded on a Perkin-Elmer 1000 FT IR spectrometer with 4 cm^{-1} resolution. UV−visible spectra were recorded in petroleum ether using a Cary 2200 spectrometer.

Solution Photochemical Studies. *cis*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}SMe)_2$, 50 mg, was placed in a 50 mL Schlenk flask. After evacuation and backfilling the flask with nitrogen petroleum ether, 25 mL, was added. The Schlenk flask was wrapped in foil, and the laboratory was darkened. The solution was subjected to two freeze−pump−thaw cycles followed by introduction of 1 atm of ^{13}CO. The IR spectra of the solution were monitored over 1 h and showed no change over this period. After 1 h the foil was removed from the flask and the solution was photolyzed using a 300 W tungsten lamp placed about 10 cm from the flask. The flask temperature was maintained at room temperature by directing an air stream against the flask. IR spectra were recorded at 20 min intervals, during which time IR bands of *trans*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}SMe)_2$ and its ^{13}CO-substituted derivative were observed. Only a trace of ^{13}CO-labeled *cis* compound was observed.

Thermal Back-Reaction Studies. *cis*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}SMe)_2$, 25 mg, dissolved in petroleum ether was placed in a Griffin-Worden tube. The sample was subjected to two freeze−pump−thaw cycles and back-filled with nitrogen. The sample was immersed in a cold water bath and photolyzed for 30 min. After recording an IR spectrum of the *trans*-enriched solution, the sample was frozen and evacuated and one atmosphere of ^{13}CO introduced to the tube. The sample was wrapped in foil and stored in the dark at room temperature overnight.

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