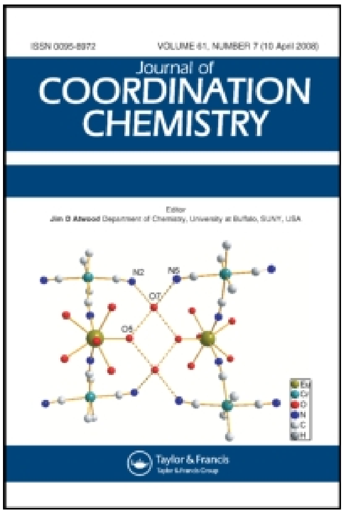

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ON THE MECHANISM OF PHOTOCHEMICAL ALKYNE INSERTION INTO CYCLOPENTADIENYLIRONDICARBONYL DIMER: ALKYNE ADDITION TO A "TIED-BACK" Cp-Fe DIMER†

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The photochemical insertion of phenylacetylene with the "tied-back" dinuclear complex $[(\eta^5\text{-}C_5H_4)_2SiMe_2]Fe_2(CO)_2(\mu\text{-}CO)_2$ (**4**) yields, by X-ray structural analysis, a dimetallacyclopentenone product entirely analogous to that obtained from the photochemical reaction of the alkyne with $(\eta^5 - C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)_2$ (**1**). This result is interpreted as evidence for an alternative pathway for photochemical alkyne addition to **1**. Attempts to identify the photochemical intermediates from **4** have been unsuccessful. A competition study between **1** and **4** indicates that photochemical alkyne insertion into **1** is preferred by approximate ratio of 2:1 over insertion into **4**.

KEYWORDS: dinuclear organometallics, photochemistry, alkyne insertion, intermediates, X-ray structure.

INTRODUCTION

The rich photochemistry of the dinuclear organometallic complex $Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$ (**1**, $Cp = \eta^5\text{-}C_5H_5$) has been and continues to be a very active area of research.[2] Like many dinuclear organometallic complexes, **1** exhibits two primary photochemical channels: (i) homolytic cleavage into 17-electron mononuclear radicals, and (ii) ligand loss to form a coordinatively unsaturated dinuclear complex. In this paper, we shall focus on the latter process and continue our ongoing mechanistic studies of photochemical substitution reactions of **1**.

Caspar and Meyer first recognized that irradiation of **1** leads to loss of CO and the formation of the unsaturated intermediate $Cp_2Fe_2(CO)_3$ (**2**).[3] Subsequent matrix studies by Rest *et al.*[4] and Wrighton *et al.*[5] indicated that **2** is formed exclusively from the trans isomer of **1**. These studies also showed that **2** has a highly symmetric structure that contains three bridging CO ligands and in which the

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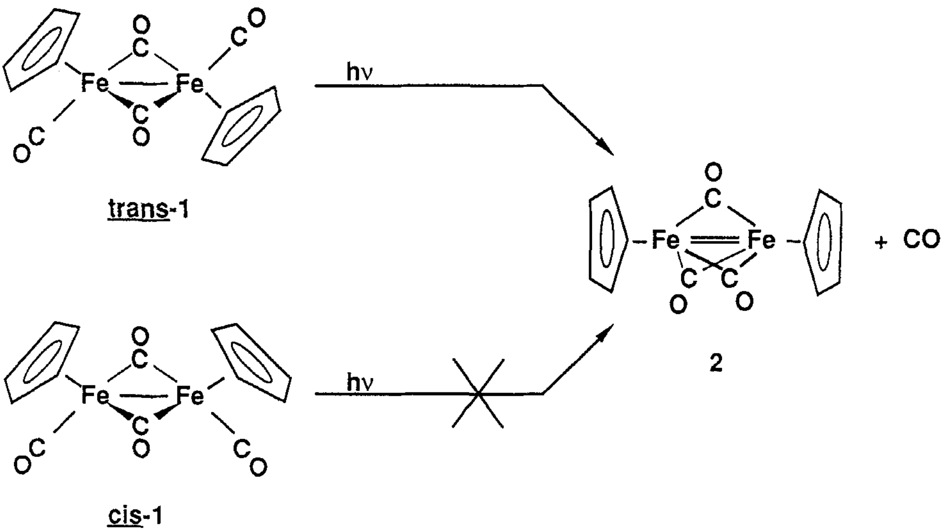
† Dedicated to Professor Theodore L. Brown, friend, colleague, and coauthor, on the occasion of his retirement.

* Author for correspondence.

centroids of the Cp ligands lie on the Fe-Fe axis (Scheme 1). Poliakoff, Turner, *et al.* have used time-resolved infrared (TRIR) spectroscopy on the microsecond time scale to monitor the formation of both **2** and $Cp(CO)_2Fe\cdot$ upon irradiation of **1** in fluid solution.[6] These studies provided strong support for the proposal that **2** is the primary intermediate in the photosubstitution chemistry of **1**, *i.e.* CO loss occurs prior to ligation of the incoming ligand. Previously, we have used microsecond laser flash photolysis to follow the generation of **2** and its irreversible reaction in the presence of alkynes,[7] a reaction that leads to the formation of a dimetallacyclopentenone *via* insertion of the alkyne into one of the Fe-(μ-CO) bonds.[8] We have also demonstrated that irradiation of the bridging-ethylidene analog of **1**, $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)$ (**3**), leads to CO loss and the formation of a similar triply-bridged intermediate, $Cp_2Fe_2(\mu\text{-}CO)_2(\mu\text{-}CHMe)$[9].

Scheme 1



Recent elegant investigations by Rest *et al.*, [10] by Poliakoff, Turner, *et al.*,[11] and by Zhang and Brown[12] have provided compelling evidence for the formation of additional CO-loss intermediates upon the irradiation of **1**. The formation of these intermediates, and the relationship of their formation to that of **2**, adds new complexity to the photochemistry of **1**, as will be discussed later in this paper.

The facts that the formation of **2** occurs exclusively from *trans*-**1** and that **2** can be effectively and irreversibly trapped by reaction with alkynes leads to an intriguing question: What will occur in the photochemical reaction of an alkyne with an analog of **1** that is constrained to be in a *cis* conformation? To address this question, we report the product formed upon irradiation of an alkyne with the "tied-back" iron dimer, $(Cp'_2SiMe_2)Fe_2(CO)_2(\mu\text{-}CO)_2$ (**4**, $Cp' = \eta^5\text{-}C_5H_4$),[13] a model of the *cis* isomer of **1**. The results provide support for the existence of additional pathways in the photochemical ligand substitution of **1**.

EXPERIMENTAL

*Synthesis and Characterization of **4***

Synthetic procedures were performed under water- and oxygen-free conditions using conventional Schlenk techniques. The ligand $(C_5H_5)_2SiMe_2$ is prepared by the reaction of Me_2SiCl_2 with NaC_5H_5 in THF.[14] The crude yellow syrup isolated from this reaction is not analytically pure, but can be used as is. The synthesis of compound **4** used a modification to the original literature methods[13] in which $Fe_2(CO)_9$[5a] and $(C_5H_5)_2SiMe_2$ were refluxed in xylenes. The product was purified by recrystallization from hexane. IR (toluene): ν_{CO} 1998(vs), 1962(m), 1787(vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.46(t), 5.04(t), 0.39(s).

Photochemical Reaction of 4 and Phenylacetylene

Irradiation experiments were carried out in a home-made cylindrical quartz photolysis cell (28 mm diameter by 150 mm length) equipped with a sidearm for connection to a Schlenk line. The source of radiation was a Hanovia 450 W medium-pressure mercury-vapor immersion lamp, which was placed in a quartz immersion well that was cooled by circulating tap water. The sample cell and immersion well were placed into a constant temperature (25±2°C) water bath during irradiation.

Under a backflow of Ar, 0.25 g (6.1×10^{-4} mole) of solid **4** was added to the photolysis cell, which had previously undergone five evacuation/refill cycles with dry Ar. Deoxygenated toluene (50 mL) was added to dissolve the solid, and 0.64 g (6.3×10^{-3} mole) of HC≡CPh (Aldrich) was added. The reaction mixture was irradiated for 10 hr under a slow Ar purge. The solution was then transferred by cannula to a deoxygenated Schlenk flask, and the solvent was removed by vacuum to yield a brown-green oil. The oil was dissolved in CH_2Cl_2 and transferred to a chromatography column (15 cm × 1 cm; Aldrich activated alumina, neutral, Brockmann I, 150 mesh). The column was packed and eluted under a stream of Ar. Elution with CH_2Cl_2 caused the separation of a red band, determined by IR to be unreacted **4**. Switching the eluent to CH_3CN removed a brown band from the column. Evaporation of the solvent yielded a brown solid (**5**). Based on the identification of **5** as $(Cp'_2SiMe_2)Fe_2(CO_3)(HCCPh)$, the yield was 31%.

Analytical data for **5**: IR (CH_2Cl_2), ν(CO) 1981(s), 1800(s), 1750(m) cm^{-1}; ^1H NMR (250 MHz, 25°C, $CDCl_3$), δ 0.34 (s, 3H), 0.55 (s, 3H), 3.85 (m, 1H), 4.32 (m, 1H), 4.71 (m, 1H), 4.82 (m, 1H), 5.23 (m, 1H), 5.72 (m, 1H), 5.82 (m, 1H), 6.39 (m, 1H), 7.19–7.69 (m, 5H), 12.47 (s, 1H); ^{13}C-{H} NMR (62.9 MHz, 25°C, $CDCl_3$), δ −3.50, −2.49 (CH_3), 31.54 (C-C_6H_5), 80.65, 83.65 (C_5H_4-Si), 87.08, 87.77, 88.43, 90.88, 92.71, 92.85, 96.55, 99.01 (C_5H_4), 127.14, 128.02, 128.80 (C_6H_5), 136.95 (ipso C_6H_5), 169.81 (C-H), 210.51 (t-CO), 231.80 (C=0), 261.82 (μ-CO). *Anal.* Calcd. for $C_{23}H_{20}Fe_2O_3Si$: C, 56.94; H, 4.36; Fe, 23.02%. Found: C, 56.50; H, 4.07; Fe, 22.77%.

*Structural Studies of **5***

X-ray quality crystals were obtained by diffusing pentane into a flask containing **5** dissolved in CH_2Cl_2 over a period of several days. A deep red crystal of approximate dimensions 0.35 × 0.28 × 0.15 mm was mounted on the tip of a glass fiber. Diffraction data were collected at −35°C on an Enraf-Nonius CAD-4 diffractometer with MoKα radiation.

Preliminary examination of the reflections unambiguously indicated the monoclinic space group $P2_1/n$ (No. 14). The unit cell parameters were obtained by least-squares refinement of the angular settings (ϕ, κ, ω) from 25 reflections lying in a 2θ range of 24–30°. Intensity data were collected in the ω-2θ scan mode with $4 \leq 2\theta \leq 50°$. No significant decay was observed during data collection. The data were corrected for Lorentz and polarization effects. The intensities were also corrected for absorption by using an empirical method based on the crystal orientation and measured ψ scans. Data reduction, including the empirical absorption correction, and all subsequent calculations were performed using the SDP Structure Determination Package.[15] Crystal and data collection details are summarized in Table 1.

The structure was solved by a combination of direct methods (MULTAN/82) and difference Fourier techniques, and was refined by full-matrix least squares. Analytical atomic scattering factors[16] were used throughout the structure refinement with both the real and imaginary components of the anomalous dispersion included for all atoms. The location of the Fe atoms became apparent on the E-map. The positions of the remaining atoms were determined from a Fourier synthesis that was phased on the metal atoms. Coordiantes of all hydrogen atoms were located directly from the difference Fourier map and were included in the last 5 cycles of refinement (both positions and thermal parameters refined).

The final refinement cycle involved 2807 unique reflections for which $I > 3\sigma(I)$ and 343 variable parameters including the extinction parameter (non-hydrogen atoms were refined anisotropically). For the final least-squares cycle, $R = 0.023$, $R_w = 0.034$, and G. O. F. = 1.503. Selected bond distances and bond angles are tabulated in Tables 2 and 3, respectively.

Table 1 Crystal and data collection details for compound **5**

formula	$C_{23}H_{20}O_3Fe_2Si$
formula weight, amu	484
a, Å	12.198(3)
b, Å	12.761(3)
c, Å	13.806(3)
β,°	109.13(2)
space group	$P2_1/n$
Z	4
d_{calc}, g/cm^3	1.54
μ, cm^{-1}	15.0
size of crystal, mm	0.35 × 0.28 × 0.15
radiation, Å	MoKα, 0.71073
2θ range,°	4–50
scan mode	ω-2θ
no. of unique data	3559
no. of unique data with $I>3\sigma(I)$	2807
variable parameters	343
R	0.023
R_w	0.034
goodness-of-fit (G.O.F.)	1.503
max/min transmission, %	99.94/82.09
extinction parameter	refined

Table 2 Selected bond distances (Å) for compound **5**

Fe1-Fe2	2.510(1)	Fe1-C11	2.137(2)
Fe1-C2	1.933(2)	Fe1-C12	2.104(2)
C2-C3	1.407(3)	Fe1-C13	2.091(2)
C3-C4	1.463(3)	Fe1-C14	2.105(2)
Fe2-C4	1.887(2)	Fe1-C15	2.134(2)
Fe2-C2	2.019(2)	Fe2-C21	2.132(2)
Fe1-C1	1.939(2)	Fe2-C22	2.107(2)
Fe2-C1	1.884(2)	Fe2-C23	2.082(2)
Fe1-C5	1.754(2)	Fe2-C24	2.095(2)
C1-O1	1.174(3)	Fe2-C25	2.090(2)
C4-O4	1.201(2)	Si-C11	1.878(2)
C5-O5	1.146(3)	Si-C21	1.857(2)
C2-H2	0.94(2)	Si-C6	1.844(3)
C3-C31	1.489(3)	Si-C7	1.851(3)

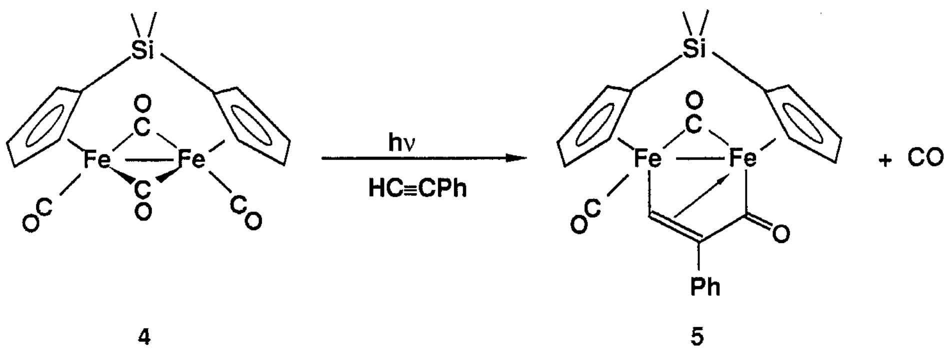
Table 3 Selected bond angles (°) for compound **5**

Fe2-Fe1-C2	52.12(6)	Fe1-C1-O1	136.9(2)
Fe1-C2-C3	126.3(2)	Fe2-C1-O1	141.0(2)
C2-C3-C4	113.6(2)	Fe2-Fe1-C5	106.90(8)
C3-C4-Fe2	76.2(1)	Fe2-C4-O4	146.2(2)
C4-Fe2-Fe1	91.76(6)	C3-C4-O4	137.1(2)
Fe1-Fe2-C1	49.91(7)	C11-Si-C21	105.81(9)
Fe2-Fe1-C1	48.04(6)	C6-Si-C7	111.0(2)
Fe1-C1-Fe2	82.05(8)		

RESULTS AND DISCUSSION

Irradiation of a toluene solution of **4** with a 10-fold excess of phenylacetylene over 10 hours results in the formation of a single product (Scheme 2). Purification of the reaction mixture by column chromatography leads to the isolation of the insertion product $Me_2Si[(\eta^5\text{-}C_5H_4)_2Fe_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1\eta^3\text{-}C(O)C(C_6H_5)C(H)\}]$ (**5**) in 31% yield. The structure of **5** was confirmed by X-ray crystallography. We have observed

Scheme 2



4 **5**

similar insertion products with dimethylacetylenedicarboxylate and diphenylacetylene, albeit with significantly lower yields and significant photochemical decomposition of the starting material.

The molecular structure of **5** (Figure 1) shows that the alkyne moiety of phenylacetylene has inserted into a Fe-CO bond to form a dimetallacyclopentenone, analogous to compounds formed by the irradiation of $Cp_2M_2(CO)_2(\mu\text{-}CO)_2$ (M = Fe, Ru) with alkynes.[8] The bonding of the C2—C3—C4 bridging unit is virtually identical to that found in $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1\eta^3\text{-}C(O)C(C_6H_5)C(C_6H_5)\}$.[8] The C2-C3 and C3-C4 distances are shorter than that expected for a single bond, suggesting "allylic" character as was reported for the ruthenium compound. Interestingly, both the Fe1-C2 and Fe2-C4 distances in **5** are shorter than expected for an Fe-C single bond,[17] suggesting partial double bond

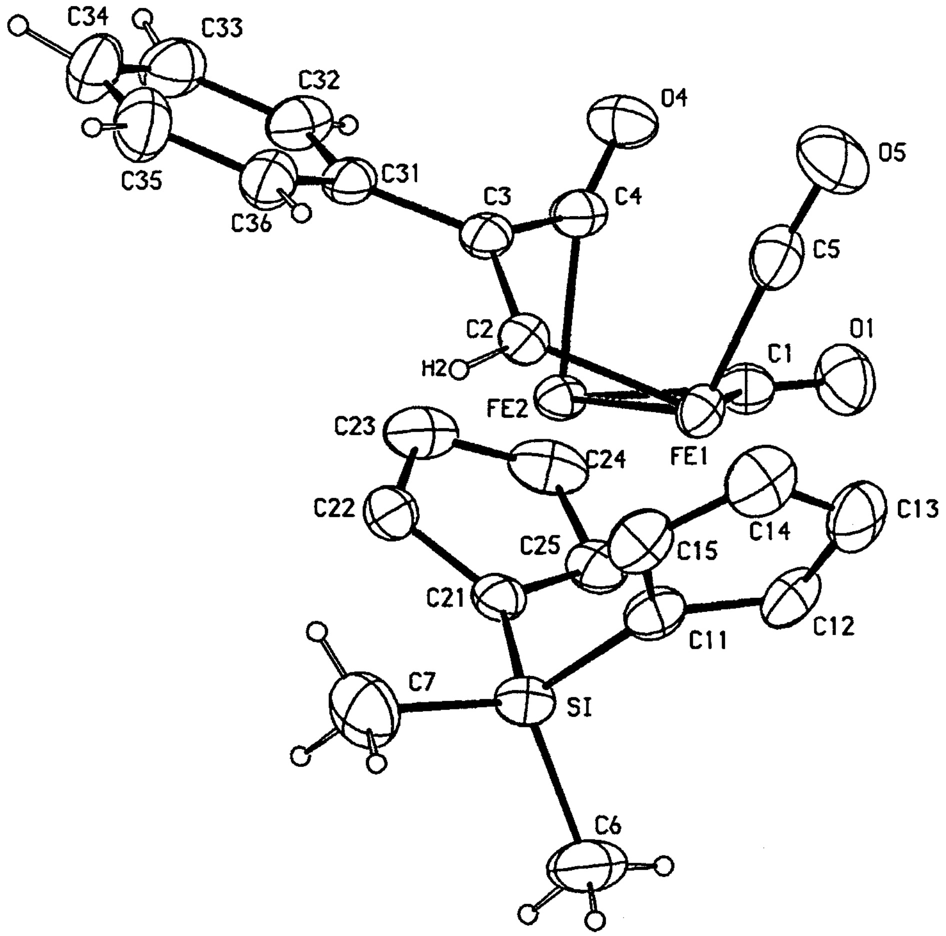
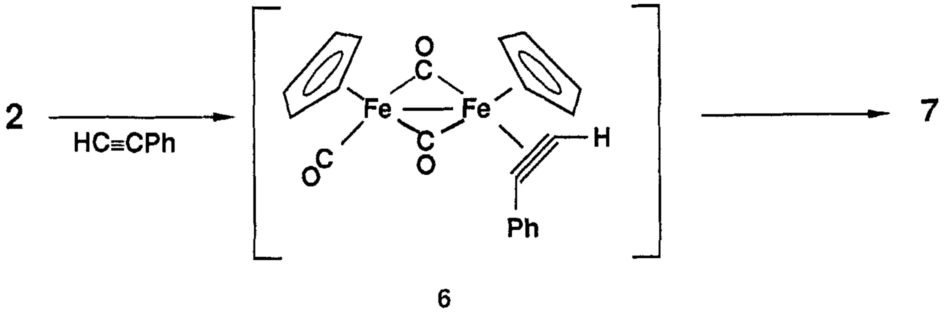


Figure 1 ORTEP drawing of **5**. The hydrogen atoms on the cyclopentadienyl ligands have been removed for clarity.

character. This metal-carbon double bond character is absent in the ruthenium system. The iron atoms are at a distance consistent with an Fe-Fe single bond, bridged almost symmetrically by a carbonyl group. The silylene-linked cyclopentadienyl groups are bound in an η^5 fashion and are, of course, constrained to a *cis* conformation. This portion of the molecule shows little deviation from the crystal structure of 4.[13a]

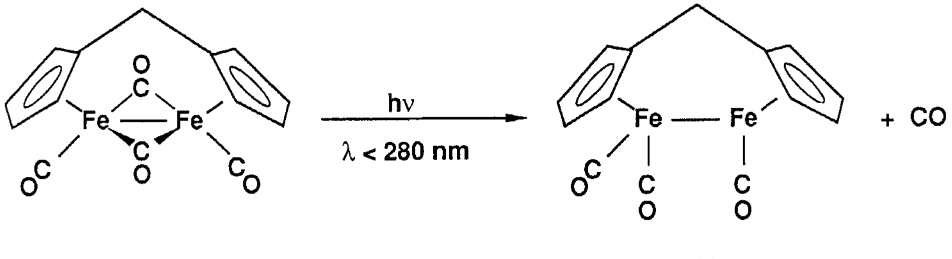
Compound **4** is electronically very similar to **1**; our spectroscopic studies (UV-*vis*, IR) indicate that the introduction of the silylene bridge is a very small electronic perturbation.[1] However, we expected the geometric constraints introduced by the silylene bridge to affect the photochemistry of **4** relative to that of **1**. On the basis of laser flash photolysis, we have previously proposed a mechanism for the irreversible photochemical insertion of alkynes into **1**.[7] This mechanism involves the photogeneration of **2**, presumably from only the *trans* isomer of **1**.[5] We proposed that **2** then reacts with an alkyne in an associative bimolecular process to form an undetected η^2-alkyne intermediate **6**, followed by rearrangement to the insertion product **7** (Scheme 3). Because the $SiMe_2$ bridge precludes the formation of an analog of **2** from irradiation of **4**, the formation of **5** from **4**, which is analogous to the product obtained when **1** is irradiated in the presence of alkynes, was quite surprising to us. Clearly a mechanism other than that shown in Scheme 3 must be proposed to explain this result.

Scheme 3



Several recent investigations suggest the formation of intermediates other than **2** upon the irradiation of **4** and its analogues. Rest *et al.* investigated the matrix photochemistry of **1**, of $Cp_2Ru_2(CO)_4$ (**8**), and of the analogues of **1** and **8** in which the Cp rings are tied back with methylene bridges, $[CH_2(\eta^5\text{-}C_5H_4)_2]M_2(CO)_4$ (**9**, M = Fe; **10**, M = Ru).[10] These studies affirm that, upon irradiation by near-UV light ($320<\lambda<390$ nm), **2** is formed exclusively from the *trans* isomer of **1**. The tied back compounds **9** and **10** exhibit behavior different from that of **1**. Near-UV irradiation of the Ru complex **10** leads to the loss of one CO ligand and the formation of an intermediate that contains three terminal CO's. The Fe complex **9** is apparently photoinert for $\lambda>280$ nm. With higher energy radiation, however, CO is lost and an all-terminal intermediate **11** is believed to be formed (Scheme 4).

Scheme 4

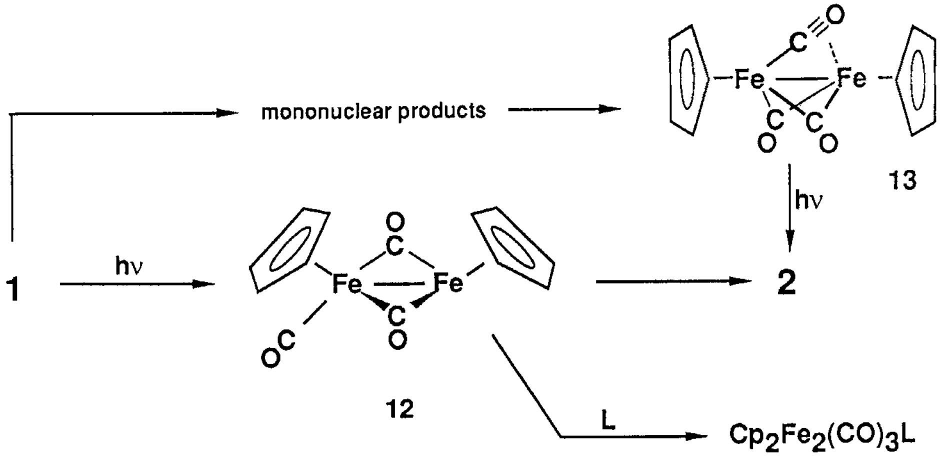


9

11

Poliakoff, Turner and coworkers reported a detailed study of the photosubstitution reactions of **1** in which TRIR spectroscopy was the primary probe.[11] They provide evidence for a short-lived (<125 ns) and thus far undetected intermediate that can rearrange rapidly to form **2**, or can react with small ligands such as THF to form substitution products. One possibility they propose for this intermediate is compound **12**, a doubly-bridged isomer of **2** that could be generated by loss of a terminal CO from **1** (Scheme 5).

Scheme 5



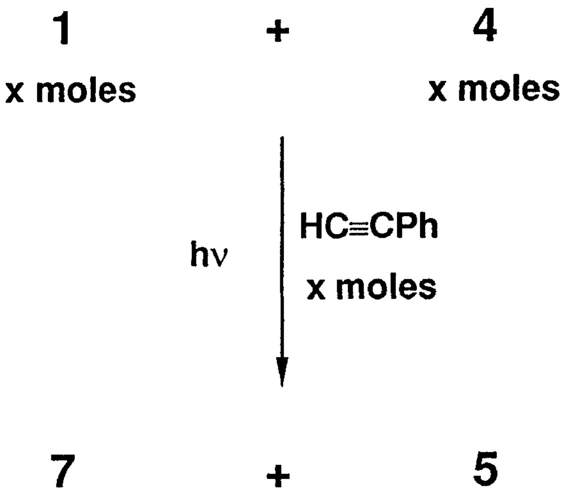
Zhang and Brown have recently detected several new long-lived intermediates upon irradiation of **1**.[12] Notable among these is yet another isomer of **2**, species **13**, which contains a semi-bridging carbonyl ligand. These authors propose that **13** is produced by the recombination of mononuclear fragments, and that **13** cannnot be produced directly from **2**; rather, irradiation of **13** converts it into **2** (Scheme 5).

The implications of these recent studies for the photochemistry of **4** are interesting to consider. First, it seems unlikely that irradiation of **4** would liberate any mononuclear intermediates, and therefore an analogue to **13** (Scheme 5) is unlikely to contribute to the observed photochemistry. An analogue to **11** (Scheme 4) would be a natural one to consider given that both **4** and **9** contain tied-back Cp ligands. Likewise, an analogue to intermediate **12** (Scheme 5) is an attractive possibility in the photochemistry of **4**, especially given its likely longer lifetime in the absence of an easy conversion to an analogue of **2**. Also, intermediate **12** is apparently formed from lower-energy photons than is intermediate **11**, and **12** satisfies the empirical rule advanced by Poliakoff *et al.* that the number of bridging or terminal CO ligands changes by ± 1 when a CO is photoejected.[18]

Our efforts to explore the nature of the intermediate produced upon irradiation of **4** have not been conclusive. Laser flash photolysis (351 nm) of **4** under the same conditions we used previously[7,9] showed no evidence for the production of a transient species. We have also explored the photochemistry of **4** in a frozen matrix composed of a 9:1 mixture of methylcyclohexane/3-methylpentane. Irradiation with either 355 nm light or broad-band radiation from an Oriel 200 W Hg lamp produced no changes in the matrix IR spectrum of **4**. Of particular interest, we observed no evidence for analogues to intermediates **11** and **12** (no change in the intensities of the CO bands, and no generation of new metal-carbonyl bands or of free CO), which would seem the most likely candidates for a CO-loss intermediate from **4**. This result seems consistent with the observations that *cis*-1 is photoinert in matrices,[4,5] and with the observation by Rest and coworkers that the low-energy photolysis of **9** failed to produce a CO-loss process.[10] We have not yet performed the matrix photochemistry with light of $\lambda < 280$ nm to determine whether the formation of an intermediate analogous to **11** is formed.

It appears that the synthesis of **5** from **4** must involve a different mechanism from the synthesis of **7** from *trans*-**1**. However, it is not unreasonable to assume that whatever mechanism allows the photochemical conversion of **4** to **5** should also allow the conversion of *cis*-**1** to **7**. It occurred to us that perhaps the conversion of *cis*-**1** to **7** was much slower than both the conversion of *trans*-**1** to **7** and the isomerization of *cis*-**1** to trans-**1** in fluid solution. Under these conditions, we could not observe the direct conversion of *cis*-**1** to **7**. If there were a significant difference in the rate of formation of alkyne-insertion product between *trans*-**1** and *cis*-**1**, there should also be a large rate difference between **1** and **4**. Because the alkyne-addition reaction is irreversible,[7] we used a photochemical competition reaction between **1** and **4** in the presence of phenylacetylene to test this notion (Scheme 6). Equimolar solutions (*ca.* 2×10^{-3} M) of **1**, **4**, and HC≡CPh were irradiated with a 450 W Hg lamp for 2–3 hr. The product mixture was analyzed by integrating the ^{1}H NMR resonances due to the β-carbon of the dimetallacyclopentenone portion of **5** and **7**. From several trials, the ratio of **7**:**5** was 2.10 ±0.35, *i.e.* alkyne insertion into **1** is preferred by about 2-to-1 over insertion into **4**. This ratio is smaller than we would have expected should there be a large difference in the rate of photochemical insertion into **1** and **4**. Of interest in this analysis would be the comparative quantum yields for the formation of the alkyne insertion product from **1** and **4**. We have not measured this value for either reaction.

Scheme 6



In conclusion, we believe that the photochemical production of **5**, an alkyne adduct of **4**, is strong evidence for an alternative mechanism for the photochemical alkyne addition to **1**. Further studies of these reactions, including their wavelength dependence, should be enlightening.

Acknowledgements

We thank Professor S. G. Shore for assistance with the X-ray crystallography and Professor M. S. Platz for many thought-provoking discussions. This research was supported by the Petroleum Research Fund (Grant 22182-AC3), administered by the American Chemical Society, and by the National Science Foundation (Grant CHE-9208703).

Supplementary Material

Supplementary information, Tables: S1 (Positional Parameters and B Values for **5**), S2 (Anisotropic Thermal Parameters for **5**), and S3 (Observed and Calculated Structure Factors for **5**) are available from the authors.

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