

Photochemical activation of metalloporphyrin carbene complexes¹

Christopher J. Ziegler, Kenneth S. Suslick^{*}

505 S. Mathews Ave., School of Chemical Sciences University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

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Abstract

While the photochemistry of simple metalloporphyrin complexes has been explored to some extent, the photoactivation of multiple-bonded axial ligands coordinated to metalloporphyrins has not been previously examined. We report here the photochemistry of several iron porphyrin carbene and vinylidene complexes. Irradiation of these complexes with visible light cleaves the iron–carbon double bond and produces a four coordinate iron(II) porphyrin and a free carbene, which can be trapped in high yield with a variety of alkenes. This photochemistry is unique among organo transition metal complexes of carbenes or alkylidenes. For these metalloporphyrin carbene complexes, the presence of the porphyrin ring alters the photoreactivity of the metal–carbon bond. This is probably due to the mixing between the π^* orbitals of the porphyrin ring and the iron–carbon orbitals, which is also responsible for the hypso-type spectrum (i.e. blue-shifted) seen in these complexes. Hypso spectra are a common trait in other photodissociative porphyrin complexes, most notably CO complexes.

Keywords: Porphyrin; Metalloporphyrin; Carbene; Photochemistry; Iron

1. Introduction

Since the discovery in 1964 of the first transition metal carbene complexes, the chemistry of this class of compounds has blossomed into a rich and exciting field of organometallic chemistry [1]. In 1978, a new type of carbene complexes of metalloporphyrins were prepared by Mansuy et al. [2] that notably differed from the previous classes of the Fischer and Schrock carbene complexes [3]. These ‘Mansuy carbenes’ are usually synthesized by the reaction of Fe(II) or Fe(III) porphyrins with haloalkanes such as CCl_4 , CFCl_3 , CBr_4 , and CCNCl_3 in the presence of a reducing agent [4]. The iron carbon double bond is orthogonal to the plane of the porphyrin macrocycle, and the sixth coordination site can be either vacant or occupied (Fig. 1).

The Mansuy carbenes have an unusual distinction among organometallic compounds for their relationship to biological systems [5]. $\text{Fe}(\text{TPP})\text{CCl}_2$ (TPP = 5,10,15,20-tetraphenylporphyrinate) was first synthe-

sized in an attempt to understand the mechanism for the catalytic reduction of CCl_4 by (normally) oxidative enzymes such as cytochrome P-450. The reaction of CCl_4 with the heme protein cytochrome P-450 under low oxygen conditions produces a permanently deactivated form of the enzyme in a low spin (EPR silent) form that has been shown to be the dichlorocarbene complex [6]. Haloalkanes are toxic because of this reaction with heme enzymes, and through the same chemistry, the hydrodehalogenation of haloalkanes are catalyzed by similar heme proteins. In addition, the once ubiquitous pesticide DDT also can irreversibly bind to heme cofactors, and it was found that, in the presence of excess reductant, DDT will form a vinylidene complex with iron porphyrins, e.g. $\text{Fe}(\text{TPP})(\text{C}=\text{C}(p\text{-C}_6\text{H}_4\text{Cl}_2))$ (Fig. 1) [7].

There have been many reports on the photochemistry of both Fischer and Schrock carbene complexes [8]. A large body of work has been produced by Hegedus and coworkers concerning the photochemistry of chromium Fischer carbene complexes in organic synthesis [9]. These species have the ability under photoexcitation to behave like modified α -heteroatom ketenes, due to migration of a carbonyl, and have been used to create a variety of compounds including β -lactams, cyclobu-

^{*} Corresponding author.

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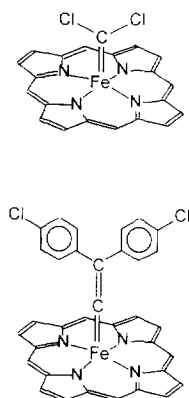


Fig. 1. The structure of $\text{Fe}(\text{TPP})\text{CCl}_2$ and $\text{Fe}(\text{TPP})(\text{C}=\text{C}(p\text{-C}_6\text{H}_4\text{Cl})_2)$. The phenyl groups have been omitted for clarity.

tanones, α -amino acid esters, dipeptides, captodative allenes, and dioxocyclams in high yield. Other Fischer carbenes, such as tungsten compounds, undergo loss of CO as their primary photochemical process. Once a CO has dissociated, the resulting fragment can undergo reactions such as solvent coordination, disproportionation, or substrate addition [10]. In cases where CO loss cannot occur, such as $[\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}=\text{CHPh}]^+$, the species experiences photoisomerization about the carbene bond [11]. In contrast, although the reactivity and spectroscopy of the Mansuy carbenes have been extensively examined, to date there have been no reports of the photochemistry of these systems.

Our interests in the photochemistry of iron porphyrin carbene complexes came from previous work in metalloporphyrin photochemistry [12]. It has been found that a variety of $\text{M}(\text{porph})\text{X}$ species (where X is a singly bound axial ligand) are photoactive [13]. When excited, porphyrins containing metals such as Cr, Mn, Fe, Ru, and Os can undergo photosensitization, photoreduction, and photo-oxidation reactions, and the nature of the photochemistry depends both on the characteristics of the metal and the axial ligand. As with many metal carbonyl compounds, irradiation of $\text{M}(\text{porph})(\text{L})(\text{CO})$ complexes liberates the carbonyl, which can either rebind or be replaced by a new ligand. Metalloporphyrin halide complexes such as $\text{Fe}(\text{TPP})\text{X}$ and $\text{Mn}(\text{TPP})\text{X}$ both undergo photoinduced homolytic bond cleavage to produce the reduced metalloporphyrin and a halogen atom, which can initiate oxidative chain reactions. Iron, manganese and chromium porphyrin complexes of oxoanions (e.g. perchlorate, nitrate, nitrite, etc.) also undergo photochemical bond cleavage, which can be either homolytic or heterolytic. This can result in highly oxidizing terminal oxo metal complexes, which can epoxidize olefins and hydroxylate alkanes. In the light of these findings, we became interested in investigating the possible photochemistry of metalloporphyrins with multiply bound axial ligands.

In this paper we will discuss our recent work examining the photochemistry of four iron porphyrin carbene complexes and one vinylidene complex. We have found that such complexes are indeed photoactive and possess a unique photochemistry. In addition, by looking at substrate reactivity in the form of cyclopropanation, we have elucidated the mechanism of the photochemical reaction: the liberation of a free carbene in solution.

2. Experimental

2.1. Preparation of porphyrin complexes

The syntheses and characterization of $\text{Fe}(\text{TPP})\text{L}$, where $\text{L} = \text{CCl}_2$, CClF , CBr_2 , CClCN , and $\text{CC}(\text{C}_6\text{H}_4\text{Cl})_2$ have been described previously [2,4,6]. The four carbene complexes are air sensitive and were synthesized and manipulated using anaerobic Schlenk line and glove box techniques. $\text{Fe}(\text{TPP})\text{Cl}$ (360 mg, 0.5 mmol) was dissolved in 30 ml of an anaerobic (freeze–pump–thaw degassed, then placed under argon) CH_2Cl_2 – CH_3OH (9:1) solution in the presence of an excess of iron powder (100 mg). The 0.5 mmol of the carbene precursor (CCl_4 , CCl_3F , CBr_4 , and CCl_3CN) was then added, and the resultant mixture was stirred under argon for approximately 1 h, during which time the solution turned from brown to bright red-violet. Filtration of the solution, evaporation of the solvent, redissolution in CH_2Cl_2 and recrystallization by addition of CH_3OH produced the desired carbene complex in greater than 90% yield. The crude products were then taken into the glove box, dissolved in benzene, filtered on a fine frit, and recrystallized by addition of pentane to produce the carbenes in high purity. $\text{Fe}(\text{TPP})\text{CCl}_2$, $\text{Fe}(\text{TPP})\text{CClF}$, $\text{Fe}(\text{TPP})\text{CBr}_2$, and $\text{Fe}(\text{TPP})\text{CClCN}$ were all prepared in this fashion and fully characterized by elemental analysis, NMR and mass spectrometry. We found that the dibromocarbene complex, $\text{Fe}(\text{TPP})\text{CBr}_2$, was somewhat unstable towards the formation of the μ -carbido dimer, $(\text{Fe}(\text{TPP}))_2\text{C}$, when impure, but preparative silica TLC could be used to obtain pure porphyrin for analysis and photolysis.

The vinylidene complex, $\text{Fe}(\text{TPP})(\text{C}=\text{C}(p\text{-C}_6\text{H}_4\text{Cl})_2)$ was prepared in an analogous fashion to that of the carbene complexes; however, the resultant complex is stable to air when pure. $\text{Fe}(\text{TPP})\text{Cl}$ (360 mg, 0.5 mmol) was reacted with 1,1-bis(chlorophenyl)-2,2,2-trichloroethane (DDT, 350 mg, 1.0 mmol) in the presence of iron powder as above. The reaction solution was then filtered, the solvent removed, and the product recrystallized three times from CHCl_3 – CH_3OH under argon. Excess DDT was removed from the microcrystalline product by washing generously with hot petroleum ether to produce the pure vinylidene iron porphyrin in 37% yield.

2.2. Photolysis studies

Dilute solutions of the above carbenes and vinylidenes (ca. 1×10^{-5} M) were used to examine their photochemical behavior. These solutions were made up in benzene (Fisher Scientific, distilled over CaH_2 , freeze–pump–thaw degassed, and purged with argon) in ground glass sealed optical cells in an inert atmosphere box. Photolyses were carried out using a 300 W xenon arc lamp (Eimac, 300LF) using both IR and less than 360 nm long pass filters. During excitation, the optical cells were thermostated to an internal cell temperature of ca. 20°C using a circulating constant temperature bath. The photochemical reactions were monitored by a Hitachi 3300 UV–visible double monochromator spectrophotometer.

Photolyses were also conducted in the presence of substrates to detect the formation of cyclopropanes. These benzene solutions were 25 wt.% alkene, and had a higher porphyrin concentration (ca. 2.5×10^{-4} M). These solutions were also monitored by UV–visible absorption, with optical characterization of the Q-band spectral region (500–700 nm) used to determine reactant and product concentrations. Cyclopropane formation was quantitatively determined by FID detection gas chromatography.

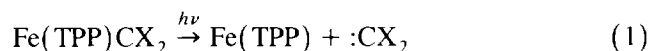
2.3. Base-induced cyclopropane formation

Standards for GC analysis of cyclopropane formation were synthesized using base/haloform procedures found in the literature in conjunction with microscale techniques [14]. The product oils were purified by chromatography and characterized by GC and GCMS. Base/haloform reactions were conducted at the same temperature as the photolyses (ca. 20°C) in order to compare the free carbene mechanism of base/haloform reactions with that found in the iron porphyrin photolyses.

3. Results and discussion

Upon irradiation in non-coordinating solvents, three of the iron porphyrin carbenes ($\text{L} = \text{CCl}_2$, CBr_2 , and CClF) and the vinylidene complex cleanly produced the four-coordinate $\text{Fe}(\text{TPP})$ ($\lambda_{\text{max}} = 419, 442, 537$ nm), as shown in Eq. (1). The spectrophotometry of this reaction is shown in Fig. 2 for $\text{Fe}(\text{TPP})\text{CCl}_2$. Both the Soret and Q-bands of the parent compounds are photoactive, and selective irradiation of either of these bands gives the same photochemistry. These photolyses demonstrate isosbestic behavior, eliminating the possibility of a long-lived porphyrinic intermediate in this reaction. The production of $\text{Fe}(\text{TPP})$ in this reaction is indicative of homolytic cleavage of the metal–carbon double bond and production of a free carbene. The formation of

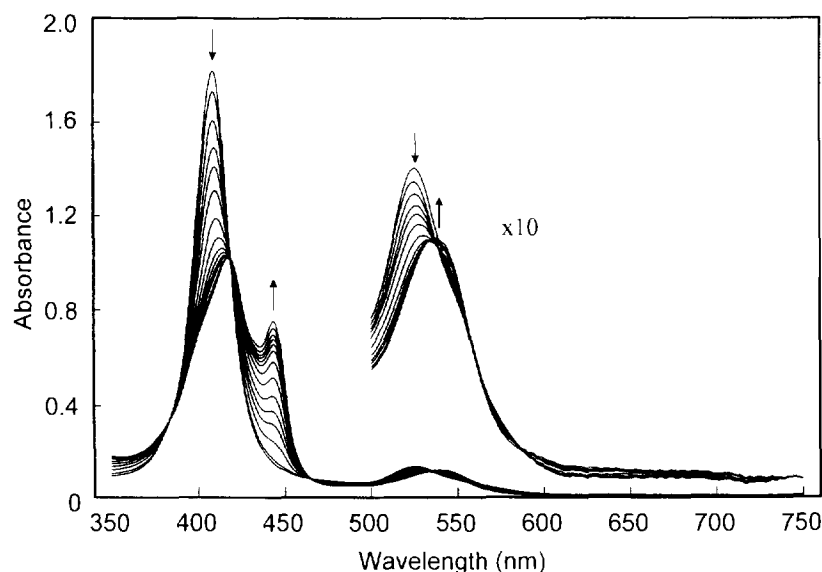
$\text{Fe}(\text{TPP})$ was confirmed by addition of pyridine after photolysis of the carbene or vinylidene complexes, yielding the bispyridine complex, $\text{Fe}(\text{TPP})(\text{py})_2$. Also, as expected, exposure of photolyzed solutions to oxygen resulted in the formation of the μ -oxo dimer species, $[\text{Fe}(\text{TPP})]_2\text{O}$. While this is a new photochemical reaction for metallocarbene complexes, the photoreductive loss of the axial ligand is not uncommon in porphyrin photochemistry, as can be seen in the photochemical reaction of $\text{Fe}(\text{TPP})\text{X}$ (where X is a halide) to form unligated $\text{Fe}(\text{TPP})$ [13].



While the UV–visible spectrum clearly shows the fate of the porphyrin in this reaction, the fate of the organic fragment must be determined by other means. Free carbenes or carbenoid intermediates are unstable and will rapidly react with a variety of substrates. The most common substrates for carbene additions are olefins [15], which can be used to trap the reactive intermediates in these photolyses.

A number of alkenes were selected to confirm the release of carbenes from the photolysis of the metalloporphyrin carbene complexes, as shown in Table 1. Irradiation of $\text{Fe}(\text{TPP})\text{CCl}_2$, $\text{Fe}(\text{TPP})\text{CBr}_2$, or $\text{Fe}(\text{TPP})\text{CClF}$ in the presence of alkenes produced the corresponding dihalocyclopropanes. In dilute solution these reactions occurred in high yield, but the yield diminished with increasing porphyrin concentration. At higher porphyrin concentrations but low alkene concentration, photolysis initiated the formation of $\text{Fe}(\text{TPP})\text{X}$ in addition to $\text{Fe}(\text{TPP})$ and dihalocyclopropanes. The production of $\text{Fe}(\text{TPP})\text{X}$ in solution probably results from halocarbene or carbenoid attack on unreacted $\text{Fe}(\text{TPP})\text{CX}_2$; this is inhibited by photolysis in the presence of higher alkene concentrations. It is important to note that the relative yields from the three complexes reflect the relative reactivity of the three free carbene fragments in solution.

Although the loss of the axial ligand and relative yields from the above three compounds implies the release of a free carbene, its actual production cannot be conclusively determined from the above data alone. For example, an excited state $\text{Fe}(\text{TPP})\text{CCl}_2$ could react with alkene in solution, for example, in a [2 + 1] cycloaddition. Such reactions are not uncommon for transition metal carbene species, as can be seen in the stabilized carbene cycloadditions catalyzed by metals such as Cu, Pd, Ni, Co, and Rh [16]. Thus, loss of the carbene from irradiation might occur through two possible pathways: direct photoinduced lysis of the metal–carbon double bond to produce the reduced iron porphyrin and a free carbene that would then react with substrates, or through a metal mediated addition to a substrate, analogous to the Simmons–Smith-type zinc carbenoid reaction [17].

Fig. 2. Photolysis of $\text{Fe}(\text{TPP})\text{CCl}_2$ in benzene under Ar.

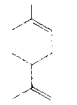
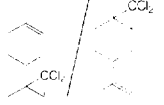
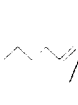
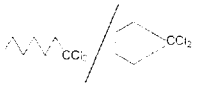






Fortunately, substrate reactivity studies can clearly determine which mechanism is present in these photolyses. Free carbenes and carbenoid reactions have distinctly different selectivities towards alkenes. In the case of free singlet carbenes, the long-lived diradical will selectively react with the alkene with the greatest electron density. The reactivity of free carbenes with alkene substrates has been thoroughly investigated, and the selectivity of product formation can be used as a test

of the formation of free carbenes [14,18]. It is well established that the reactivity of free singlet carbenes are independent of the mechanism of production (pyrolysis, photolysis, base-induced, etc.). In a metal-mediated carbenoid reaction, the steric bulk of the ligands about the metal will restrict the approach of the alkene to the metal and thus alter the observed selectivity. This effect would even manifest itself in a relatively unbulky porphyrin like $\text{Fe}(\text{TPP})\text{CCl}_2$. In addition, bulky olefins

Table 1
Photolysis of $\text{Fe}(\text{TPP})\text{CX}_2$ in the presence of alkene substrates

Porphyrin	Substrates, Products, and Yields			
$\text{Fe}(\text{TPP})\text{CCl}_2$	 82%	 80%	 80%	 79%
$\text{Fe}(\text{TPP})\text{CBr}_2$	 59%	 59%	 64%	 55%
$\text{Fe}(\text{TPP})\text{CClF}$	 90%	 89%	 85%	 86%

Table 2
Photolysis of $\text{Fe}(\text{TPP})\text{CX}_2$ under competitive conditions

Porphyrin	Substrate	Product	Photolysis Product Ratio	Base Induced Product Ratio
$\text{Fe}(\text{TPP})\text{CCl}_2$			0.22	0.22
$\text{Fe}(\text{TPP})\text{CCl}_2$			0.14	0.14
$\text{Fe}(\text{TPP})\text{CClF}$		 <i>syn F vs. syn Cl products</i>	0.55	0.55
$\text{Fe}(\text{TPP})\text{CClF}$		 <i>syn F vs. syn Cl products</i>	0.82	0.82
$\text{Fe}(\text{TPP})\text{CClF}$		 <i>syn F vs. syn C products</i>	0.50	0.50

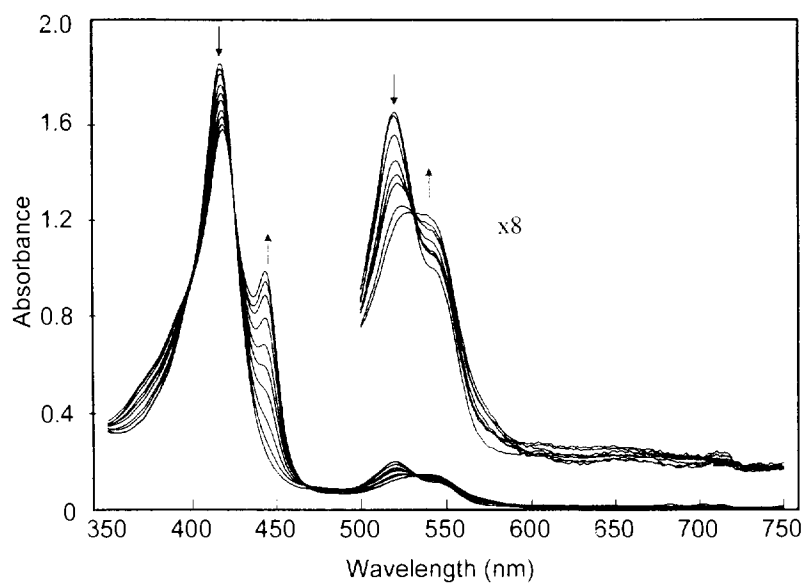
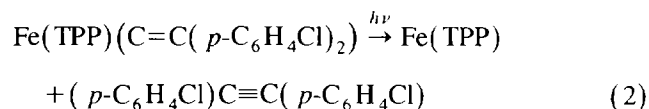


Fig. 3. Photolysis of $\text{Fe}(\text{TPP})(\text{C}=\text{C}(p\text{-C}_6\text{H}_4\text{Cl})_2)$ in benzene under Ar.

generally will have higher electron density (e.g. have more alkyl substituents), so there should be a distinct difference between the selectivity of a free carbene and a metal-mediated process. Both intra- and inter-molecular competitions can be used to probe this selectivity. With metalloporphyrin catalytic oxidations, a similar approach has been used to determine the mechanism of epoxide formation [19].

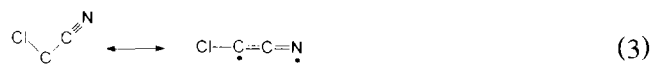
In the photochemical reaction of Fe(TPP)CCl₂ with alkenes, both the selectivity of an intramolecular competition, ((*S*)-(-)-limonene; entry 1 in Table 2), and of an intermolecular competition (cyclohexene vs. 1-hexene; entry 2 in Table 2) were examined. We compared these reactions with a known free carbene reaction, base-induced carbenes from haloforms. In both cases, the product ratios from the photochemical reaction matched exactly that of free CCl₂ produced from the reaction of base with CHCl₃ conducted at the same temperature (20 °C). In addition, photolysis of Fe(TPP)CClF with alkene substrates produced both *syn*-fluoro and *syn*-chloro products (entries 3, 4, and 5 in Table 2), whose ratios could also be compared with the reaction of CHCl₂F with base. Again, no significant difference in product ratios was found between the metalloporphyrin complex photolysis and the free carbene reactions. This similarity in selectivity indicates that upon photoactivation, the metalloporphyrin carbene complexes undergo homolytic dissociation with the formation of free carbene. A metal-mediated reaction would demonstrate a much different selectivity owing to the steric constraints of the substrate molecules.

The photolysis of the vinylidene complex, Fe(TPP)(C=C(*p*-C₆H₄Cl)₂), also produced the four-coordinate Fe(TPP) species in solution, as can be seen in Fig. 3. However, the fate of the resulting organic fragment is not identical to those from the carbene complexes: the vinylidene complex Fe(TPP)(C=C(*p*-C₆H₄Cl)₂) did not liberate a reactive fragment that added to alkenes. Instead, upon photolysis the vinylidene complex produced di(*p*-chlorophenyl)acetylene, as shown in Eq. (2). We presume that the vinylidene [C=C(*p*-C₆H₄Cl)₂] rapidly rearranges to form the more stable diarylacetylene. The yield of this acetylene, confirmed by GCMS of photolyzed solutions of the parent porphyrin, occurred quantitatively (ca. 99%). Such rearrangements are not uncommon for these organic fragments, and phenyl migration has been seen before in organic reactions that produce the vinylidene diradical [20].



In contrast to the photoactivity of the previous carbene complexes, Fe(TPP)CClCN is surprisingly unreactive to photolysis. The complex does react slowly to

form the unligated Fe(TPP), but does not go to completion even after extended irradiation (several hours). In addition, we were unable to detect any cycloalkane product formation even when the porphyrin was photolyzed in neat alkene. The lack of formation of a clean cyclopropane adduct was corroborated by the fact that we could not synthesize chlorocyanocyclopropanes using the base/haloform free carbene methodology. The lack of observed free carbene reactivity of the ClCCN fragment is not inconsistent with what is known about the electronic structure and reactivity of cyanocarbenes in general [21]. The anti-bonding orbitals of the cyano group contribute to the instability of the singlet ground state of the molecule. Singlet carbenes are stabilized by π donation into the carbon orbitals, and thus halocarbenes have singlet ground states. Thus, even though ClCCN has a halide functionality, the CN group may induce a triplet ground state, or at least minimize the singlet–triplet gap. To the best of our knowledge, there has been no ab initio calculation to date of the singlet–triplet gap in ClCCN, but such calculations on FCCN predict a triplet ground state [22]. In addition to the questions concerning its singlet–triplet character, the actual geometry of the molecule is also unresolved. There has been an extended debate on the linearity of the fragment HCCN and whether it forms a discrete carbene or has an allene-like structure [23], as shown in Eq. (3).



The allene structure has a diradical character and its stability and reactivity would be much different from that of a free singlet carbene.

Perhaps owing to the instability of the resultant carbene fragments, the quantum yields for the iron porphyrin carbenes are significantly lower than those of iron porphyrin carbonyl complexes, which can approach unity, but similar to the quantum yields of other metalloporphyrin systems that produce radical species. The quantum yields for photochemical reactions of five carbene complexes, listed in Table 3, were measured by irradiating by laser at the Soret band (406.7 nm). A

Table 3
Quantum yields of photolysis of iron porphyrin carbene and vinylidene complexes

Porphyrin	Quantum yield
Fe(TPP)CClCN	4.0×10^{-5}
Fe(TPP)CBr ₂	1.1×10^{-4}
Fe(TPP)CCl ₂	2.0×10^{-4}
Fe(TPP)(C=C(C ₆ H ₄ Cl) ₂)	1.1×10^{-3}
Fe(TPP)CClF	4.2×10^{-3}

similar trend was seen earlier in the relative yields of the cyclopropanation reactions, and these numbers may also reflect the relative stabilities of the fragments.

The source of the photoactivity of these complexes is significantly different from the previous porphyrins we have examined. The Cr(III), Mn(III), and Fe(III) systems that have been previously studied all have d-type hyper spectra according to the classification system of Gouterman [12,24]. These porphyrins have additional bands in the Q-band region of the visible spectrum. Low lying π to π^* transitions on the porphyrin ring do not produce photochemical behavior in these molecules. Instead, only irradiation into high energy porphyrin to metal or axial ligand to metal charge transfer transitions induce the homolytic bond cleavage observed [12,13].

The metalloporphyrin carbene complexes, however, belong to a different class and have hypso spectra [12,23], where the Q-band is shifted to a wavelength of less than 570 nm. In these porphyrins, the d_{yz} and d_{xz} orbitals overlap with the empty π^* levels of the porphyrin, which are therefore pushed up in energy. This creates a hypsochromic shift in the porphyrin π to π^* transitions with respect to the normal porphyrin spectrum. Both the d_{yz} and d_{xz} orbitals are involved in π bonding with axial ligands such as CO or carbene fragments, which presumably explains the photodissociative behavior of these complexes.

As well-known examples of photolabile hypso complex, six-coordinate Fe(porph)(L)(CO) species demonstrate axial ligand photodissociation, as do the CO complexes of myoglobin and hemoglobin (which was first noted by Haldane and Lorraine-Smith in 1895 [25]). Hoffman and coworkers determined that CO can labilize at an energy as low as 14300 cm^{-1} and concluded that this occurred directly from (π - π^*) configurations [26]. Much of the Fe-CO bond stabilization occurs from π -back-bonding from the (d_{xz} , d_{yz}) of the iron, and these d orbitals in turn back-bond with the highest filled porphyrin π levels [27]. Therefore, an excitation in these porphyrin π orbitals would significantly decrease the strength of the Fe-CO bond. There are distinct similarities between the bonding proposed for CO and carbene complexes of iron porphyrins [28]. The large difference in quantum yield between iron porphyrin carbonyl compounds (which can be as high as ca. 1) and iron porphyrin carbene complexes can be partially explained by considering the relative stabilities of the resulting fragments, as well as the decrease in back bonding.

4. Conclusions

Photolysis in the visible or UV of iron porphyrin carbene complexes liberates free carbenes into solution, which can react with olefins to form cyclopropanes. To

the best of our knowledge, the photochemical generation of a free carbene fragment from a transition metal carbene complex has not been previously observed [1,8–11]. Although the photochemistry of both Fischer and Schrock-type carbene complexes has been investigated, no examples of homolytic carbene dissociation have yet been found. In the case of the metalloporphyrin carbene complexes, which we refer to as 'Mansuy-type' carbene complexes, the lack of other coordinatively labile species and the stability of the resulting fragment both contribute to the reactivity of the iron-carbon double bond.

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