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Photochemistry of Metalloporphyrin Carbene Complexes

Christopher J. Ziegler and Kenneth S. Suslick*

School of Chemical Sciences
University of Illinois at Urbana-Champaign
Urbana, Illinois 61801

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The photochemistry of metalloporphyrins and other tetrapyrrolic systems continues to attract considerable interest.[1] There have been numerous studies on the photoactivity of various porphyrin complexes with single-bonded axial ligands, including halogens, oxo-anion species, molecular oxygen,[2] and a variety of metals, including chromium, manganese, and iron.[3] The photochemistry of metalloporphyrins with multiple-bonded axial ligands has not been explored. 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, resulting in a four-coordinate iron(II) porphyrin and a free carbene. This chemistry is unique in the area of transition metal carbene or alkylidene compounds.

Porphyrins with multiple-bonded axial ligands are especially relevant to both biological and catalytic oxidative processes.[4] Iron porphyrin carbene and nitrene species are isoelectronic with a terminal iron−oxo complex, the proposed intermediate of the cytochrome P-450 monooxygenases and its synthetic analogs. Most recently, the catalytic cyclopropanation of olefins by iron porphyrins using ethyl diazoacetate was thought to involve a porphyrin carbene complex.[5]

We prepared $\mathrm{Fe(TPP)CCl_2}$, $\mathrm{Fe(TPP)CBr_2}$, Fe(TPP)CClF, and $\mathrm{Fe(TPP)CC(}p\mathrm{\text{-}C_6H_4Cl)_2}$ under anaerobic conditions following Mansuy's procedure using iron metal as the reductant (TPP = 5,10,15,20-tetraphenylporphyrinate).[6] These compounds were further purified via crystallization from benzene/pentane under argon in an inert atmosphere box and then fully characterized.[7] To examine the photochemistry of these complexes, degassed benzene solutions ($\sim 1 \times 10^{-4}$ M) were irradiated with a 300 W Xe arc lamp, which was filtered to remove both infrared and ultraviolet (<360 nm) light in order to prevent sample heating and porphyrin bleaching, respectively. In addition, the photolysis cells were thermostated to an internal solution temperature of 20 °C.

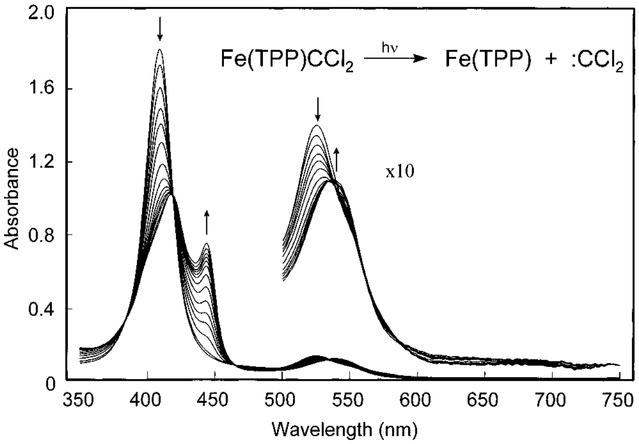
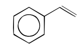
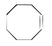
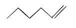
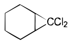
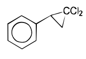
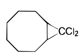
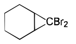
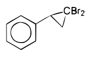
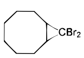
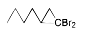
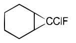
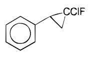
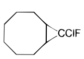
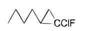


Figure 1. Photolysis of $\mathrm{Fe(TPP)CCl_2}$ in benzene under argon at 25 °C.

Table 1. Photolysis of $\mathrm{Fe(TPP)CX_2}$ in the Presence of Alkene Substrates

	Substrates, Products, and Yields			
Porphyrin				
$\mathrm{Fe(TPP)CCl_2}$	 82%	 80%	 80%	 79%
$\mathrm{Fe(TPP)CBr_2}$	 59%	 59%	 64%	 55%
Fe(TPP)CClF	 90%	 89%	 85%	 86%

In all cases, irradiation of the parent compounds cleanly produced a new porphyrin identified as Fe(TPP) ($\lambda_{\max} = 419$, 442, and 537 nm), as shown in Figure 1 for $\mathrm{Fe(TPP)CCl_2}$. Both the Soret and Q-bands of the parent compounds are photoactive.[8] The formation of Fe(TPP) was confirmed by addition of pyridine after photolysis of the carbene or vinylidene complexes, yielding the bispyridine complex, $\mathrm{Fe(TPP)(py)_2}$. Also as expected, exposure of photolysed solutions to oxygen resulted in the formation of the μ-oxo dimer species, $\mathrm{[Fe(TPP)]_2O}$.

The production of Fe(TPP) in this reaction is indicative of homolytic cleavage of the metal−carbon double bond and production of a carbene, as in the following reaction:

$$\mathrm{Fe(TPP)CX_2} \xrightarrow{h\nu} \mathrm{Fe(TPP)} + :\mathrm{CX_2}$$

The transient formation of free carbenes was confirmed by addition to various substrates (Tables 1 and 2), with products monitored by capillary GC and GCMS. The reactivity of free carbenes with alkene substrates has been thoroughly investi-

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(7) UV-Vis, ^{1}H NMR, FDMS, and elemental analysis were used to confirm the identity and purity of these species, which agreed completely with the prior literature.

(8) The quantum yields for these compounds are comparable to those of other metalloporphyrins with axial ligands. These yields upon irradiation of the Soret band ranged from 1×10^{-4} to 4×10^{-3} with $\mathrm{CBr_2} < \mathrm{CCl_2} < \mathrm{CC(C_6H_4Cl)_2} <$ CClF, which tracks the relative stabilities of the four resulting carbene fragments. The Q-bands, upon selective irradiation, were also found to be photoactive.

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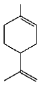
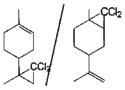
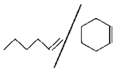
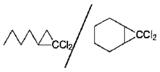
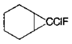
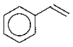
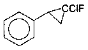
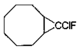
Table 2. Photolysis of $Fe(TPP)CX_2$ under Competitive Conditions

Porphyrin	**Substrate**	**Product**	**Photolysis Product Ratio**	**Base Induced Product Ratio**
$Fe(TPP)CCl_2$			0.22	0.22
$Fe(TPP)CCl_2$			0.14	0.14
Fe(TPP)CClF		 *syn* F vs. *syn* Cl products	0.55	0.55
Fe(TPP)CClF		 *syn* F vs. *syn* Cl products	0.82	0.82
Fe(TPP)CClF		 *syn* F vs. *syn* Cl products	0.50	0.50

gated,[9,10] and the selectivity of product formation can be used as a test of the formation of free carbenes. A number of alkenes were selected to corroborate the formation of carbenes from the photolysis of the metalloporphyrin carbene complexes. Irradiation of $Fe(TPP)CCl_2$, $Fe(TPP)CBr_2$, or Fe(TPP)CClF in the presence of alkenes produced dihalocyclopropanes (Table 1). All of these additions occurred in good yield in dilute solution, and the relative yields from the three complexes reflect the relative reactivity of the three free carbene fragments in solution. The photolysis of more concentrated solutions of these three species resulted in the formation of Fe(TPP)X in addition to the cyclopropanes and Fe(TPP). The production of Fe(TPP)X in solution results from halocarbene attack on unreacted $Fe(TPP)CX_2$ and can be inhibited by photolysis in the presence of high alkene substrate concentration.

In the photochemistry of $Fe(TPP)CX_2$, cyclopropanation could conceivably occur either through free dihalocarbene production or through a metal-mediated carbenoid intermediate. In the first case, photoexcitation would liberate the carbene fragment, which would then go on to react with the alkene substrate. In the second possibility, the metal center would play a distinct role in the reaction, perhaps via a metallocycle intermediate. The mechanism of photochemical cyclopropanation with these complexes was determined by competitive substrate addition, from either intra- or intermolecular selectivity. Similar approaches have been found useful in mechanistic studies of epoxidations by metalloporphyrin oxo complexes.[11]

In the irradiation of $Fe(TPP)CCl_2$, both the selectivity of an intramolecular competition, (*S*)-(−)-limonene (first entry in Table 2), and an intermolecular competition, cyclohexene vs 1-hexene (second entry in Table 2), were examined. In both cases, the product ratios matched exactly that of free CCl_2 produced from the reaction of base with $CHCl_3$ 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, whose ratios could also be compared to the reaction of $CHCl_2F$ with base. As before, 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 parent compound undergoes homolytic dissociation with the formation of free carbene.

Unlike the photolyses of the dihalocarbene iron porphyrins, the vinylidene complex $Fe(TPP)CC(p\text{-}C_6H_4Cl)_2$ did not liberate a reactive fragment that added to alkene substrates. Instead, upon photolysis the vinylidene complex produced di(*p*-chlorophenyl)acetylene:

$$Fe(TPP)CC(p\text{-}C_6H_4Cl)_2 \xrightarrow{h\nu} Fe(TPP) + (p\text{-}C_6H_4Cl)C{\equiv}C(p\text{-}C_6H_4Cl)$$

The yield of the above acetylene, confirmed by GCMS, occurred in quantitative yield (99%). This phenyl migration has been seen before in a number of other organic reactions that produce the vinylidene fragment as an intermediate.[12]

The photochemical generation of a free carbene fragment from a transition metal carbene complex has not been observed previously.[13] Although the photochemistry of both Fischer and Schrock type carbene complexes has been investigated, no examples of homolytic carbene dissociation have been found. In Fischer type carbenes, photoexcitation often leads to loss of carbonyl and subsequent reaction with substrates,[14] or migration and insertion of a carbonyl into the metal-carbon bond, as seen in the recent chemistry of Hegedus and co-workers.[15] In other carbene and alkylidene compounds, such as $(CO)_5W{=}C(OR)R'$ and $[Cp(NO)(PPh_3)Re{=}ChPh]^+$, isomerization of the metal−carbon double bond occurs.[16] In the case of the metalloporphyrin carbene complexes, which should be referred to as "Mansuy type" carbene complexes, the porphyrin excitation initates the metal carbon bond cleavage. We believe that this is 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[17] (i.e., blue-shifted) seen in these complexes.[18] *Hypso* spectra are a common trait in other photodissociative porphyrin complexes, most notably CO complexes.[1]

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