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Photoreactivity of σ-Bonded Metalloporphyrins. 1. Formation of Zwitterionic Indium and Gallium Porphyrin Complexes in Tetrahydrofuran

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Continuous irradiation and laser-flash photolysis experiments were carried out in THF on σ-bonded indium and gallium porphyrins of the type (P)M(R), where P is the dianion of tetraphenylporphyrin (TPP) or octaethylporphyrin (OEP), M is In or Ga, and R is CH$_3$, C$_2$H$_5$, C$_4$H$_9$, CH(CH$_3$)$_2$, C(CH$_3$)$_3$, CH$=$CHC$_6$H$_5$, or C$\equiv$CC$_6$H$_5$. Steady-state photolysis of (P)M(R), where R = CH$_3$, C$_2$H$_5$, C$_4$H$_9$, CH(CH$_3$)$_2$, or C(CH$_3$)$_3$, leads to photodissociation of the metal–carbon bond. In contrast, indium and gallium porphyrins with σ-bonded CH$=$CHC$_6$H$_5$ or C$\equiv$CC$_6$H$_5$ groups do not undergo this photodissociation reaction. Laser photolysis studies were carried out both in the presence and in the absence of ferrocene and indicate that the photoreaction occurs via a triplet state originating from the porphyrin macrocycle. The resulting ESR spectra obtained after photolysis of (TPP)In(C$_2$H$_5$) in THF are compared with ESR spectra obtained after electrochemical reduction of (TPP)InCl. On the basis of these results, a photochemical generation of zwitterionic metalloporphyrin radicals of the type (P)$^-$In$^+$ is demonstrated to occur in THF. Similarly, the (P)Ga(R) complexes also form a zwitterionic photoproduct upon irradiation as evidenced by ESR and UV-visible spectra. The photoreactivity of (P)In(R) and (P)Ga(R) is discussed with respect to the porphyrin macrocycle, the σ-bonded R group, and the solvent polarity.

Introduction

Numerous metalloporphyrins containing σ-bonded alkyl and aryl groups have now been synthesized and characterized.[1-13] Some of the complexes are stable toward light while others undergo photochemical reactions under visible-light irradiation.[7,14-18] For example, a photochemical reaction involving (OEP)Rh(CH$_3$) (where OEP is the dianion of the octaethylporphyrin) results in reduction of Rh(III) and the formation of dimeric [(OEP)Rh]$_2$.[18] In contrast, the photoproduct of (TPP)In(C$_2$H$_5$) (where TPP is the dianion of tetraphenylporphyrin) in 2-methyltetrahydrofuran (MTHF) has been described[15] as a zwitterionic porphyrin of the type (TPP)$^-$In$^+$. This latter finding has led to the conclusion that the 5s orbital of the central indium atom in (TPP)$^-$In$^+$ is higher in energy than the π^* orbital of the TPP ligand.[19]

The nature of the metalloporphyrin ground and excited states is affected by the type of central metal ion and the nature of the axially bound ligand. In this regard, an investigation of the photochemical reactivities of group 13 and group 14 metalloporphyrins containing σ-bonded alkyl or aryl ligands is of interest. Main-group metalloporphyrins containing σ-bonded alkyl or aryl groups are also of considerable interest with respect to their light-induced organometallic reactivity and their possible use as anticancer agents.[2-4] Germanium porphyrins that contain σ-bonded alkyl or aryl ligands show considerable activity toward neoplastic tissues both in vivo and in vitro.[4] In addition, carbon dioxide insertion into the metal–carbon bond of (TPP)In(C$_2$H$_5$) or (TPP)Al(C$_2$H$_5$) has been reported to be light activated.[2,3]

This paper investigates the laser-flash and steady-light photolysis of indium and gallium metalloporphyrins of the form (P)M(R), where P = TPP or OEP, M = In or Ga, and R = CH$_3$, C$_2$H$_5$, C$_4$H$_9$, CH(CH$_3$)$_2$, C(CH$_3$)$_3$, CH$=$CHC$_6$H$_5$, or C$\equiv$CC$_6$H$_5$. Quenching experiments using ferrocene (Fc) as the quencher were also performed in order to elucidate the reactive state responsible for the photoreaction. The photochemical generation of zwitterionic porphyrins is demonstrated to occur, and the photoreactivity of the (P)In(R) and (P)Ga(R) complexes is discussed with respect to the σ-bonded R group, the porphyrin macrocycle, and the solvent. This theme is also continued in the following paper, which presents data from steady-state and laser flash photolysis studies on germanium porphyrins containing σ-bonded alkyl, aryl, and ferrocenyl groups.

Experimental Section

Materials. The investigated (P)M(R) and (TPP)InCl complexes were synthesized by literature methods.[9,13] A complete characterization of these compounds is reported in the literature.[5,13,15]

All solvents were distilled under an inert atmosphere prior to use. Tetrahydrofuran (THF, Aldrich) was purified by distillation, first from CaH$_2$ and then from sodium/benzophenone. Benzene (Bz, Aldrich) was distilled from sodium. Dimethylformamide (DMF) was distilled from molecular sieves (4 Å). Tetra-*n*-butylammonium perchlorate (TBAP, Alfa) was recrystallized twice from absolute ethanol, dried, and stored under vacuum at 40 °C.

Instrumentation. UV–visible spectra were taken with an IBM Model 9430 spectrophotometer. A 1000-W xenon arc lamp was used in conjunction with a Model 7240 monochromator (Oriel Corp.) to irradiate the samples at desired wavelengths. Water having a temperature of 20 °C was constantly circulated through a metal jacket surrounding the cell holder. Ferrioxalate actinometry was employed to determine the light intensity, I_0. Quantum yields (Φ) were determined on the basis of the disappearance of absorbance due to the initial complex as described in the literature.[19] The value of Φ obtained for the photoreaction of (TPP)In(C$_2$H$_5$) in benzene is 0.044 and is close to the value reported in the literature.[19] Transient absorption spectral measurements and kinetic analysis of transient decays were performed at the Centre for Fast Kinetics Research (CFKR) at the University of Texas at Austin. The utilized laser and detection systems have been described previously.[20] The possibility that the transient spectra of the photoreactive (P)M(R) complexes are due to laser light and/or a flash-light-induced steady-state product was eliminated by using low laser energies (<5 mJ) and $\sim 10^{-4}$ M solutions of samples. Furthermore, the steady-state absorption spectra of the sample solutions were continuously monitored in order to ascertain the absence of a photoreaction during laser-flash photolysis. The majority of (P)M(R) complexes showed identical absorption species before and after the experiment but (P)M(CH$_3$) and (P)M(C$_2$H$_5$) showed steady-state spectral changes during the laser-flash experiments. In these

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Table I. Q-Band Peak Absorbance Wavelengths before and after Irradiation, Quantum Yields for Photoreaction (Φ), and Transient Decay Rate Constants (k°_T) of (P)M(R) Complexes in THF at 25 °C

			λ_{max}, nm						
complex	porphyrin, P	R	before irradn		after irradn[a]			Φ[b]	$10^{-4}k^\circ_T$,[c] s^{-1}
(P)In(R)	TPP	C_2H_5	581	627	560	604	790	0.20	8.11
		C_4H_9	578	623	561	605	785	0.16	7.44
		$CH(CH_3)_2$	583	628	560	605	824	0.06	12.40
		$C(CH_3)_3$	588	633	560	605	788	0.07	4.14
		$CH{=}CHC_6H_5$	574	615	574	615		*d*	0.95
		$C{\equiv}CC_6H_5$	565	606	565	606		*d*	0.12
	OEP	C_2H_5	554	589	538	576	784	0.30	8.62
		C_4H_9	554	588	537	575	782	0.13	6.52
		$CH{=}CHC_6H_5$	549	586	549	586		*d*	2.09
		$C{\equiv}CC_6H_5$	543	581	543	581		*d*	0.95
(P)Ga(R)	TPP	CH_3	568	609	552	624	771	0.28	6.67
		C_4H_9	571	615	551	625	775	0.06	1.10
		$CH{=}CHC_6H_5$	568	609	568	609		*d*	0.62
		$C{\equiv}CC_6H_5$	553	592	553	592		*d*	3.30
	OEP	CH_3	545	582	531	570	763	0.46	8.44
		C_2H_5	550	584	531	570	765	0.07	6.59
		$C(CH_3)_3$	550	571	530	570	765	0.02	0.51
		$CH{=}CHC_6H_5$	535	571	535	571		*d*	1.30
		$C{\equiv}CC_6H_5$	535	572	535	572		*d*	0.19

[a] Irradiation was carried out at 580 and 550 nm for (P)In(R) and (P)Ga(R), respectively. [b] Error limits ± 0.02. [c] Error limit ± 15%. [d] No reaction.

cases, the sample solutions were often replaced with fresh solutions while measuring their transient spectra.

ESR spectra were recorded with an IBM Model ER 100 D spin resonance system. DPPH was used as a *g* marker ($g = 2.0036$). Oxygen was rigorously excluded from the samples during both steady-light and laser-flash irradiation experiments. This was achieved by purging the solutions with argon for 15–20 min before carrying out the experiments or by preparing the solutions in a Vacuum Atmospheres glovebox.

Cyclic voltammetry measurements were performed under a N_2 atmosphere with a conventional three-electrode system. The working electrode was a platinum button (0.02 cm^2). A saturated calomel electrode (SCE) was used as the reference electrode and was separated from the bulk solution by a fritted glass bridge that contained the nonaqueous solvent and supporting electrolyte. An IBM Model EC 225 voltammetric analyzer was used to control the potential. Current–voltage curves were recorded on a Houston Instruments Model 2000 X-Y recorder.

Results and Discussion

Steady-State Photolysis of (P)M(R) in THF. Figure 1a shows the UV–visible spectral changes that occur during irradiation of (OEP)In(C_4H_9) in deoxygenated THF at 580 nm. (OEP)In(C_4H_9) initially exhibits peak maxima at 554 and 588 nm. Both peaks disappear upon irradiation, and new peaks appear at 537, 575, and 782 nm. Isobestic points are present at 541, 582, and 599 nm.

(OEP)InClO$_4$ has Q-band peaks at 535 and 573 nm in CH_2Cl_2, while the porphyrin π anion radicals $[(OEP)InCl]^{\bullet-}$ and $[(OEP)InClO_4]^{\bullet-}$ have bands in the region 700–900 nm.[21] Thus, the irradiation of (OEP)In(C_4H_9) results in a species that has dual spectral properties; i.e., the 538- and 575-nm bands suggest an In(III) complex of the type (OEP)InX ($X = ClO_4^-$, Cl^-, OH^-, or F^-),[21] but the 782-nm band suggests a porphyrin π-ring anion radical.[21,22] Similar dual spectral properties have been reported for solutions of (TPP)In(C_2H_5) that were irradiated at wavelengths greater than 400 nm in MTHF.[15]

(P)Ga(R) complexes show a similar spectral evolution during steady-state photolysis at 550 nm. This is shown in Figure 1b, which illustrates the UV–visible changes observed for (OEP)Ga(CH_3) in THF upon irradiation at 550 nm. The initial spectrum has absorption maxima at 545 and 582 nm while the product has peaks at 531 and 570 nm. The final spectrum is close to that of (OEP)GaCl in benzene (530 and 567 nm),[6] but there is also another broad peak in the spectrum at 763 nm, which may be attributed to a porphyrin π-anion radical.[6,22]

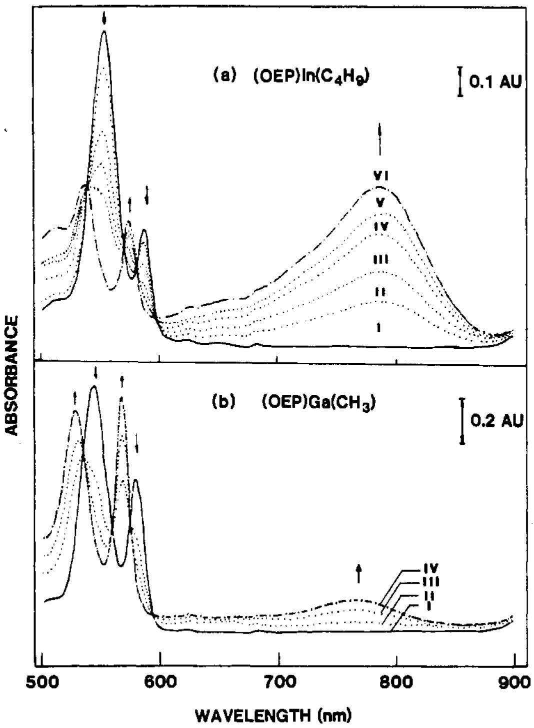

Figure 1. Spectral changes observed during irradiation of (a) (OEP)In(C_4H_9) in THF at (I) 0, (II) 2, (III) 5, (IV) 10, (V) 15, and (VI) 20 min (λ irradiation 580 nm) and (b) (OEP)Ga(CH_3) in THF at (I) 0, (II) 2, (III) 6, and (IV) 10 min (λ irradiation 550 nm).

The absorption maxima of each (P)M(R) complex before and after irradiation and the corresponding quantum yields of photoreaction in THF are listed in Table I. The (P)In(R) complexes were irradiated at 580 nm while (P)Ga(R) was irradiated at 550 nm. However, a variation in the irradiation wavelength over the range 450–600 nm did not result in changes of the final spectrum.

The spectral changes observed at 10 °C upon irradiation of THF solutions containing (OEP)In(C_4H_9) or (OEP)Ga(CH_3) were similar to the spectral changes shown in Figure 1, and warming these solutions to 40 °C in the absence of light did not produce any spectral changes. These observations indicate that no thermal reactions are involved in the spectral changes observed for the (P)M(R).

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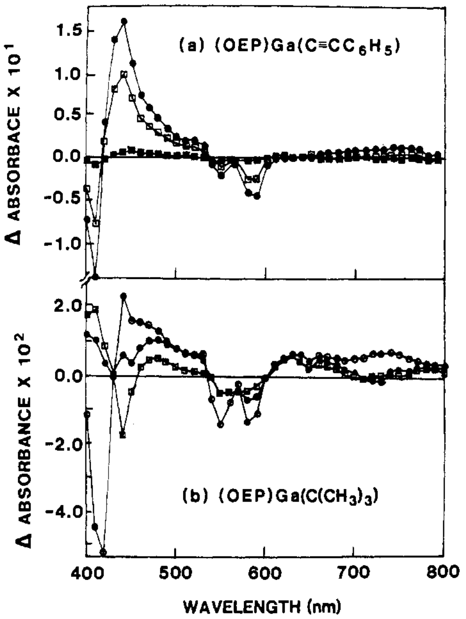

Figure 2. Transient absorption spectra of (a) (OEP)Ga($C{\equiv}CC_6H_5$) in THF at (●) 2, (□) 64, and (■) 269 μs after the laser flash and (b) (OEP)Ga($C(CH_3)_3$) in THF at (○) 2, (●) 20, and (□) 269 μs after the laser flash.

The (P)M(R) complexes in a given metal series (In or Ga) with the same porphyrin ring (OEP or TPP) have an identical spectral product independent of the R group after photolysis. This suggests a cleavage of the metal–carbon σ-bond and formation of the same zwitterionic $(P)^-M^+$ species as a final photoproduct[15] as shown in eq 1. The fate of $R^\bullet$ was not investigated in any of the reactions.

$$(P)M(R) \xrightarrow{h\nu} (P)^-M^+ + R^\bullet \qquad (1)$$

According to a conventional oxidation state formalism, the photolytic homolysis of (P)M(R) should generate $[(P)M^{III}]^\bullet$ and $R^\bullet$. σ-Bonded alkyl metalloporphyrins having cobalt, aluminum, and rhodium as central metals undergo photoinduced dissociation of the metal–carbon bond upon irradiation, producing $(P)M^{II}$.[18,19] The photolytic homolysis of (TPP)In(C_2H_5) does not produce $(TPP)In^{II}$, and an intramolecular electron transfer takes place to generate $(TPP)^-In^+$ as the final product. This has been ascribed to the fact that the 5s orbital of the central indium atom is higher in energy than the π^* orbital of the TPP ligand.[19] As will be shown in this paper, the product of each photoreactive (P)M(R) complex undergoes an intramolecular electron transfer upon photohomolysis of the metal–carbon bond and $(P)^-M^+$ is produced as a result of this reaction.

Additional evidence for photochemical cleavage of the metal–carbon bond in (P)M(R) comes from ^1H NMR spectra taken during photolysis of (TPP)In(C_4H_9) in deoxygenated THF-d_8 solutions. The peaks due to the C_4H_9 group at −4.36 (t), −2.25 (m), −1.58 (q), and −0.50 (t) ppm decrease in intensity during irradiation and disappear upon completion of the reaction. The same phenomenon has been reported to occur during photolysis of (TPP)In(C_2H_5) in benzene-d_6.[14]

Laser Photolysis. Laser photolysis of the (P)M(R) complexes leads to an identification of the reactive state and to the primary photoprocesses involved in the photoreaction. The time-resolved absorption spectra of (OEP)Ga($C{\equiv}CC_6H_5$) and (OEP)Ga($C(CH_3)_3$) in THF at time intervals between 2 and 269 μs after the flash are shown in Figure 2. The spectra of both complexes are identical 2 μs after the laser flash and have peak maxima in the ranges 440–480 and 750–800 nm. Similar spectra were obtained for each of the (P)Ga(R) and (P)In(R) complexes, and these spectra are similar to those obtained after laser-flash irradiation of (P)MCl, where M = Ga or In.

The transient spectrum of (TPP)In(C_2H_5) in MTHF has peak maxima at 470 and 800 nm and has been ascribed to the triplet–triplet absorption spectrum of the complex.[16] A similar assignment is given for the spectra of (OEP)Ga($C{\equiv}CC_6H_5$) and (OEP)Ga($C(CH_3)_3$) obtained 2 μs after the laser flash. However, the transient spectra taken for (OEP)Ga($C{\equiv}CC_6H_5$) and (OEP)Ga($C(CH_3)_3$) at longer time periods (20–269 μs) are different from each other. The spectrum of (OEP)Ga($C{\equiv}CC_6H_5$) decays without complications (see Figure 2a) while the spectrum of (OEP)Ga($C(CH_3)_3$) (Figure 2b) shows absorptions at 420, 470, 525, 570, and 750 nm that still exist 269 μs after the flash. Thus, although the absorption of the pure triplet partly contributes to the spectrum, the residual absorbances shown in Figure 2b largely correspond to a photoproduct obtained under steady-light irradiation of (OEP)Ga($C(CH_3)_3$) (see Table I). Similarly the residual absorbances at longer time periods after the laser flash (269 μs or more) are nearly identical with absorbances in the final spectrum obtained after steady-light irradiation of the photoreactive (P)M(R) complexes.

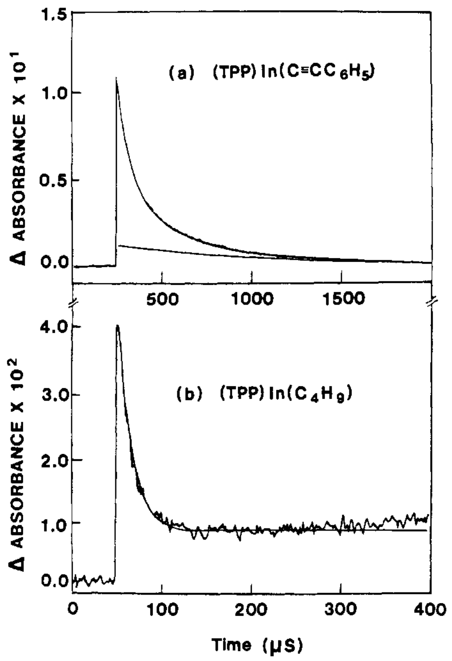

Figure 3. Transient decay of (a) (TPP)In($C{\equiv}CC_6H_5$) and (b) (TPP)In(C_4H_9) in THF at 480 nm.

Figure 3 shows the triplet absorption decay at 480 nm for THF solutions of (TPP)In($C{\equiv}CC_6H_5$) and (TPP)In(C_4H_9). The profile of (TPP)In($C{\equiv}CC_6H_5$) (Figure 3a) is first order with a rate constant of $0.12 \times 10^4\ s^{-1}$. Similar decay curves were obtained for (P)M(R) where R = $CH{=}CHC_6H_5$ or $C{\equiv}CC_6H_5$. However, the transient decay due to (TPP)In(C_4H_9) (Figure 3b) differs from that due to (TPP)In($C{\equiv}CC_6H_5$) (Figure 3a) in that the signal does not reach the base line within 400 μs or even at longer periods. The residual absorbance is due to a photoproduct that absorbs at 480 nm and is in agreement with the data in Figure 2b. The transient decays for (P)M(R), where R = CH_3, C_2H_5, $CH(CH_3)_2$, or $C(CH_3)_3$, are similar to the decay profile for (P)In(C_4H_9) in that each decay profile shows a residual absorbance at 480 nm that may or may not reach the base line on the millisecond time scale.

The observed rate constants for the transient decays (k°_T) of the photoreactive (P)M(R) complexes are given in Table I and parallel the steady-state quantum yields (Φ), which are obtained from the observed spectral changes during continuous irradiation.

Oxygen quenches the lifetime of the transients and reduces the steady-state photoreaction quantum yields. For example, the photoreactions of (OEP)Ga($C(CH_3)_3$) have Φ values of 0.013 and 0.004 in deoxygenated and aerated benzene solutions, respectively. These observations, coupled with the fact that similar absorption spectra are obtained for each of the (P)M(R) complexes at short time periods (2 μs or less), indicate that the photoreaction occurs from the triplet manifolds of these complexes.

Compelling evidence for triplet-state participation in the photocleavage reactions comes from quenching experiments. Fer-

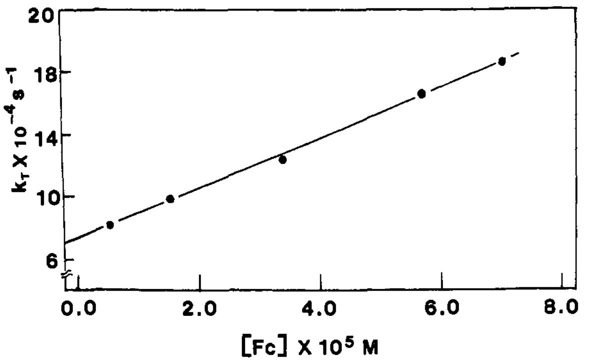

Figure 4. Transient decay rate (k_T) of (TPP)In(C_4H_9) absorbance at 480 nm as a function of ferrocene concentration.

rocene is reported to quench the triplet state of (TPP)In(C_2H_5) and to reduce the quantum yield of the photoreaction in benzene.[14] This was confirmed for (TPP)In(C_2H_5) in THF as well as for several other photoreactive (P)M(R) complexes in the same solvent. The dependence of k_T in the quenching of (TPP)In(C_4H_9) on ferrocene concentration is given in Figure 4. A linear relationship is obtained between k_T and [Fc], and the slope of this plot gives a quenching rate constant (k_q) of 1.7×10^9 M^{-1} s^{-1}. Analogous plots were constructed for quenching of the other (P)M(R) complexes by ferrocene, and the calculated values of k_q are listed in Table II. Each k_q value is nearly diffusion controlled, and this implies an efficient quenching of the (P)M(R) triplets by ferrocene.

Metallocenes have been shown to quench organic triplets by both energy-transfer and electron-transfer mechanisms.[23-25] A quenching of metalloporphyrin triplets by ferrocene has been shown to proceed via an energy-transfer mechanism,[14] and a similar mechanism probably occurs in quenching of the (P)M(R) complexes. However, independent of the exact nature of the energy-transfer between the (P)M(R) triplets and ferrocene, a mechanism for the photoreaction of these complexes in the presence of ferrocene can still be written. This mechanism is shown in Scheme I where ^{3}[(P)M(R)] is the triplet state of (P)M(R) and k_b, k_r, and k_q represent the rate constants for reactions 3, 4, and 5, respectively.

Scheme I

$$\text{(P)M(R)} \xrightarrow{h\nu} {}^3\text{[(P)M(R)]} \quad (2)$$

$$^3\text{[(P)M(R)]} \xrightarrow{k_b} \text{(P)M(R)} \quad (3)$$

$$^3\text{[(P)M(R)]} \xrightarrow{k_r} \text{(P)}^-\text{M}^+ + \text{R}^\bullet \quad (4)$$

$$^3\text{[(P)M(R)]} + \text{Fc} \xrightarrow{k_q} \text{(P)M(R)} + {}^*\text{Fc} \quad (5)$$

The observed transient decay rate of (P)M(R) in the absence of Fc ($k°_T$) can be expressed as shown in eq 6 while in the presence

$$k°_T = k_b + k_r \quad (6)$$

of Fc, the observed transient decay rate (k_T) is given by eq 7.

$$k_T = k°_T + k_q[\text{Fc}] \quad (7)$$

Dividing equation 7 by 6, gives eq 8. A similar relation is obtained

$$k_T/k°_T = 1 + (k_q/k°_T)[\text{Fc}] \quad (8)$$

by using quantum yields. This relationship is given in eq 9 where

$$\Phi°/\Phi = 1 + (k_q/k°_T)[\text{Fc}] \quad (9)$$

Table II. Rate Constants (k_q) for the Quenching of the (P)M(R) Triplet States by Ferrocene in THF at 25 °C

porphyrin, P	central metal	R	$10^{-9}k_q$,[a] M^{-1} s^{-1}
TPP	In	C_2H_5	2.1
		C_4H_9	1.7
		$CH(CH_3)_2$	2.0
		$C(CH_3)_3$	2.0
OEP	In	C_2H_5	2.0
		C_4H_9	1.3
TPP	Ga	CH_3	b
		C_4H_9	0.8
OEP	Ga	CH_3	b
		C_2H_5	2.0
		C_4H_9	2.1

[a] Error limits ±10%. [b] k_q values could not be determined owing to the extreme photosensitivity of these complexes.

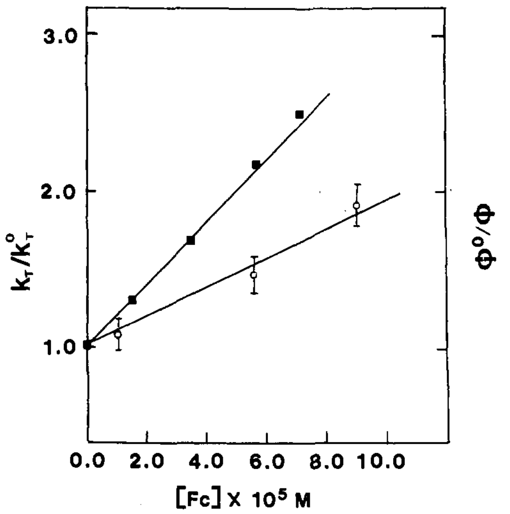

Figure 5. $k_T/k°_T$ (■) and $\Phi°/\Phi$ (○) for the quenching of (TPP)In(C_4H_9) in THF as a function of ferrocene concentration.

$\Phi°$ and Φ are the steady-state quantum yields for the photoreactions in the absence and the presence of Fc, respectively. Equations 8 and 9 indicate that $k_T/k°_T$ or $\Phi°/\Phi$ is linearly dependent on ferrocene concentration and that a plot of $k_T/k°_T$ or $\Phi°/\Phi$ vs [Fc] will have a slope of $k_q/k°_T$ and an intercept of 1.0.[14] This is indeed the case as shown in Figure 5 for the quenching of (TPP)In(C_4H_9) by ferrocene in THF. The value of $k_q/k°_T$ determined from the plot of $k_T/k°_T$ vs [Fc] is 2.0×10^4 M^{-1} while the plot of $\Phi°/\Phi$ gives a $k_q/k°_T = 9.2 \times 10^3$ M^{-1}. Within the experimental error limits, the values obtained by each method are close to each other and indicate that a photoexcited triplet is responsible for the photoreaction of (TPP)In(C_4H_9).

An analogous set of steady-state and laser-flash photolysis experiments were conducted for (OEP)Ga(C_4H_9) and gave values of $k_q/k°_T$ of 3.0×10^4 M^{-1} and 2.6×10^4 M^{-1} from plots of $\Phi°/\Phi$ vs [Fc] and $k_T/k°_T$ vs [Fc], respectively. These data indicate that the photoreaction of (OEP)Ga(C_4H_9) originates from its excited triplet state.

ESR Spectra of Photochemically and Electrochemically Reduced (TPP)In(C_2H_5) and (TPP)InCl in THF. Figure 6a displays the ESR spectrum of irradiated (TPP)In(C_2H_5) in THF at room temperature. Almost identical spectra are observed for the other photoreactive (TPP)In(R) complexes.

The spectrum in Figure 6a exhibits 10 hyperfine lines due to an interaction between one unpaired electron and the central indium atom ($I = {}^9/_2$) of the porphyrin. The g value and hyperfine coupling constants are 2.004 and 10.5 G, respectively. A similar ESR spectrum was reported for (TPP)In(C_2H_5) in degassed MTHF after irradiation (λ > 400 nm) for 30 s at room temperature.[15] However, the same solution at 115 K gives an ESR spectrum with a different shape (see Figure 6b). The g value of

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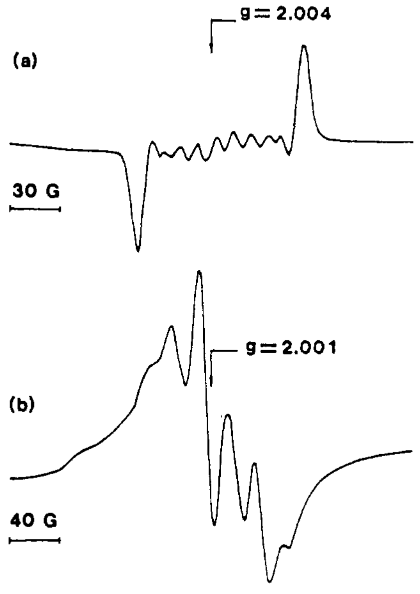

Figure 6. ESR spectra of the product obtained after exposure of (TPP)In(C_2H_5) in THF to visible light, at (a) 300 and (b) 115 K.

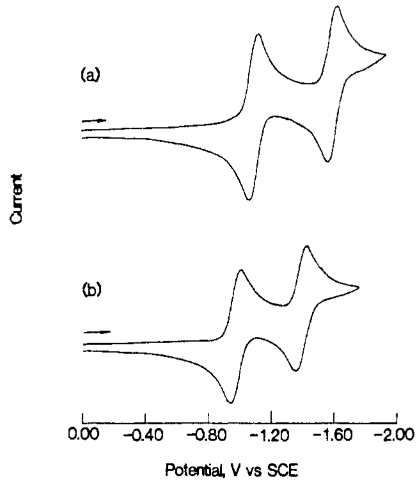

Figure 7. Cyclic voltammograms of (a) (TPP)In(C_2H_5) and (b) (TPP)InCl in THF containing 0.2 M TBAP. Scan rate = 0.1 V/s.

the signal is 2.001, the total width is 113 G, and the width between points of the maxima is 11 G.

Electrochemistry was also used to generate a singly reduced indium porphyrin, which was then examined by ESR spectroscopy. Figure 7 illustrates the cyclic voltammograms for (TPP)In(C_2H_5) and (TPP)InCl in THF containing 0.2 M TBAP. The voltammograms of (TPP)In(C_2H_5) were taken in the dark under a nitrogen atmosphere. As seen in this figure, reversible one-electron-transfer processes are observed for (TPP)In(C_2H_5) at $E_{1/2}$ = −1.09 and −1.59 V (Figure 7a) while (TPP)InCl is reversibly reduced at $E_{1/2}$ = −0.97 and −1.39 V (Figure 7b).[26] Each reaction occurs at the porphyrin π-ring system. These assignments are based on the potential separations between the first and second reduction of the complex, which are consistent with formation of π anion radicals and dianions,[27] and are also supported by data from thin-layer spectroelectrochemistry.[5,21] Thus, the electrode reductions of (TPP)In(C_2H_5) and (TPP)InCl in THF can be expressed by eq 10 and 11, where L = C_2H_5 or Cl^-.

$$(TPP)In(L) + e^- \rightleftarrows [(TPP)In(L)]^- \quad (10)$$

$$[(TPP)In(L)]^- + e^- \rightleftarrows [(TPP)In(L)]^{2-} \quad (11)$$

An assymetric ESR spectrum is recorded at 115 K after bulk electrolysis of (TPP)In(C_2H_5) at −1.30 V (the first electroreduction) in THF containing 0.2 M TBAP under a nitrogen atmosphere and in the dark. This ESR spectrum is shown in Figure 8a. The measured values of *g* factors are 2.002 and 1.968, respectively, and are in good agreement with an assymmetry of the [(TPP)In(C_2H_5)]$^-$ anion radical.

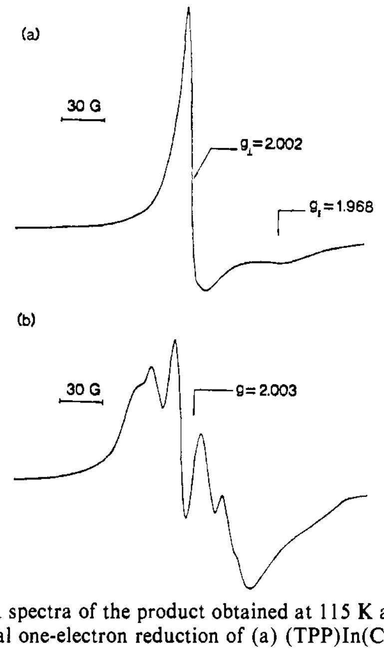

Figure 8. ESR spectra of the product obtained at 115 K after the controlled-potential one-electron reduction of (a) (TPP)In(C_2H_5) and (b) (TPP)InCl in THF containing 0.2 M TBAP.

The ESR spectrum shown in Figure 8b was obtained at 115 K after the controlled-potential one-electron reduction of (TPP)InCl in THF containing 0.2 M TBAP. The *g* value is 2.003, and the total width of the signal is 81 G. The shapes of the ESR spectrum for a (TPP)InCl solution that has been electrochemically reduced by one electron (Figure 8b) and that for (TPP)In(C_2H_5) which has been photoreduced (Figure 6b) are almost identical at 115 K. In contrast, the shape of the ESR spectra for electrochemically reduced (TPP)In(C_2H_5) (Figure 8a) is totally different from that of photoreduced (TPP)In(C_2H_5) at room temperature or at 115 K (Figure 6a,b).

It has been reported that the product of (TPP)InCl reduction on the thin-layer spectroelectrochemical time scale (about 1 min) is a neutral (TPP)In radical.[21] Thus, the ESR data are consistent with the fact that (TPP)In(C_2H_5) undergoes cleavage of the indium–carbon σ-bond upon irradiation and that the generated photoproduct is a four-coordinated (TPP)In anion radical which is in the zwitterionic form $(TPP)^-In^+$. On the basis of the UV-visible spectral data in Table I, it can be concluded that the remaining photoreactive (P)In(R) complexes should also exhibit zwitterionic character for their respective photoproducts.

Electrode reactions of the type shown in eq 10 and 11 also occur for metal–carbon- and metal–chloride-bonded gallium porphyrins.[6] However, the electrochemically generated $[(P)Ga(Cl)]^{\bullet-}$ product is stable and does not undergo chloride dissociation as is the case for $[(P)In(Cl)]^{\bullet-}$.[5] For this reason, a comparison of the ESR spectra obtained by electrochemical reduction of (P)GaCl to ESR spectra obtained after irradiation of (P)Ga(R) would not provide evidence for the zwitterionic character of the photoproduct. However, the combined ESR and UV–visible data might suggest formation of a zwitterionic $(P)^-Ga^+$ product upon irradiation of (P)Ga(R).

A $\sim 10^{-4}$ M solution of (TPP)Ga(CH_3) in degassed THF shows an ESR signal at 298 K that has a *g* value of 2.010 and a $\Delta H_{p,p}$ value of 26 G. Similar ESR signals are also obtained upon irradiation of photoreactive (P)Ga(R) complexes. These signals are characteristic of porphyrin anion radicals[22] and indicate the ionic character of the photoproducts. This fact, coupled with the observation of dual spectral characteristics in their UV–visible spectra, suggests a zwitterionic form for the photoproducts of (P)Ga(R).[15]

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(26) For these waves $|E_{pa}-E_{pc}|$ = 60 mV, i_{pa}/i_{pc} = 1.0 and $i_p/v^{1/2}$ = a constant over the potential scan rate range 0.05–5.0 V/s.

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Photoreactivity of (P)M(R) Complexes in THF. The metal-carbon σ-bond of (P)In(R)[5] or (P)Ga(R)[6] also breaks upon electrooxidation of the complex, and this leads to irreversible cyclic voltammograms. The irreversible peak potential, E_p, for this oxidation has been related to the relative rate of metal-carbon σ-bond cleavage and is expected to parallel the electron donicity of the R group:[5,6]

$$C(CH_3)_3 > CH(CH_3)_2 > C_4H_9 > C_2H_5 > CH_3 > CH{=}CHC_6H_5 > C{\equiv}CC_6H_5$$

The peak potential is a measure of the rate constant for the chemical reaction following the electron transfer (an electrochemical EC type mechanism[28]), and thus (P)M(R) complexes with more negative irreversible peak potentials should have faster metal-carbon bond cleavage rates. The data in Table I indicate that the trend in magnitude of the photochemical quantum yield for a given series of complexes is opposite to that determined from the electrochemical peak potentials.

The bulkiness of the axially ligated alkyl ligand leads to two different effects that are opposite to each other in terms of how they influence the photoreactivity of (P)M(R) where R = CH_3, C_2H_5, C_4H_9, $CH(CH_3)_2$, or $C(CH_3)_3$. The first effect involves the electron donicity of the ligated R group and its repulsive interaction with the equatorial ligand, P. This effect increases the rate of metal-carbon bond homolysis upon irradiation. However, the diffusion rate of the photogenerated radical species, $R^\bullet$, from the coordination sphere will become smaller as the bulkiness of the alkyl ligand increases. A slow diffusion rate favors recombination of $R^\bullet$ with the transiently reduced central metal. The trend in quantum yields indicate that this latter effect dominates the photochemical reactions of the (P)M(R) complexes and is similar to what has been reported for the photoreduction of (TPP)MoO(OR).[29]

The UV-visible spectra, the ^1H NMR spectra, and the electrochemical data reveal an evolution from pure σ-bonded character of the metal-carbon bond in (P)M($C(CH_3)_3$) to an ionic-like character in (P)M($C{\equiv}CC_6H_5$).[5,6] (P)M(R) complexes, where R = $CH{=}CHC_6H_5$ or $C{\equiv}CC_6H_5$, do not undergo any photodissociation reaction and this may be attributed to the electron-withdrawing ability of these two alkyl ligands that results in an ionic-like character of the metal-carbon bond.

The photoproduct of (TPP)In(C_2H_5) has been postulated to exist as a zwitterionic species $(TPP)^-In^+$[15] that has separate positive and negative charges. As such, the quantum yield for the photochemical reactions of (P)M(R) should be solvent dependent; the more polar the solvent, the larger should be the quantum yield. This is indeed the case as shown for the reaction of (TPP)In($CH(CH_3)_2$) where the observed Φ for the reaction roughly parallels the solvent dielectric constant. The lowest yield is obtained in benzene ($\Phi = 0.02$) and the highest in DMF ($\Phi = 0.22$). Similarly, quantum yields for the photocleavage reactions of (OEP)Ga($C(CH_3)_3$) are ~0.01, 0.02, and 0.04 in benzene, THF, and DMF, respectively. These trends are thus consistent with formation of a zwitterionic species after photocleavage of the metal-carbon σ-bond in (P)M(R).

A recent study[19] indicates that axial ligation of pyridine by (TPP)In(C_2H_5) in the excited triplet state results in an increased quantum yield for the photoreaction. An axial ligation of the electron-donating THF or DMF molecules in the excited triplet states may also contribute to enhanced quantum yields of (P)M(R). Also, it is likely that the photoproduct may not be stabilized as a zwitterionic species in benzene due to the low dielectric constant of this solvent.

It is significant to note that the quantum yields of the OEP complexes are generally larger than those of the TPP complexes that have the same axial alkyl ligand and the same metal center. This is in good agreement with the increased electron donicity of the OEP ring with respect to that of TPP. Finally, the data in Table I do not show any dependence of the metal ion on the photoreactivity of the (P)M(R) complexes.

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Registry No. (TPP)In(C_2H_5), 63036-65-7; (TPP)In(C_4H_9), 63036-66-8; (TPP)In[$CH(CH_3)_2$], 72340-10-4; (TPP)In[$C(CH_3)_3$], 63036-67-9; (TPP)In($CH{=}CHC_6H_5$), 72340-11-5; (TPP)In($C{\equiv}CC_6H_5$), 72340-12-6; (OEP)In(C_2H_5), 63036-69-1; (OEP)In(C_4H_9), 63036-70-4; (OEP)In($CH{=}CHC_6H_5$), 72340-08-0; (OEP)In($C{\equiv}CC_6H_5$), 72340-09-1; (TPP)Ga(CH_3), 87607-76-9; (TPP)Ga(C_4H_9), 87607-78-1; (TPP)Ga($CH{=}CHC_6H_5$), 98943-16-9; (TPP)Ga($C{\equiv}CC_6H_5$), 98943-17-0; (OEP)Ga(CH_3), 87607-71-4; (OEP)Ga(C_2H_5), 87607-72-5; (OEP)Ga[$C(CH_3)_3$], 98943-18-1; (OEP)Ga($CH{=}CHC_6H_5$), 98943-19-2; (OEP)Ga($C{\equiv}CC_6H_5$), 98943-20-5; (OEP)Ga(C_4H_9), 87607-73-6; (TPP)InCl, 63128-70-1; $(TPP)^-In^+$, 102513-31-5; $(OEP)^-In^+$, 108294-69-5; $(TPP)^-Ga^+$, 119273-07-3; $(OEP)^-Ga^+$, 119273-08-4; $[(TPP)In(C_2H_5)]^-$, 96363-91-6; $[(TPP)InCl]^-$, 97644-33-2; $[(TPP)In(C_2H_5)]^{2-}$, 119273-09-5; $[(TPP)InCl]^{2-}$, 97644-34-3; ferrocene, 102-54-5.

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