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MLCT Photodissociation of Low-Spin Ferrous Bis(dioximate) Complexes. Comparison of Ground- and Excited-State Reactivity

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Photochemical axial ligand substitution reactions of low-spin FeN$_4$XY complexes, N$_4$ = bis(dimethylglyoximate) or bis(naphthoquinone dioximate) and X or Y = CO, PBu$_3$, P(OBu)$_3$, BzNC, or MeIm, are shown to proceed via a dissociative mechanism in toluene solution. Quantum yields generally decrease as the π-acceptor strength of the axial ligand decreases: CO $\gg$ BzNC $\sim$ P(OBu)$_3$ > PBu$_3$ $\geq$ MeIm. Ratios of quantum yields for loss of X vs. Y from the same FeN$_4$XY complex provide a measure of excited-state rate constant ratios. These ratios are similar to corresponding ground-state values. Apparent activation energies for Fe(DMGH)$_2$(MeIm)X for X = CO, P(OBu)$_3$, BzNC, and PBu$_3$ of $\sim$1, 4.3, 4.6, and 8.1 kcal/mol, respectively, are obtained from the temperature dependence of the quantum yields. The wavelength, temperature, and ligand dependence of quantum yields in a variety of FeN$_4$XY systems, including hemes, are most consistent with a common low-lying ligand field photoactive state, involving d$_{z^2}$ population, with a lifetime in the picosecond range. Higher quantum yields for π acceptors are rationalized in terms of a substantial decrease in π bonding in the axially elongated excited-state complex. A strong case is made for a common photochemical mechanism for all FeN$_4$ systems including hemes wherein the axial ligand bonding in the excited state resembles that of a cobalt(II) ground-state analogue.

Introduction

While reactions of hemes were one of the first photochemical reactions investigated,[2] only recently have detailed questions concerning the nature of the photoactive state responsible for ligand dissociation been addressed. Hemes show a wavelength-independent (280–620 nm for MbCO) quantum yield approaching 1.0 for CO photolysis but substantially lower for other ligands.[3,4] Flash photolysis studies reveal a nonemitting transient with a lifetime on the picosecond time scale.[5] The identity of the photoactive state is by no means established, but the prevailing view is that it is a ligand field state reached via efficient internal conversion or intersystem crossing from π^* states.[4–10]

If ligand field states are in fact responsible for the photolability of axial ligands in hemes, it makes sense to treat them as one member of a variety of structurally analogous FeN$_4$XY complexes. A similar array of low-lying ligand field states perhaps differing somewhat in their exact ordering in energy is common to all FeN$_4$XY complexes. Understanding the inorganic photochemistry in these low spin d^6 systems then involves the following problems:[11–13] The first problem is establishing if a thermally equilibrated excited state is present. Release of CO from hemes is said to be complete within a picosecond or less,[7] placing this system close to the limit wherein ligand release competes with vibrational relaxation. Quantum yields in this limit will depend upon quantum mechanical selection rules that are not well established.[13] The question of which electronic state the ligand is lost from may become blurred or irrelevant in this case. (2) If a specific thermally equilibrated (thexi) photoactive state is involved, identifying it in systems whose absorption spectrum is dominated by $\pi \rightarrow \pi^*$ or MLCT bands and where no emission is observed is difficult. These difficulties account for the fact that almost every conceivable state has been invoked at some point to account for the photolability in hemes. (3) To explain differences in quantum yields, systematic trends in photophysical and photochemical parameters must be elucidated. A common strategy is to assume that photophysical properties are invariant in similar complexes and then try to relate differences in quantum yields to excited-state bonding.

Studies of photochemical substitution reactions of Fe(II) complexes have been limited[11,14–17] owing to the general lack of suitable low-spin substitution-inert complexes. We have reported a remarkable similarity between the photosubstitution reactions of simple FeN$_4$XY systems and those of hemes where N$_4$ = phthalocyanine, bis(dioximes), tetraimines, etc.[14] Having completed an extensive characterization of a wide variety of substitution inert derivatives of ferrous dimethylglyoxime[18] and naphthoquinone[19] dioxime complexes, we undertook a survey of their photosubstitution reactions. These complexes are neutral, and can be studied in noncoordinating solvents. Their thermal substitution reactions have been extensively studied, and they proceed via a classic dissociative mechanism with rate parameters reflective of metal–ligand bond strength uncomplicated by solvation effects.[20] These systems offer a number of advantages over more conventional studies, primarily of photoaquation of Werner complexes (especially with regard to solvent participation). The existence of a clearly established dissociative process for both thermal and photochemical ligand substitution reactions makes it possible to directly compare ground- and excited-state reactivities in a case where the reaction coordinate for both processes differs only in the electronic state of the six-coordinate complex. Reports of such comparisons are rare.[11]

Theoretical models for photosubstitution reactions have attempted to predict bond weakening in ligand field excited states by using spectroscopically derived parameters for the ground-state complexes.[21,22] The availability of data more directly related to

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(1) Abbreviations: DMGH, dimethylglyoximate; NPQH, naphthoquinone dioximate; MeIm, 1-methylimidazole; BzNC, benzyl isocyanide; PBu$_3$, tributylphosphine; P(OBu)$_3$, tributyl phosphite. Rate constants for dissociation of ligand L trans to T are designated $k^{\mathrm{T}}_{-\mathrm{L}}$. The shortened forms N(MeIm), P(PBu$_3$), and PO (P(OBu)$_3$) are used as subscripts and superscripts. Quantum yields are similarly denoted by $\phi^{\mathrm{T}}_{-\mathrm{L}}$. Rate constants for addition of L trans to T are designated $k^{\mathrm{T}}_{+\mathrm{L}}$.

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metal–ligand bond energies in both the ground and excited states would provide a test of these models.

Experimental Section

Materials. All complexes were available from previous work or generated in situ as described previously.[18,19] All ligands and solvents were from standard sources and used as received.

Photolysis Procedures. Photolysis experiments were performed with a Oriel 200-W quartz halogen lamp. Monochromatic light was selected by using interference filters of 100-Å band-pass (Optically Thin Film, North Andover, MA). Typical light intensities were 10^{-7} to 10^{-6} einstein/min as determined by the actinometers $Fe(DMGH)_2(MeIm)(CO)$ at 400 nm, $Fe(DMGH)_2(MeIm)(BzNC)$ at 450 nm, FeTIM(MeIm)(BzNC) at 500 nm, and 550 nm with quantum yields reported for these complexes previously.[14]

An Alphametrics radiometer (Model dc1010) was used to monitor the lamp output on a daily basis. White light irradiations were carried out by using a 410 nm cutoff filter.

Thermostated and magnetically stirred toluene solutions of the complex (10^{-4}–10^{-5} M) were irradiated in the presence of a large excess of entering ligand (0.02–0.4 M) in 2-cm optical glass cells contained in a close-fitting brass block. All solutions had absorbances greater than 2 at the wavelength irradiated. For low temperatures, a Pyrex Dewar cell was used employing chlorobenzene (45 °C) or carbon tetrachloride (−23 °C) slush baths. The photolyses were followed by periodically taking the visible spectra of the solution being irradiated in a 1-cm pathlength cell at 10 or 25 °C using an Aminco DW2a UV/vis spectrophotometer. The extent of reaction for periods of photolysis indicates no correction is required for inner-filter effects or product absorption up to 30% conversion. The reactions could be conveniently driven to 100% completion by irradiating with white light for a few minutes. Corrections were made for thermal dark reactions, which were typically less than 10% of the photochemical reaction. The contributions of thermal reactions were verified experimentally by running blanks and also were in good agreement with that calculated by using rate constants previously reported for the reactions. Quantum yields were calculated from (1), where ΔA is

$$\phi = (\Delta A)V/t(\Delta\epsilon)I \qquad (1)$$

the absorbance change measured in a 1-cm cell and corrected for thermal reaction and $\Delta\epsilon$ is the difference in extinction coefficients between the reactant and the product at the wavelength of analysis, V is the volume of the solution, and t and I are the time of irradiation and incident light intensity, respectively. The reproducibility of quantum yields in separate experiments was typically ±15%.

Results

Spectral Features. Visible spectral data for $Fe(DMGH)_2XY$ and $Fe(NPQH)_2XY$ are given in Table I. The assignments have been discussed in detail previously.[18,19] The spectra for both systems are dominated by an intense MLCT band assigned to metal $d_{xz,yz}$ to oxime π^*. Substantial red shifts (~150 nm) in this band are observed when DMGH is replaced by NPQH. The band is also sensitive to the nature of the axial ligands shifting to higher energy as ligands of increased π-acceptor strength are introduced. The NPQH system shows an additional internal ligand band (IL) at higher energy (~400 nm), which does not shift appreciably with axial ligands. Ligand field bands have not been observed in these systems.

Photochemical Reactions. The thermal substitution reactions of FeN_4XY complexes have been previously described in detail.[18,19] Dissociation rates of 10^{-7}–10^{-2} s^{-1} at 25 °C are observed depending upon N_4, X, and Y. These complexes also show rich photosubstitution chemistry with spectral changes identical with those for the corresponding thermal reactions. The photoproduct is readily identified from the visible spectrum. Axial ligand substitution reactions were the only photochemical reactions observed. Both white light and monochromatic light irradiation of a complex FeN_4XY in the presence of X or Y result in reaction to give FeN_4X_2 or FeN_4Y_2, respectively, with clean isosbestic points (see Figure 1). However if a different ligand Z is used as entering ligand, there are two potential products, FeN_4XZ and FeN_4YZ.

$$FeN_4XY + Z \begin{cases} \longrightarrow FeN_4XZ + Y \\ \longrightarrow FeN_4YZ + Y \end{cases} \qquad (2)$$

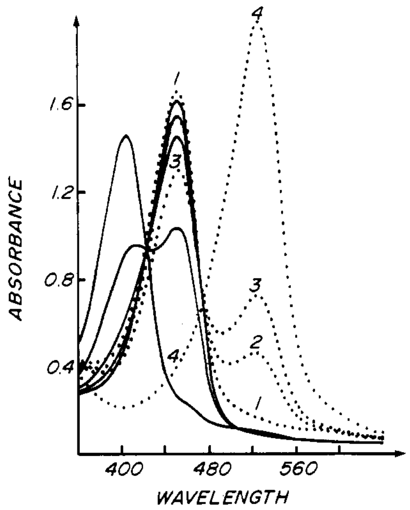

Figure 1. Spectral changes accompanying successive photolysis of $Fe(DMGH)_2(MeIm)(P(OBu)_3)$ in the presence of either 0.1 M MeIM(···) or 0.1 M $P(OBu)_3$ (—).

Table I. Visible Spectral Data for FeN_4LT Complexes in Toluene

		DMGH		NPQH	
L	T	λ_{max}, nm	$10^{-3}\epsilon$, M^{-1} cm^{-1}	λ_{max}, nm	$10^{-3}\epsilon$, M^{-1} cm^{-1}
MeIm	MeIm	531	6.9	702	25
	PBu_3	499	6.1	642	23
	$P(OBu)_3$	460	5.8	592	22
	BzNC	445	5.9	567	20
	CO	385	3.8	485	16
PBu_3	PBu_3	468	5.5	594	26
	$P(OBu)_3$	436	5.5	558	
	CO	376	4.3	470	
$P(OBu)_3$	$P(OBu)_3$	414	5.2	527	23
	CO	360	5.4	455	
BzNC	BzNC	392	6.0	505	

Table II. Survey of Primary Photoproducts[a,e] from Reactions of $Fe(DMGH)_2XY$ with Trapping Ligand Z

axial ligands				thermal rates[b]	
X	Y	Z	ligand lost	10^4k_{-X}, s^{-1}	10^4k_{-Y}, s^{-1}
MeIm	PBu_3	$P(OBu)_3$	MeIm	158	13
MeIm	CO	$P(OBu)_3$	CO	slow	5.2
MeIm	$P(OBu)_3$	PBu_3	$P(OBu)_3$	5.7	68
MeIm	BZNC	PBu_3	BZNC	0.1	3.1
PBu_3	$P(OBu)_3$	MeIm	$P(OBu)_3$	0.2	40
PBu_3	BZNC	MeIm	BZNC	0.23[d]	34[d]
PBu_3	CO	MeIm	CO	slow	230
$P(OBu)_3$	CO	MeIm	CO	slow	160

[a] The primary photoproduct corresponds to the complex in which the ligand lost is replaced by Z. See Table I for spectral details. [b] Thermal rates at 60 °C in toluene unless indicated otherwise.[18] [c] 65 °C. [d] 80 °C. [e] Corresponding reactions of the NPQH analogues give identical results.

The ligand that is more photolabile is inferred from the product. For example, irradiation of $Fe(DMGH)_2(P(OBu)_3)(PBu_3)$ in the presence of MeIm results in a clean conversion to $Fe(DMGH)_2(MeIm)(PBu_3)$, indicating that $P(OBu)_3$ is more photolabile than PBu_3 (Figure 2). In some cases the primary photosubstitution product can undergo secondary photochemical reactions. These secondary reactions can be minimized if monochromatic light is used. While white light irradiation of $Fe(NPQH)_2(P(OBu)_3(BZNC)$ gives largely $Fe(NPQH)_2(MeIm)_2$, irradiation at 500 nm results in clean conversion to $Fe(NPQH)_2(P(OBu)_3)(MeIm)$ with insignificant secondary reactions up to 30% conversion.

Results of a survey of photochemical reactions are collected in Table II. In all cases studied, one reaction mode accounts for >90% of the photoproduct.[23] A general pattern of high quantum

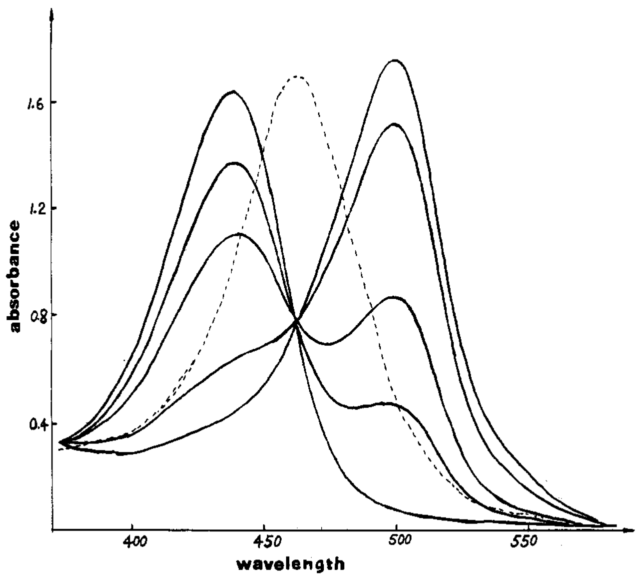

Figure 2. Spectral changes during successive photolysis of Fe-$(DMGH)_2(PBu_3)(P(OBu)_3)$ in the presence of 0.1 M MeIm. The dashed line shows the spectrum of $Fe(DMGH)_2(MeIm)(P(OBu)_3)$, which is not formed in the above reaction.

yields for π-acceptors has been noted previously.[14] However, the thermal lability seems to be a more reliable indicator of which ligand is preferentially labilized in the excited state. In FeN_4-$(MeIm)(PBu_3)$, the thermally more labile MeIm is photolyzed in preference to the better π acceptor, PBu_3. These qualitative observations are supported by quantitative quantum yields described later. Before discussing the quantum yields, we first provide a careful analysis of the mechanism of the photosubstitution reactions and consider in detail the thermal-following reactions, which, if overlooked, can lead to erroneous interpretations of photoreactivity.

Evidence for a Dissociative Mechanism. In flash photolysis experiments of six-coordinate heme complexes, the five-coordinate intermediate has been detected and characterized by both visible spectroscopy and kinetic studies,[5,8,25] proving that the basic mechanism for photosubstitution reactions for hemes is dissociative. It is reasonable to expect that these oxime systems also follow a D mechanism. In this mechanism the photoactive state FeN_4TL^* undergoes a ligand dissociation generating as the primary photoproduct, a presumably ground-state pentacoordinate complex FeN_4T, which subsequently adds ligands rapidly to give six-coordinate products.

$$\begin{tikzcd} FeN_4TL \arrow[r, "h\nu"] & FeN_4TL^* \arrow[r, "k^{T^*}_{-L}"] & FeN_4T \arrow[r, "k_{+E}", "+E"'] \arrow[ll, bend left, "k_{+L}", "+L"'] & FeN_4TE \end{tikzcd} \qquad (3)$$

Recombination rate constants in hemes[8,25] are typically 10^7–10^8 $M^{-1}\ s^{-1}$, and it is established that relative rates of ligand addition to $Fe(DMGH)_2$ complexes parallel those of hemes.[18] The hypothesis of dissociative reaction of the photoactive state was experimentally tested in several ways. For the case of a simple photodissociation of a ligand, the observed quantum yield for formation of product is given by

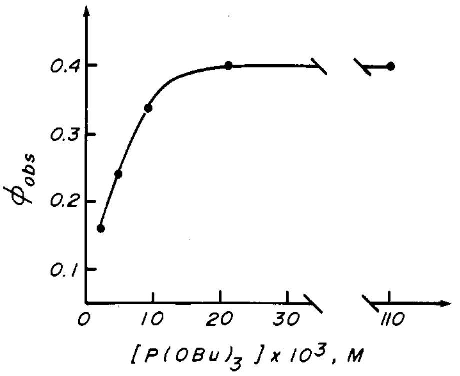

Figure 3. Dependence of ϕ_{obsd} on $[P(OBu)_3]$ for the photochemical (λ = 400 nm) reaction $Fe(DMGH)_2(MeIm)(CO) + P(OBu)_3 \rightarrow Fe$-$(DMGH)_2(MeIm)(P(OBu)_3) + CO$ in CO-saturated toluene at 25 °C.

$$\phi_{obsd} = \alpha\phi^{T}{}_{-L} \tag{4}$$

where $\phi^{T}{}_{-L}$ is the quantum yield for formation of the pentacoordinate intermediate, FeN_4T, and α is the efficiency of trapping the intermediate as the final product. The reactions of the pentacoordinate intermediate are exactly analogous to those of the same intermediate involved in thermal substitution reactions where the pseudo-first-order rate constant for ligand substitution also involves the product of a limiting dissociative rate constant multiplied by the trapping efficiency, α.

$$k_{obsd} = \frac{k^{T}{}_{-L}k_{+E}(E)}{k_{+L}(L) + k_{+E}(E)} = \alpha k^{T}{}_{-L} \tag{5}$$

The parameter α has the same meaning in both cases and is given by eq 6 if only E and L are present.

$$\alpha = \frac{k_{+E}(E)}{k_{+L}(L) + k_{+E}(E)} \tag{6}$$

The concentration dependence of ϕ_{obsd} for the photochemical reaction

$$Fe(DMGH)_2(MeIm)(CO) + P(OBu)_3 \xrightarrow{h\nu} Fe(DMGH)_2(MeIm)(P(OBu)_3) + CO \tag{7}$$

was studied at 1 atm of CO and varying $[P(OBu)_3]$. As shown in Figure 3, the quantum yield increases with increasing $[P(OBu)_3]$ and reaches a limiting value of 0.40. A plot of $1/\phi_{obsd}$ vs. $[CO]/[P(OBu)_3]$ is linear as expected from (6) with a slope = 1.4 ± 0.2 and intercept = 2.5 ± 0.1 from which we derive $k_{+PO}/k_{+CO} = 1.4 \pm 0.2$ and $\phi^{N}{}_{-CO} = 0.4$.

When [E] is large and [L] is negligible, eq 4 reduces to $\phi_{obsd} = \phi_{-L}$ ($\alpha = 1$). This "limiting" quantum yield should be independent of both the concentration and nature of the entering ligand providing E does not quench the excited state. Reactions 8 and 9 were found to have ϕ_{obsd} independent of the concentration of

$$Fe(DMGH)_2(MeIm)(CO) + MeIm \rightarrow Fe(DMGH)_2(MeIm)_2 + CO \tag{8}$$

$$Fe(NPQH)_2(MeIm)(P(OBu)_3) + MeIm \rightarrow Fe(NPQH)_2(MeIm)_2 + P(OBu)_3 \tag{9}$$

entering ligand for a 10-fold variation in [MeIm]. Furthermore the quantum yield for reaction 8 is identical with the limiting quantum yield for reaction 7 described above, demonstrating that ϕ_{obsd} is independent of the nature of the entering ligand. These observations are fully consistent with a dissociative mechanism.

As an additional test of the dissociative mechanism, a competitive trapping method was used. In the presence of two potential entering ligands E_1 and E_2, the ratio k_{+E_1}/k_{+E_2} can be obtained

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(23) For each reaction listed in Table II, we have carefully examined the known rate constants for dissociation of both axial ligands from the starting material and all potential primary and secondary products. For reaction of FeN_4XY with entering ligand E, this includes $k^{Y}{}_{-X}$, $k^{X}{}_{-Y}$, $k^{E}{}_{-X}$, $k^{E}{}_{-Y}$, $k^{X}{}_{-E}$, $k^{Y}{}_{-E}$, and $k^{E}{}_{-E}$. These rate constants are all given in previous work.[18,19] Other workers[17] have erroneously assigned thermal-following chemistry to photochemical reactions in cases where kinetic data was not available.[24]

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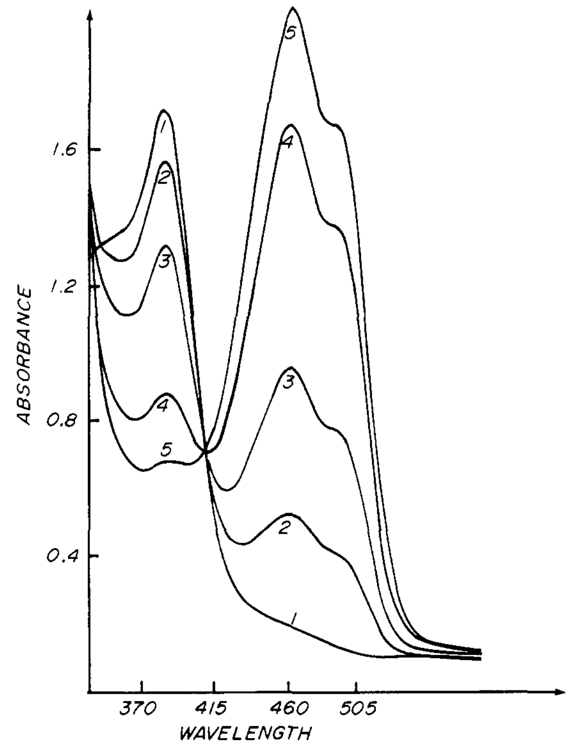


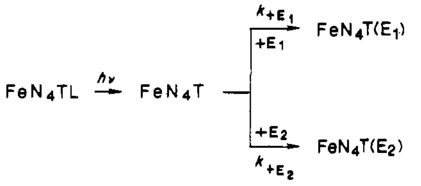
Figure 4. Competition experiment in which Fe(DMGH)$_2$(MeIm)(CO) is irradiated at 400 nm in the presence of 0.034 M PBu$_3$ and 0.031 M P(OBu)$_3$ at 25 °C in toluene. The two products Fe(DMGH)$_2$(MeIm)(PBu$_3$) and Fe(DMGH)$_2$(MeIm)(P(OBu)$_3$) absorb at 499 and 460 nm, respectively.

Table III. Comparisons of Rate Constant Ratios for Reaction of the Photochemically and Thermally Generated Pentacoordinated Intermediate Fe(DMGH)$_2$X[a]

X	ratios	photochemical	thermal[c]
MeIm	k_{+P}/k_{+PO}	1.0 (3)[b]	0.7 (3)
	k_{+PO}/k_{+CO}	1.4 (2)	1.4 (2)
PBu$_3$	k_{+N}/k_{+PO}	7 (2)[b]	5 (2)
	k_{+N}/k_{+P}	6 (2)	4 (1)

[a] 25 °C in toluene unless otherwise indicated. [b] Obtained from phototrapping methods as described in text under the following conditions: [PBu$_3$] = 0.034 M, [P(OBu)$_3$] = 0.031 M; [P(OBu)$_3$] = 0.062 M, [MeIm] = 0.021 M. [c] Calculated from data in ref 18.

from the ratio of the two products FeN$_4$T(E$_1$) and FeN$_4$T(E$_2$) formed on photolysis of FeN$_4$TL.



(10)

Thus, when a solution of Fe(DMGH)$_2$(MeIm)(CO) was irradiated at 400 nm in the presence of both P(OBu)$_3$ and P(Bu)$_3$, a mixture of Fe(DMGH)$_2$(MeIm)(P(OBu)$_3$) and Fe(DMGH)$_2$(MeIm)(PBu$_3$) was generated as shown in Figure 4. The presence of an isosbestic point indicates that the two products are formed in a constant ratio. Concentrations of the two products were deduced from the absorbance at 460 and 499 nm.

The rate constant ratios for ligand additions to the photointermediate FeN$_4$T and to the corresponding thermally generated intermediate, compared in Table III, are within experimental error of each other indicating that the pentacoordinate intermediates generated by the two methods are identical, or at least have the same reactivity. This constitutes reasonable evidence that the pentacoordinate complex is generated in its ground electronic state.

Quantum Yield Measurements. For a given complex FeN$_4$XY both quantum yields ϕ_{-X} and ϕ_{-Y} may be obtained. The following reactions carried out by using a large excess of the entering ligand ($\phi_{obsd} = \phi_{-L}$) afford the limiting quantum yields shown. Note that photolysis of the "wrong ligand" (loss of X in reaction 11 or Y in reaction 12) merely results in exchange, thus allowing a direct determination for photolysis of the less photolabile ligand. Results are collected in Table IV.

Table IV. Quantum Yields for Dissociation of L from Fe(DMGH)$_2$TL and Fe(NPQH)$_2$TL[a]

trans ligand	leaving ligand	DMGH		NPQH	
		λ_{irr}, nm	$10^2\phi$	λ_{irr}, nm	$10^2\phi$
MeIm	CO	400	41	450	20
Meim[b]	BzNC	450	5.3	550	1.2
BzNC[b]	BzNC	400	3.3		
MeIm	P(OBu)$_3$	450	2.6	600	0.25
PBu$_3$	P(OBu)$_3$	450	5.0		
P(OBu)$_3$	P(OBu)$_3$	400	4.0	500	0.79
MeIm	PBu$_3$	500	0.04	650	≤0.004
PBu$_3$	PBu$_3$	450	1.5		
P(OBu)$_3$	PBu$_3$	450	0.03		
PBu$_3$	MeIm	500	0.5		
P(OBu)$_3$	MeIm	450	0.6	600	0.047
BzNC	MeIm	450	0.3	550	0.11

[a] 10 °C in toluene, this work. Entering ligand is the same as the trans ligand in all cases. [b] Reference 14, 25 °C.

$$\mathrm{FeN_4XY} + \mathrm{X} \xrightarrow{\phi^{X}_{Y}} \mathrm{FeN_4X_2} + \mathrm{Y} \tag{11}$$

$$\mathrm{FeN_4XY} + \mathrm{Y} \xrightarrow{\phi^{Y}_{-X}} \mathrm{FeN_4Y_2} + \mathrm{X} \tag{12}$$

$$\mathrm{FeN_4X_2} + \mathrm{Y} \xrightarrow{\phi^{X}_{-X}} \mathrm{FeN_4XY} + \mathrm{X} \tag{13}$$

Significant absorbance changes were typically observed for monochromatic irradiation times of 1–40 min. However in some cases white light irradiations (which typically require 20-fold smaller irradiation times compared to those using narrow bandpass filters) were used to avoid possible thermal contributions that might lead to errors in cases of prolonged irradiation.

In white light irradiations, two identical solutions of FeN$_4$XY containing excess X or Y (which neither absorb in visible region or quench) were irradiated under identical conditions such that the number of photons absorbed is the same. A wavelength-averaged quantum yield over the absorption spectra of the complex is obtained by this method. The average quantum efficiency of reaction 11 can then be obtained relative to that of reaction 12. If both processes show an identical wavelength dependence, one expects to obtain identical ratios of quantum yields with either monochromatic or white light. This is found to be the case for FeN$_4$(MeIm)(BzNC) where the ratio of quantum yields for dissociation of MeIm vs. BzNC obtained with white light are within experimental error of those obtained with monochromatic irradiation.

Temperature Dependence of Quantum Yields. The quantum yields for dissociation of X (X = CO, BzNC, P(OBu)$_3$, PBu$_3$) trans to MeIm (ϕ^{N}_{-X}) were studied over a wide temperature range by using MeIm as the entering ligand. Results are collected in Table V.

The temperature dependence of ϕ^{N}_{-P} from Fe(DMGH)$_2$(MeIm)(PBu$_3$) was also studied by using white light irradiation of identical solutions. A possible complication that may arise is the change of the area under the absorption spectrum as a function of temperature leading to a change in the number of photons absorbed by identical solutions at different temperatures. This does not appear to be a significant problem for the case of Fe(DMGH)$_2$(MeIm)(P(OBu)$_3$) for which the same value of ΔE_{app} was obtained by using white light or monochromatic light irradiation.

Discussion

Quantum yields shown in Table IV show a rough correlation with the energy of irradiation. However, it does not seem that the photon energy is the major factor in determining the quantum

Table V. Temperature Dependence of Quantum Yields[a] in Toluene for the Reaction

$$FeN_4(MeIm)L + MeIm \xrightarrow{h\nu} FeN_4(MeIm)_2 + L$$

L	λ, nm	$10^2\phi_{-L}$ T = 25 °C	T = 10 °C	T = 0 °C	T = −23 °C	T = −45 °C
			DMGH			
CO	400	41	41	...	39	35
BzNC	450	5.3	4.2	3.1	1.7	0.5
$P(OBu)_3$	450		2.6	1.9	1.0	0.4
PBu_3	>410[b]	0.04		0.016	...	0.0007
			NPQH			
CO	450		20	15	14	15
$P(OBu)_3$	600	0.43	0.25	0.14	0.023	
$P(OBu)_3$	400	0.22	0.11	0.06	0.02	

[a] Reproducibility of separate trials was typically ±15%. [b] White light irradiation was used.

Table VI. Comparison of Ground-State and Excited-State Reactivity of FeN_4XY Complexes

		$Fe(DMGH)_2XY$			$Fe(NPQH)_2XY$		
X	Y	λ_{irr},[c] nm	ϕ_{-X}/ϕ_{-Y}[a]	k_{-X}/k_{-Y}[b]	λ_{irr},[c] nm	ϕ_{-X}/ϕ_{-Y}[a]	k_{-X}/k_{-Y}[b]
MeIm	PBu_3	500/w	12.5	23	w	~100	250
4CN(py)	$P(OBu)_3$	450	2.5	2.5			
$P(OBu)_3$	MeIm	450	5	13	600	5.3	16
BzNC	MeIm	450	18	23	550	11	18
		w	13	23	w	15	18
$P(OBu)_3$	PBu_3	w	170	200			

[a] Ratio of quantum yields for loss of X vs. Y. [b] Ratio of thermal rate constants for dissociation of X vs. Y. [c] w indicates white light irradiation ≥410 nm.

yields. Relative magnitudes of ϕ show a much stronger correlation with the nature of the ligand lost. Thus quantum yields for CO dissociation are found between 0.2 and 1.0 for irradiations from 280 to 620 nm in hemes, phthalocyanines, TIM, and NPQH and DMGH complexes.[14] Corresponding quantum yields for isocyanides are in the range 0.02–0.10, and values for methylimidazole are substantially lower than those for CO in all systems.

Within the oxime systems, values for the NPQH complexes, while typically lower than the DMGH analogue, are not lowered enough to be explained in terms of the photon energy alone. Irradiation into the ligand band of NPQH at 400 nm also gives quantum yields and temperature dependences that strongly suggest that both MLCT and intraligand irradiation result in similar photochemical behavior in spite of a 20 kcal/mol difference in photon energy.

Two limiting cases for photoreaction have been considered. In the "fast" limit,[12a] the excess energy provided by the photon is rapidly converted into vibrational energy and ligand dissociation competes with vibrational relaxation.[11-13] One characteristic of this model is that the quantum yield increases with increasing energy of the photon. In addition, the excited state does not persist long enough to thermally equilibrate with its surroundings.[26] Neither the wavelength dependence nor the temperature dependence of the quantum yield in our systems is consistent with this model. Also, there is virtually no precedent for how one should compare quantum yields in different complexes using this model.

Therefore, the results will be interpreted in terms of the "slow" or thexi case wherein a thermally equilibrated excited state (thexi), generally the lowest energy excited state, reached by a series of internal conversions or intersystem crossings, is responsible for the photochemistry. The obvious advantage of this model is that reactions of the excited state may then be treated by using the same concepts as those applied to reactions of ground state molecules.

Nature of the Photoactive State. There is no convincing proof concerning the nature of the photoactive state in hemes, which have been studied in some detail, let alone other FeN_4XY systems for which only limited data exists. While MLCT and other non ligand field states have sometimes been considered as the photoactive state, the prevailing speculation favors ligand field states. For a d^6 system with D_{4h} or C_{4v} symmetry, there will be a number of low-energy ligand field states. Since the predominant reactivity mode involves axial ligand dissociation, a ligand field state (either a singlet, triplet, or quintet) involving population of d_{z^2} is proposed as the photoactive state in these systems. Loew has implicated the singlet d_{z^2} state to account for the photochemistry of hemes.[9]

Theoretical models and experimental facts support the idea that substantial axial bond weakening occurs on population of d_{z^2}. Structural data for high, low, and intermediate-spin hexacoordinate hemes[27] shows that axial bonds are lengthened by 0.2–0.3 Å on population of d_{z^2}. It is extremely doubtful that axial bond weakening of this magnitude would be achieved in MLCT or π^* excited states.

Quantum Yields. A careful analysis of quantum yield data requires that several factors be considered before attempting to relate the quantum yields in Table IV to metal–ligand bonding in the excited state. Thermal-following reactions, which may contribute to apparent quantum yields, have been already discussed. We also note that the pentacoordinate species will have a lifetime of the order of 10^{-7} s ($k_{+X} \simeq 10^8$ M^{-1} s^{-1} at 1 M [X]), which is too short for further ligand loss to give a four-coordinate species.[25] Possible cage recombination effects have been shown not to be a complication in picosecond heme photolyses.[5]

Even after all complicating thermal-following processes are factored out, the quantum yield is not a simple quantity. It is a complex ratio of rate constants involving photochemical and photophysical processes, each of which may vary with conditions in structurally similar complexes.

$$\phi_{-X} = \phi_{IC}\frac{k^*_{-X}}{k^*_{-X} + k^*_{-Y} + k_{other}} \qquad (14)$$

For our purposes, equation 14 may be used,[11] where ϕ_{IC} is the efficiency of population of the photoactive state, k^*_{-X} and k^*_{-Y} are excited state rate constants for ligand dissociation, and k_{other} is the rate constant for all other modes of decay of the excited state. Differences in ϕ_{-X} in different complexes could result from changes in one or all of the parameters shown. Cautious comparison of closely related systems can be made, assuming that ϕ_{IC} and k_{other} do not vary, and thus quantum yield differences will

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Table VII. Comparison of Measured[a] Thermal and Derived Photochemical Rate Parameters for $Fe(DMGH)_2(MeIm)X$ Complexes

X	ΔE_{App}, kcal/mol	k^{*}_{-X},[b] s^{-1}	ΔH^{*}_{-X}, kcal/mol	ΔS^{*}_{-X}, cal/mol	k^{298}_{-X}, s^{-1}
CO	0.9	2×10^{11}	27	7	4×10^{-6}
BzNC	4.6	9×10^{9}	~30	~18	6×10^{-6}
$P(OBu)_3$	4.3	4×10^{10}	29.0	18.4	4×10^{-5}
PBu_3	8.1	8×10^{8}	32.5	25.3	3×10^{-6}

[a] Thermal data from ref 18 in toluene. [b] Calculated from Eyring equation assuming excited-state activation parameters $\Delta H^{*}_{-X}{}^{*} = \Delta E_{App} + 2.5$ and $\Delta S^{*}_{-X}{}^{*} = 0.7\ (\Delta S^{*}_{-X})$.

reflect differences in excited-state bond strengths.

The ratio of the quantum yields ϕ_{-X}/ϕ_{-Y} gives a less ambiguous measure of the ratio of excited-state rate constants since all other parameters must be the same if only one photoactive state is responsible for both reactions.

$$\phi_{-X}/\phi_{-Y} = k^{*}_{-X}/k^{*}_{-Y} \tag{15}$$

These ratios are summarized in Table VI along with corresponding ground-state ratios obtained from the kinetics of thermal substitution reactions also proceeding via the same D mechanism. Taking into account that the thermal studies are at different temperatures, the similarity in the ground- and excited-state reactivities is remarkable. The results are consistent with a model in which all the bonds considered in Table VI experience a similar weakening in the excited state.

Temperature Dependence. The temperature dependence of the quantum yields was subjected to an Arrhenius plot, giving apparent activation energies shown in Table VII. The quantum yields are found to correlate directly with ΔE_{app} as shown in Figure 5. This is considered strong evidence for the existence of a well-defined bound state in which the metal–ligand bond energy is the principal determinant of ϕ_{-X}. If transition-state theory is applied, the rate constant in the excited state may be calculated[13] from excited-state activation enthalpy and entropies by using the Eyring equation.

$$k_{-X} = \frac{kT}{h} e^{-(\Delta H^{*} - T\Delta S^{*})/RT} \tag{16}$$

The value of ΔE_{app} (or the analogous ΔH^{*}_{App}) unfortunately includes small effects due to the temperature dependence of ϕ_{IC} and k_{other} in eq 14. Correction for these effects would lead to ΔH^{**}_{-X} somewhat higher than ΔE_{App}. In a $Rh(NH_3)_5Cl^{2+}$ system, it has been established that photophysical processes contribute 2–3 kcal/mol.[28] Since the excited-state dissociation process is essentially the same as the corresponding ground-state reaction, except involving weaker bonds, ΔS^{**}_{-X} may be roughly estimated from previously reported[34,35] values of ΔS^{*}_{-X}. For $\Delta H^{*}_{-X} = \Delta E_{App}$ and $\Delta S^{**}_{-X} = \Delta S^{*}_{-X}$ in eq 16, excited-state rate constants k_{-P} of $\sim 10^{9}$ and $k_{-CO} \geq 10^{13}\ s^{-1}$ are obtained. The result for CO would mean that ligand loss would compete with vibrational relaxation, placing the system outside the thexi limit and in a region where the Eyring equation would not apply. However, if one includes a correction for the temperature dependence of k_{other} to the apparent activation energy of ~3 kcal/mol and an entropy 70% of the ground-state value, the calculated excited-state rate constant is $\sim 10^{11}$, within the thexi limit. Estimates of the excited-state rate constants using this crude approach at least demonstrate that the observed quantum yields are not inconsistent with this model. Assuming $\phi_{IC} = 1$, one may then calculate k_{other} from eq 14 from which we infer a common excited-state lifetime in the picosecond regime, similar to that found in hemes.[5]

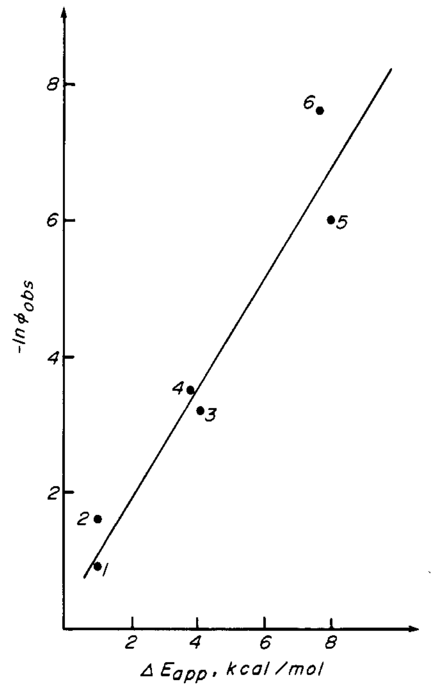

Figure 5. Correlation of quantum yields for dissociation of X trans to methylimidazole in $FeN_4(MeIm)X$ at 10 °C with ΔE_{App}. (1) $N_4 = (DMGH)_2$, X = CO; (2) $N_4 = (NPQH)_2$, X = CO; (3) $N_4 = (DMGH)_2$, X = BzNC[(4) $N_4 = (DMGH)_2$, X = $P(OBu)_3$; (5) $N_4 = (NPQH)_2$, X = $P(OBu)_3$; (6) $N_4 = (DMGH)_2$, X = PBu_3.

An alternative interpretation of the temperature dependence for MLCT photochemistry commonly invoked in systems where no low-lying LF states are likely,[9] is that the ΔE_{App} reflects a thermal process to reach a LF state lying *above* the nonreactive MLCT state. These explanations invariably ignore any barriers within the LF state. While the energies of LF states in these systems are not known, we believe they are more likely to lie below than above the MLCT states. The numerous parallels with ground-state chemistry are also more easily rationalized in terms of a barrier associated with a lowest energy LF excited state. In fact the existence of lower LF states is typically invoked to account for the lack of emission in these systems![30] An apparent activation energy of 3.8 kcal/mol for $P(OEt)_3$ loss from $FeTIM(P(OEt)_3)_2{}^{2+}$ was explained in terms of the LF state lying above the MLCT state.[17] The value is quite similar to those reported here and could also be due to a barrier that reflects the metal ligand bond energy in the excited state.

The admittedly crude estimates of the excited-state rate constants in Table VII represent one of the few cases, where excited-state and ground-state reactivities may be directly compared. The excited state is about 10^{15} more labile than the ground-state complex. This order of magnitude is remarkably the same as that found for aquation of $Rh(NH_3)_5Cl^{2+}$ where a common D mechanism for both states is not easily demonstrated.[28] Emission in the $Rh(NH_3)_5Cl^{2+}$ however, allows a more precise determination of the excited-state constant in this system.

The reactivity of the proposed ligand field photoactive state seems entirely consistent with what is expected for a singlet d_{z^2} state based on ground-state analogues. The proposed photoactive state is electronically similar to a d^7 low-spin Co(II) complex. The enthalpy for piperidine binding to cobalt(II) porphyrin is −1.7 kcal/mol (K^{L}_{L}),[31] and it is well-known that cobalt porphyrins and cobalt dimethylglyoximes do not readily add a sixth ligand.[32] The dissociation rate for imidazole from a high-spin pentacoordinate

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heme[25] is 2×10^5 s^{-1}. However, as in the cobalt case, one expects the corresponding rate constant for a hexacoordinate analogue to be several orders of magnitude faster[33] owing to the destabilizing effect of the electron in d_{z^2}.

The very weak bonds suggested for the photoactive state are a necessary condition for photochemical lability. It is important to recognize that *no* significant quantum yield is possible for a dissociative process from a thexi state with a subnanosecond lifetime *unless* the bonds are weak.

Bonding Effects in the Excited State. We have already seen in Table VI that ratios of excited-state rate constants *within a given complex* parallel ground-state values. However, there is no direct relationship between thermal lability and quantum yields *in different complexes.* For example CO is more labile than PBu_3 in $Fe(NPQH)_2(MeIm)(X)$ and has a ground-state activation enthalpy 7 kcal/mol smaller, yet the $\phi^{N}{}_{-CO}$ is 10^3 times greater than $\phi^{N}{}_{-P}$. Generally π-acceptor ligands show substantially greater photolability than strictly sigma bonding ligands. The observation is not limited to CO. Quantum yields for PBu_3 vs. $P(OBu)_3$ also indicate that the better π-acceptor typically has a higher quantum yield even though ground state rates show $k^{N}{}_{-P} < k^{N}{}_{-PO}$. These observations suggest than π-bonding is less important in the excited state.

An angular overlap model[22] has been applied to the prediction of photochemical reactivity in coordination complexes. This model uses ground-state ϵ_σ and ϵ_π parameters to evaluate d orbital contributions to metal–ligand bonding in the excited state. These parameters are not available for the systems described here, nor are they likely to be useful. It is noted that spectroscopic parameters are very poor indicators even of ground-state bond strengths. We suggest that bond lengthening in the excited state will dramatically alter these ϵ_σ and ϵ_π parameters. For example, in a series of sterically hindered nickel complexes, ϵ_σ decreases by a factor of 2 for a 0.2 Å increase in Ni–N bond length.[35]

One expects π bonding to decrease even more in the excited state because of the more rapid decrease of π overlap with distance. This may explain the apparent contradiction that an excited state which is primarily σ^* results in the greatest labilization of π-acceptor ligands.

Perhaps also related to the diminished importance of π bonding in the excited state are the observations for DMGH in Table IV of a very small dependence of ϕ_{-N} on the trans ligand. In thermal reactions 10^4 $k^{T}{}_{-N}$ values at 60°C are 158, 5.7, and 0.1 for T = PBu_3, $P(OBu)_3$, and BzNC, respectively, while 10^3 $\phi^{T}{}_{-N}$ values are 5, 6, and 3, respectively. We have previously proposed that the large trans delabilizing effects of π-acid ligands is due to the loss of synergistic π bonding in the transition state. In the photochemical process, most of the π bonding would already be lost in the photoactive state prior to ligand dissociation.

Summary

In summary, the following points are emphasized.

1. Thermal and photochemical axial ligand substitution in FeN_4XY systems both occur via a dissociative mechanism.
2. The temperature dependence of ϕ indicates that the potential well for the excited state of these complexes is well-defined and ϕ_{-X} is primarily dependent on the bond strength in the excited state.
3. Rate constant ratios for loss of X vs. Y in the excited state can be unequivocally established in these systems for a wide range of ligands.
4. The high quantum yields for CO photodissociation is attributed to a dramatically diminished importance of π bonding in the axially elongated excited state, which results in very weak metal–CO bonding.
5. A common photoactive state of picosecond lifetime involving d_{z^2} population is likely responsible for the gross similarities in photolability in a variety of FeN_4XY systems, including hemes, independent of the nature of the initial excitation. This state should parallel the ligation characteristics of the analogous cobalt (II) complex.

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Registry No. $Fe(DMGH)(MeIm)_2$, 57804-36-1; $Fe(DMGH)(MeIm)(PBu_3)$, 100485-22-1; $Fe(DMGH)(MeIm)(P(OBu)_3)$, 100485-23-2; $Fe(DMGH)(MeIm)(BzNC)$, 59575-74-5; $Fe(DMGH)(MeIm)CO$, 61395-33-3; $Fe(DMGH)(PBu_3)_2$, 100485-25-4; $Fe(DMGH)(PBu_3)(P(OBu)_3)$, 100485-26-5; $Fe(DMGH)(PBu_3)CO$, 100485-29-8; $Fe(DMGH)(P(OBu)_3)_2$, 100485-30-1; $Fe(DMGH)(P(OBu)_3)CO$, 100485-33-4; $Fe(DMGH)(BzNC)_2$, 59575-75-6; $Fe(NPQH)(MeIm)_2$, 101915-88-2; $Fe(NPQH)(MeIm)(PBu_3)$, 101915-94-0; $Fe(NPQH)(MeIm)(P(OBu)_3)$, 101915-95-1; $Fe(NPQH)(MeIm)(BzNC)$, 101915-92-8; $Fe(NPQH)(MeIm)CO$, 101915-97-3; $Fe(NPQH)(PBu_3)$, 101915-90-6; $Fe(NPQH)(PBu_3)(P(OBu)_3)$, 101915-98-4; $Fe(NPQH)(PBu_3)CO$, 101916-00-1; $Fe(NPQH)(P(OBu)_3)_2$, 101915-91-7; $Fe(NPQH)(P(OBu)_3)CO$, 101916-02-3; $Fe(NPQH)(BzNC)_2$, 101915-96-2.

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Electronic Ground States, Chemical Reactivity, and Related Properties of Square-Planar Platinum(II) Dithio Complexes

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EHMO-SCCC calculations have been used in the analysis of the electronic structure, chemical reactivity, and related properties of four model platinum(II) complexes representing the set of compounds formed in the reactions of planar d^8 bis(1,1-dithiolato)platinum(II) complexes with phosphine bases. From the calculated molecular orbital description of the complexes and the frontier molecular orbital approach of chemical reactivity, plausible mechanisms of their formation reactions and fluxional behavior have been deduced. According to these mechanisms a frontier-controlled nonrigid quasi-five-coordinated four-center transition state is formed via a direct nucleophilic attack of the coordinated bidentate dithio ligand by the phosphine nucleophile. The role of sulfur and/or phosphorus 3d functions on the chemical bonding and reactivity of the complexes is also discussed. Overlap populations, two-center energy terms, and computed atomic charges of the complexes, compared to those of the corresponding free of metal ligand systems, were found to provide adequate information on the mechanism of the charge-transfer interactions involved in the bonding of the complexes.

Introduction

The interaction of Lewis bases with nickel triad dithiolates is a topic of considerable interest,[1-4] a variety of species being isolated, several of which have been structurally characterized. In particular, the reaction of phosphine bases with square-planar d^8

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