

## Axial Ligand Substitution Reactions of Phosphite Derivatives of Fe(II) Macrocyclic Complexes

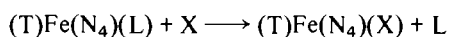
MOHAMED A. KHALIFA

Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, Egypt

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### Abstract

Kinetic studies of ligand substitution reactions of six-coordinated Fe(II) macrocyclic complexes were investigated



where  $N_4$  = DMGH, BQDH and Tim. The T, L and X ligands include nitrogen and phosphorous donors. The reaction mechanism is strictly dissociative (D), and the five-coordinate intermediate  $(T)Fe(N_4)$  possesses little or no ability to discriminate between nucleophiles. *cis* effect as well as *trans* group and leaving group effects are reported.

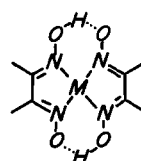
### Introduction

Very little is known about the chemistry of phosphine and phosphite derivatives of iron(II) complexes. Angelici [1] reported that  $Fe(CO)_4PPh_3$  reacts with  $PPh_3$  via CO dissociation above 160 °C to give *trans*- $Fe(CO)_3(PPh_3)_2$ . Recently, Atwood [2] reported the reaction of  $Fe(CO)_3L_2$  and  $Fe(CO)_4L$  where  $L = PPh_3, P(OPh)_3$  and  $PPh_3$  with CO. The complexes were found to be relatively inert, requiring temperatures above 100 °C. The order of lability from  $Fe(CO)_3L_2$  was reported to be  $AsPh_3 > PPh_3 > P(OPh)_3$  which was explained in terms of the general bond strength to low valent metal centers.

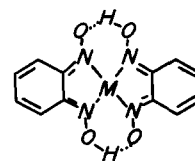
Another class of phosphine and phosphite derivatives of Fe(II) porphyrin and phthalocyanine complexes was investigated by Sweigart and co-workers [3, 4]. The reaction of Fe(II)(Pc) with  $P(OBu)_3, P(Bu)_3, Im, MeIm, Py$  and  $Pip$  was reported and the reaction mechanism was found to be dissociative. A comparative study with some inert ruthenium(II) phthalocyanine complexes has also been reported [5].

Iron macrocyclic complexes are biologically important systems since they are extremely important in enzymatic oxidation as well as in reactions involving electron transfer. This study involves the synthesis, characterization and the kinetics of axial ligand substitution of a series of Fe(II) macrocyclic com-

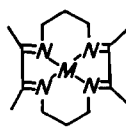
plexes\*. The axial ligands are phosphorus and nitrogen donors. Thus the Fe(II) is situated in a six-coordinate environment via a quadridentate in-plane macrocyclic ligand and two axial monodentate ligands. The study is designed to help to explore the similarities and differences between various Fe(II) complexes which mimic the heme group in order to determine the features of the porphyrin ligand which give rise to the binding characteristics of the heme group in terms of both stability (equilibria) and lability (kinetics).



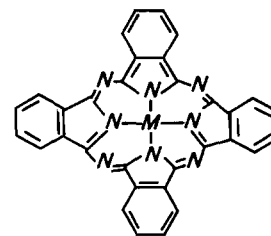
M(DMGH)<sub>2</sub>



M(BQDH)<sub>2</sub>



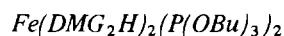
M(Tim)



M(Pc)

### Experimental

#### Synthesis



Chloroform–methanol mixture (50:50 by volume), was placed in a 3-neck-flask fitted with a serum

\*Ligand abbreviations: DMGH = dimethylglyoximate; BQDH = benzoquinone dioximate (3,5-cyclohexadiene-1,2-dione dioximate); Tim = Me<sub>4</sub>[14]1,4,8,11-tetraene N<sub>4</sub>; Pc = phthalocyanine; TPP = tetraphenylporphyrin; MeIm = 1-methyl imidazole, P(OBu)<sub>3</sub> = tri-n-butylphosphite.

stopper, nitrogen inlet and bubbler. Nitrogen was bubbled through the solvent mixture for 30 min and  $\text{Fe}(\text{DMGH})_2(\text{MeIm})_2$  (0.01 mol) was then added. After stirring for a few minutes  $\text{P}(\text{OBU})_3$  (0.04 mol) was added and the reaction mixture was refluxed overnight. The volume was reduced under vacuum and the complex was precipitated by adding hexane. The product was filtered off, washed with hexane and dried *in vacuo*. Yield 40%.

$\text{Fe}(\text{DMGH})_2(\text{P}(\text{OBU})_3)(\text{MeIm})$

To a solution of  $\text{Fe}(\text{DMGH})_2(\text{MeIm})_2$  (0.01 mol) in deaerated chloroform–methanol (50:50 by volume),  $\text{P}(\text{OBU})_3$  (0.015 mol) was added. The reaction mixture was refluxed under nitrogen for a few hours and monitored spectrophotometrically until the formation of the mixed complex was completed. The volume was then reduced under vacuum and the complex was precipitated by adding petroleum ether. The product was filtered off, washed with petroleum ether and dried *in vacuo*. Yield 61%.

$\text{Fe}(\text{BQDH})_2(\text{P}(\text{OBU})_3)_2$

A solution of  $\text{Fe}(\text{BQDH})_2(\text{MeIm})_2$  (0.01 mol) in chloroform was placed in a 250-ml round-bottom schlenk flask under a stream of  $\text{N}_2$  for 30 min. Tributylphosphite (0.04 mol) was then added and the reaction mixture was refluxed for 5 h. The resulting red solution was then concentrated under vacuum. The product was precipitated from hexane, filtered off and dried *in vacuo*. Yield 48%.

$\text{Fe}(\text{BQDH})_2(\text{P}(\text{OBU})_3)(\text{MeIm})$

A solution of  $\text{Fe}(\text{BQDH})_2(\text{MeIm})_2$  (0.01 mol) in chloroform–methanol mixture (50:50 by volume) was placed in a 250-ml round-bottom flask fitted with a serum stopper,  $\text{N}_2$  inlet and bubbler. Nitrogen was bubbled for 30 min and  $\text{P}(\text{OBU})_3$  (0.015 mol) was then added. The reaction mixture was refluxed and monitored until the formation of the mixed complex was completed. The solution was concentrated under vacuum and the product was precipitated from petroleum ether. The complex was filtered off, washed with petroleum ether and then dried *in vacuo*. Yield 54%.

$\text{Fe}(\text{Tim})(\text{P}(\text{OBU})_3)_2(\text{PF}_6)_2$

To a solution of  $\text{Fe}(\text{Tim})(\text{CH}_3\text{CN})_2(\text{PF}_6)_2$  (0.01 mol) in acetone,  $\text{P}(\text{OBU})_3$  (0.03 mol) was added. The reaction mixture was stirred at the ambient temperature for 30 min, then filtered off. Ethanol was added slowly to the filtrate and the red–violet solid formed was filtered off, washed with ethanol and dried *in vacuo*. Yield 51%.

$\text{Fe}(\text{Tim})(\text{P}(\text{OBU})_3)(\text{MeIm})(\text{PF}_6)_2$

To a solution of  $\text{Fe}(\text{Tim})(\text{CH}_3\text{CN})_2(\text{PF}_6)_2$  (0.01 mol) in acetone, about 3 ml of  $\text{MeIm}$  was added. Upon stirring at the ambient temperature for 30 min the color changed from pink to blue, characteristic of the bis  $\text{MeIm}$  complex. Tributylphosphite (0.01 mol) was then added and the volume was reduced under vacuum. The product was precipitated from ethanol–acetone (50:50 by volume) which was then filtered off and dried *in vacuo*. Yield 63%. Elemental analysis data are presented in Table I.

Other Compounds

Iron(II) acetate [6] was prepared by refluxing iron powder (Anachemia) with glacial acetic acid (Anachemia) under nitrogen. Benzoquinone dioxime was prepared by borohydride reduction of benzo-furazon oxide [7, 8].  $\text{Fe}(\text{BQDH})_2(\text{MeIm})_2$  was prepared as described for Fe, Ni, Pd, and Pt complexes [10, 12].  $\text{Fe}(\text{DMGH})_2(\text{MeIm})_2$  complex was prepared as reported [13].  $\text{Fe}(\text{Tim})(\text{CH}_3\text{CN})_2^{2+}$  was prepared by the method of Rose [14]. 1-Methylimidazole ( $\text{MeIm}$ ) (Aldrich) was distilled from  $\text{KOH}$  prior to use. Tributylphosphite ( $\text{p}(\text{OBU})_3$ ) (Aldrich) and dimethylglyoxime (Analar) were used without further purification. Toluene (Aldrich) was freshly distilled from  $\text{CaH}_2$  before use. Methyl ethyl ketone (Aldrich) and chloroform (Aldrich) were dried over molecular sieves prior to use. Methanol (Aldrich) was used without further purification.

Kinetic Measurements

Reactions were monitored spectrophotometrically using an Aminco DW-2a UV–Vis spectrophotometer or a Perkin-Elmer Hitachi 340 recording spectrophotometer. Deaerated solutions in 1 cm quartz cells

TABLE I. Microanalyses for Substituted Iron Macrocyclic Complexes

Complex	Found (%)				Calculated (%)			
	C	H	N	P	C	H	N	P
$\text{Fe}(\text{DMGH})_2(\text{P}(\text{OBU})_3)_2$	48.55	8.81	7.31	7.67	48.86	8.71	7.12	7.87
$\text{Fe}(\text{DMGH})_2(\text{P}(\text{OBU})_3)(\text{MeIm})$	47.36	5.21	14.05	5.30	47.78	5.35	13.93	5.12
$\text{Fe}(\text{BQDH})_2(\text{P}(\text{OBU})_3)_2$	51.90	7.85	6.88	7.34	52.06	7.77	6.75	7.44
$\text{Fe}(\text{BQDH})_2(\text{P}(\text{OBU})_3)(\text{MeIm})$	48.60	6.12	12.01	8.75	48.51	6.25	12.12	8.91
$\text{Fe}(\text{Tim})(\text{P}(\text{OBU})_3)_2(\text{PF}_6)_2$	41.53	7.30	5.23	11.45	41.70	7.18	5.12	11.29
$\text{Fe}(\text{Tim})(\text{P}(\text{OBU})_3)_2(\text{MeIm})(\text{PF}_6)_2$	39.12	6.12	9.22	9.93	38.89	6.20	9.07	10.00

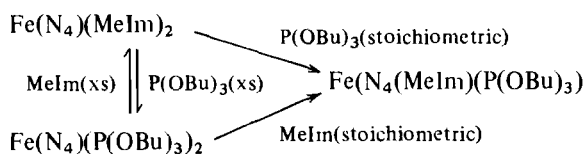
were thermostated in a close-fitting brass block. The temperature of the block was maintained by a constant flow of circulating water by means of a Lauda circulator (K-21R). Solutions were thermostated for approximately 15 min prior to the reaction measurements. The slower reactions were followed by periodically scanning the spectrum between 350 and 800 nm. The faster reactions were monitored at an absorbance maximum or minimum and the absorbance was recorded continuously. Chart speeds were adjusted to suit the rate of the reaction.

Concentrations of Fe(II) complexes were typically about  $1.0 \times 10^{-4}$  M. Reactions were run under pseudo-first-order conditions with the added nucleophile in large excess. The nucleophile was injected into the serum-capped cell, containing the Fe(II) complex, with a Hamilton gas tight syringe. All the reactions were followed until the absorbance at infinite time could be correctly read off or calculated. Final spectra were recorded. Plots of  $\log(A - A_\infty)$  vs. time were linear over 3-half-lives. Reproducibility of separate runs was typically  $\pm 5\%$  or less. The observed rate constant  $K_{\text{obs}} = 2.303 \times \text{slope}$  of the line. Plots of  $\log K/T$  vs.  $1/T$  gave straight lines. The activation parameters,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ , were calculated from the slopes and the intercepts of the lines, respectively.

## Results and Discussion

### Stoichiometry and Spectral Data

The reaction of  $\text{Fe}(\text{N}_4)(\text{MeIm})_2$  with excess of  $\text{P}(\text{OBU})_3$  affords the bis phosphite complex  $\text{Fe}(\text{N}_4)(\text{P}(\text{OBU})_3)_2$ , where  $\text{N}_4 = \text{Tim}, \text{DMGH}$  and  $\text{BQDH}$ . On using stoichiometric amounts of the phosphite, the reaction gives the mixed complex of the general formula  $\text{Fe}(\text{N}_4)(\text{P}(\text{OBU})_3)(\text{MeIm})$ . Moreover, these mixed complexes can also be obtained from the reaction of the bis phosphite complexes with stoichiometric amounts of MeIm as shown in Scheme 1.



Scheme 1.

The isolated bis phosphite and the mixed complexes together with their elemental analyses are listed in Table I. The spectral data for these complexes as well as those for bis MeIm are given in Table II.

An inspection of the spectral data, Table II, reveals a systematic variation in properties with variation in structure. Thus  $\lambda_{\text{max}}$  depends on the ligand field

TABLE II. Electronic Absorption Spectra of Fe(II) Macro-cyclic Complexes

Complex	Solvent	$\lambda_{\text{max}}$ (nm)
$\text{Fe}(\text{BQDH})_2(\text{MeIm})_2$	chloroform	444, 743
$\text{Fe}(\text{BQDH})_2(\text{MeIm})(\text{P}(\text{OBU})_3)$	chloroform	435, 620
$\text{Fe}(\text{BQDH})_2(\text{P}(\text{OBU})_3)_2$	chloroform	415, 533
$\text{Fe}(\text{DMGH})_2(\text{MeIm})_2$	toluene	530
$\text{Fe}(\text{DMGH})_2(\text{MeIm})(\text{P}(\text{OBU})_3)$	toluene	460
$\text{Fe}(\text{DMGH})_2(\text{P}(\text{OBU})_3)_2$	toluene	420
$\text{Fe}(\text{Tim})(\text{MeIm})_2^{2+}$	methylethylketone	667
$\text{Fe}(\text{Tim})(\text{MeIm})(\text{P}(\text{OBU})_3)^{2+}$	methylethylketone	580
$\text{Fe}(\text{Tim})(\text{P}(\text{OBU})_3)_2^{2+}$	methylethylketone	520

exerted by the macrocyclic in-plane ligand and both  $\sigma$ - and  $\pi$ -effects of the axial ligands. The bands for the bis MeIm complexes were assigned by analogy to the previously reported data [15 - 17]. The longer wavelength band was assigned to charge transfer from iron to the in-plane macrocyclic ligand. The much lower energy of this transition in the BQDH complexes relative to the Tim or DMGH complexes is consistent with a lowering of the  $\pi^*$  level of the dioxime moiety as a result of conjugation with the hexadiene group. On replacement of the MeIm which is a good  $\sigma$ -donor by  $\text{P}(\text{OBU})_3$  which is a good  $\pi$ -acceptor, the long wavelength band shifts to higher energy. The shift is greater with the formation of the bis phosphite complex. Tributylphosphite, being a good  $\pi$ -acceptor accepts electron density from filled  $t_{2g}$  orbitals, thus reducing the ease of charge transfer from Fe(II) to Tim, DMGH and BQDH. On the other hand, MeIm being a good  $\sigma$ -donor would increase the ease of such charge transfer. Thus, for bis phosphite complexes more energy is required to make such charge transfer possible and hence gives lower wavelength absorption maxima.

Table II shows in the three systems Tim, DMGH and BQDH a shift to higher energy from the bis MeIm complex, the mixed complex and to the bis  $\text{P}(\text{OBU})_3$  complex which is consistent with the above interpretation. Similar behaviour has been observed with carbon monoxide and benzoyl isocyanide Fe complexes of macrocyclic ligands [18].

### Kinetic Data

The reactions investigated can be categorized as follows

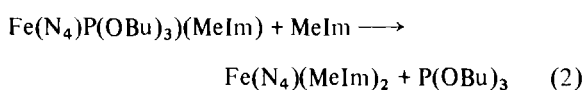
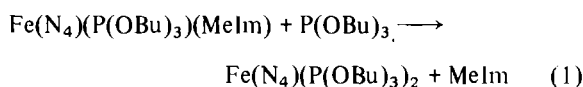
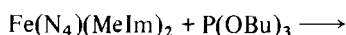
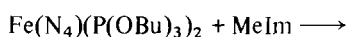


TABLE III. Kinetic Data for the Reaction (T)Fe(N<sub>4</sub>)L + X → (T)Fe(N<sub>4</sub>)X + L

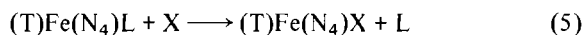
Macrocyclic (N <sub>4</sub> )	<i>trans</i> Group (T)	Leaving group (L)	Nucleophile (X)	Solvent	Temperature (°C)	k <sub>1</sub> (s <sup>-1</sup> )
(BQDH) <sub>2</sub>	p(OBu) <sub>3</sub>	MeIm	p(OBu) <sub>3</sub>	chloroform	2.8	2.4 × 10 <sup>-4</sup>
	p(OBu) <sub>3</sub>	MeIm	p(OBu) <sub>3</sub>	chloroform	10	6.80 × 10 <sup>-4</sup>
	MeIm	p(OBu) <sub>3</sub>	MeIm	chloroform	10	1.28 × 10 <sup>-4</sup>
	p(OBu) <sub>3</sub>	p(OBu) <sub>3</sub>	MeIm	chloroform	3.1	7.90 × 10 <sup>-5</sup>
	p(OBu) <sub>3</sub>	p(OBu) <sub>3</sub>	MeIm	chloroform	10	2.68 × 10 <sup>-4</sup>
	p(OBu) <sub>3</sub>	p(OBu) <sub>3</sub>	MeIm	chloroform	25	2.07 × 10 <sup>-3</sup>
(DMGH) <sub>2</sub>	p(OBu) <sub>3</sub>	MeIm	p(OBu) <sub>3</sub>	toluene	45	6.60 × 10 <sup>-5</sup>
	p(OBu) <sub>3</sub>	MeIm	p(OBu) <sub>3</sub>	toluene	60	5.67 × 10 <sup>-4</sup>
	p(OBu) <sub>3</sub>	MeIm	p(OBu) <sub>3</sub>	toluene	70	2.50 × 10 <sup>-3</sup>
	MeIm	p(OBu) <sub>3</sub>	MeIm	toluene	45	8.40 × 10 <sup>-4</sup>
	MeIm	p(OBu) <sub>3</sub>	MeIm	toluene	60	6.88 × 10 <sup>-3</sup>
	MeIm	p(OBu) <sub>3</sub>	MeIm	toluene	70	2.58 × 10 <sup>-2</sup>
(Tim)	p(OBu) <sub>3</sub>	MeIm	p(OBu) <sub>3</sub>	methylethylketone	25	8.43 × 10 <sup>-6</sup>
	p(OBu) <sub>3</sub>	MeIm	p(OBu) <sub>3</sub>	methylethylketone	45	2.30 × 10 <sup>-4</sup>
	p(OBu) <sub>3</sub>	MeIm	p(OBu) <sub>3</sub>	methylethylketone	70	3.05 × 10 <sup>-3</sup>
	MeIm	p(OBu) <sub>3</sub>	MeIm	methylethylketone	25	4.90 × 10 <sup>-4</sup>
	MeIm	p(OBu) <sub>3</sub>	MeIm	methylethylketone	45	4.95 × 10 <sup>-3</sup>
	MeIm	p(OBu) <sub>3</sub>	MeIm	methylethylketone	60	3.38 × 10 <sup>-2</sup>
Pc	p(OBu) <sub>3</sub>	p(OBu) <sub>3</sub>	Im	acetone	21	S2 <sup>a</sup>
	p(OBu) <sub>3</sub>	p(OBu) <sub>3</sub>	MeIm	acetone	21	S4 <sup>a</sup>
	p(OBu) <sub>3</sub>	MeIm	p(OBu) <sub>3</sub>	acetone	21	2.3 <sup>a</sup>
	Im	p(OBu) <sub>3</sub>	Im	acetone	21	1.0 × 10 <sup>-4</sup> a
	Im	Im	p(Bu) <sub>3</sub>	acetone	21	2.0 × 10 <sup>-3</sup> a
TPP	Py	Py	p(Bu) <sub>3</sub>	toluene	25	1.2 × 10 <sup>4</sup> b
	Im	Im	p(Bu) <sub>3</sub>	toluene	25	1.7 × 10 <sup>3</sup> b

<sup>a</sup>Ref. 4. <sup>b</sup>Ref. 23.

The reaction of Fe(N<sub>4</sub>)(P(OBu)<sub>3</sub>)<sub>2</sub> with MeIm as well as the reaction of the mixed complexes with either P(OBu)<sub>3</sub> or MeIm in the appropriate solvent (see Table III) were followed spectrophotometrically. For each system the successive spectra pass through a sharp fixed isosbestic point(s), implying that these reactions proceed cleanly. The spectra of the final products is almost identical to that of the prepared authentic sample in the appropriate solvent. Typical spectral changes with time on the addition of P(OBu)<sub>3</sub> to Fe(BQDH)<sub>2</sub>(P(OBu)<sub>3</sub>)(MeIm) solution in chloroform at 2.8 °C are given in Fig. 1, reaction (1), N<sub>4</sub> = BQDH. As the absorbance of Fe(BQDH)<sub>2</sub>-(P(OBu)<sub>3</sub>)(MeIm) at 620 nm decreases, the 533 nm peak due to the bis phosphite complex increases. The analyses at 620 and 533 nm gave consistent rate

constants, Table III. Reaction (4), N<sub>4</sub> = BQDH, is characterized by the disappearance of the peak at 744 nm which is due to the bis MeIm complex and the appearance of a new peak at 620 nm due to the formation of the mixed complex. The rate of this reaction was too fast to measure using conventional spectrophotometric methods at room temperature.

Ligand substitution reactions involved in this study can be represented by the general reaction



where T is the *trans* group; L the leaving group; X the nucleophile and N<sub>4</sub> represents the quadridentate in-plane macrocyclic ligand. Kinetic results and the activation parameters are listed in Tables III and IV, respectively.

The activation enthalpies and entropies, rate retardation by excess leaving group L, and insensitivity of the rate to the nature or concentration of the nucleophile X clearly demonstrated that reaction (5) proceeds via a dissociative mechanism (D), eqns. (6) and (7), for which an overwhelming body of evidence now exists [3–5, 9, 13, 19, 22].

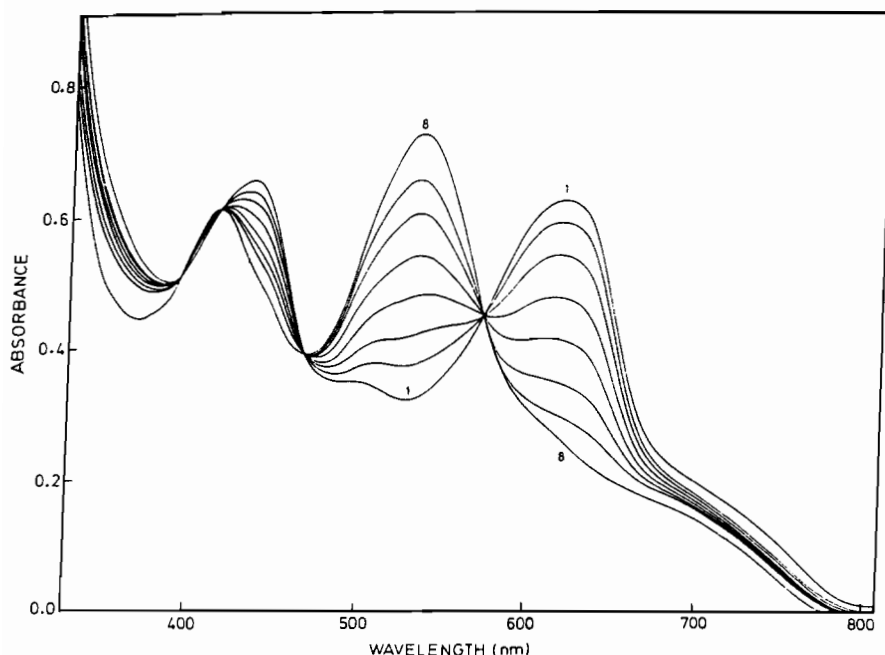


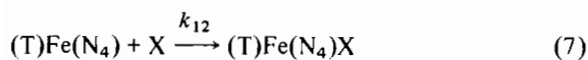
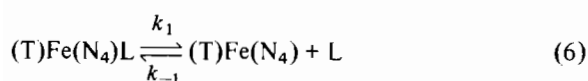
Fig. 1. Spectral changes with time for the reaction  $\text{Fe}(\text{BQDH})_2(\text{P}(\text{OBu})_3)(\text{MeIm}) + \text{P}(\text{OBu})_3 \rightarrow \text{Fe}(\text{BQDH})_2(\text{P}(\text{OBu})_3)_2 + \text{MeIm}$  in chloroform at 2.8 °C. Spectra 1–8 were recorded at times 0, 9, 19, 34, 54, 84, 125 and 275 min. Intervening spectra have been omitted for clarity.

TABLE IV. Activation Parameters for Axial Substitution Reactions<sup>a</sup>

Complex	X	Solvent	$\Delta H^\ddagger$ (kcal mol <sup>-1</sup> )	$\Delta S^\ddagger$ (cal mol <sup>-1</sup> deg <sup>-1</sup> )
$\text{Fe}(\text{BQDH})_2(\text{P}(\text{OBu})_3)\text{P}(\text{OBu})_3$	MeIm	chloroform	23 ± 1	10 ± 3
$\text{Fe}(\text{BQDH})_2(\text{P}(\text{OBu})_3)\text{MeIm}$	$\text{P}(\text{OBu})_3$	chloroform	22 ± 2	5 ± 4
$\text{Fe}(\text{DMGH})_2(\text{P}(\text{OBu})_3)\text{MeIm}$	$\text{P}(\text{OBu})_3$	toluene	29 ± 1	14 ± 4
$\text{Fe}(\text{DMGH})_2(\text{MeIm})\text{P}(\text{OBu})_3$	MeIm	toluene	28 ± 0.1	16 ± 2
$\text{Fe}(\text{Tim})(\text{MeIm})\text{P}(\text{OBu})_3$	MeIm	methylethylketone	23 ± 1	8 ± 4
$\text{Fe}(\text{Tim})(\text{P}(\text{OBu})_3)\text{MeIm}$	$\text{P}(\text{OBu})_3$	methylethylketone	26 ± 2	13 ± 5
$\text{Fe}(\text{Pc})(\text{P}(\text{OBu})_3)\text{P}(\text{OBu})_3^{\text{b}}$	$\text{P}(\text{Bu})_3$	toluene	20 ± 0.2	16 ± 0.4

<sup>a</sup>Leaving ligands without parentheses.

<sup>b</sup>Ref. 4.



For such a mechanism, the observed pseudo-first-order rate constant neglecting the reverse reaction is given by

$$k_{\text{obs}} = \frac{k_1 k_2 [\text{X}]}{k_{-1} [\text{L}] + k_2 [\text{X}]} \quad (8)$$

In this study, all reactions were carried out with a large excess of entering ligand X and negligible L. Under these conditions the above expression reduces to

$$k_{\text{obs}} = k_1 \quad (9)$$

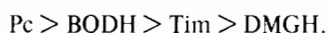
*i.e.* the pseudo-first-order rate constant corresponds to the rate constant for the dissociation of L.

A number of kinetic studies of iron porphyrin and phthalocyanine substitution reactions have been reported [3, 4, 23–25] and it is now possible to make some comparisons with the iron macrocyclic reactions described herein.

#### *cis-Effect*

Table III shows a systematic comparison of the three systems studied. Previously investigated Pc and Tpp systems are also reported for the purpose of comparison. The axial ligand lability as measured by  $k_1$  spans a large range. Considering the MeIm off rate, in the mixed complexes, it is evident from the results

that the lability of the macrocycles decreases in the following order



Both Tim and DMGH are ligands without conjugated  $\pi$ -systems, while Tpp and Pc are ligands with delocalized conjugated  $\pi$ -systems. Thus, the higher the conjugation in the equatorial macrocyclic ligand, the more labile the system. The high delocalization of the conjugated  $\pi$ -system would produce a strong ligand field from the equatorial macrocycle which in turn would result in weak and long axial bonds. Accordingly, BQDH should be more labile than both Tim and DMGH. The increased net positive charge on the Tim complex resulting from substitution of an imine for an oxime group of the macrocyclic ligand results in increased lability of  $\pi$ -acceptor ligand  $\text{P}(\text{OBU})_3$ . The extensive and high conjugation in Pc would place it as the most labile system in this *cis*-effect series. Thus the phosphite and the MeIm off rate would follow the above lability sequence.

The lack of data on the phosphite substitution on Fe(II) complexes of Tpp makes a detailed comparison with these complexes unwarranted. However, when imidazole is *trans* to imidazole Tpp is  $\approx 10^6$  more labile than Pc.

#### *trans*-Effect

For Fe(BQDH)<sub>2</sub> complexes (Table III), it has been found that when  $\text{P}(\text{OBU})_3$  is *trans* to  $\text{P}(\text{OBU})_3$ , the phosphite off rate is about two times faster than when it is *trans* to MeIm. Methyl imidazole is primarily a  $\sigma$ -donor with some  $\pi$ -donor properties, whereas tributylphosphite is both a good  $\sigma$ -donor and  $\pi$ -acceptor. This means that synergic  $\pi$ -bonding occurs in the mixed complex. Thus, *trans* to  $\text{P}(\text{OBU})_3$ , both MeIm and  $\text{P}(\text{OBU})_3$  are labilized (*trans* effect), but  $\text{P}(\text{OBU})_3$  becomes more labile because of the loss of the synergic  $\pi$ -bonding and the necessity for the  $\text{P}(\text{OBU})_3$  ligand to compete for  $\pi$ -electron density with the *trans*  $\text{P}(\text{OBU})_3$  group. Similar behaviour has been reported for iron(II) complexes of phthalocyanine [3].

Considering the mixed complexes,  $\text{Fe}(\text{N}_4)(\text{MeIm})\text{P}(\text{OBU})_3$ , where  $\text{N}_4$  is BQDH, DMGH, Tim and Pc (Table III), it is clear that the  $\text{P}(\text{OBU})_3$  off rate is higher than that of MeIm in the case of DMGH and Tim systems. The reverse is observed with BQDH and Pc systems. The higher lability of the MeIm relative to the  $\text{P}(\text{OBU})_3$  in the case of BQDH and Pc complexes can be rationalized in terms of  $\sigma$ - and  $\pi$ -effects. Both BQDH and Pc have extensively delocalized  $\pi$ -systems which increase the electron density on the central metal atom. Thus a good  $\pi$ -acceptor such as  $\text{P}(\text{OBU})_3$  which possesses vacant orbitals would easily accommodate this excessive  $\pi$ -electron density. The high electron density on the metal atom-of-necessity

in low oxidation states can thus be delocalized on the  $\text{P}(\text{OBU})_3$  ligands. A kinetically stable bis phosphite complex would be the favoured product of this reaction. The extent of  $\pi$ -bonding to phosphines and phosphites was previously reported to increase as the oxidation state is lowered [26]. These results are consistent with the  $\text{P}(\text{OBU})_3$  being a *trans* activator group in BQDH and Pc systems [3].

On the other hand the extent of electron density on the central metal ion of DMGH and Tim is much less as compared to that on the BQDH and Pc complexes. Thus a good  $\sigma$ -donor such as MeIm would donate its electrons to the empty d-orbitals of the central metal ion leading to the formation of the kinetically stable bis MeIm complex.

Structural data for Ni(DMGH)<sub>2</sub> [27] and Ni(BQDH)<sub>2</sub> [11] show surprisingly little effect of the hexadiene substituent on the metrical details of the dioxime group. This result is however consistent with these findings. That is large differences between the Fe(DMGH)<sub>2</sub> and Fe(BQDH)<sub>2</sub> complexes occur primarily in properties where the dioxime  $\pi^*$  level is important such as visible spectra and the lability of MeIm and  $\text{P}(\text{OBU})_3$ .

Iron(II) is an isoelectronic with ruthenium(II). However, the well-known  $\pi$ -donating ability of ruthenium(II) in contrast to iron(II) may produce fundamental differences between  $\text{Ru}(\text{N}_4)^{2+}$  and  $\text{Fe}(\text{N}_4)^{2+}$  towards axial ligation. Thus a comparison of the kinetic data given for iron(II) with analogous ruthenium(II) complexes [28] reveals that the Fe(II) complexes are much more labile than Ru(II) complexes implying that the  $\text{M} \rightarrow \text{L}$   $\pi$ -back bonding is more important in ruthenium(II).

Remarkably, the electrochemical investigations of a series of copper(II) [29], iron(II) [30] and ruthenium(II) [31] macrocyclic complexes of the general form *trans*- $\text{M}(\text{N}_4)\text{L}_2$  where L represents monodentate ligands such as imidazoles, pyridine, phosphine and phosphite, in a large range of solvents and at different electrodes, are in excellent agreement with these kinetic results. Polarographic studies at a dropping mercury electrode showed a wave corresponding to the formation of mercury complexes of the type  $\text{HgL}_2^{2+}$  at this electrode surface in the case of iron(II) and copper(II) macrocyclic adducts. This means the axial ligands were stripped from these macrocyclic adducts by the mercury electrode according to the overall process [32].



However, in the case of ruthenium(II), mercury complexes of these adducts were not observed. Thus the electrochemical results do support the kinetic results indicating that the iron(II) and copper(II) systems are kinetically labile while the ruthenium(II) system is kinetically inert.

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