by eq 12 and 13.

$$\phi_{py} = \frac{1}{I_0}\frac{\partial[py]}{\partial t} = \frac{1}{I_0}(2k_3' + k_5[R])[Ru^I] \tag{12}$$

$$\phi_{Cl^-} = \frac{1}{I_0}\frac{\partial[Cl^-]}{\partial t} = \frac{1}{I_0}(k_3'[Ru^I]) \tag{13}$$

$$(k_3' = k_3[CH_2Cl_2],\ [R] = [CHCl_2\cdot],\ \text{and}\ [Ru^I] = [Ru^I(pc)(py)_2^-])$$

Therefore, the ratio of the chloride ion to pyridine yield is as shown by eq 14.

$$\frac{\phi_{Cl^-}}{\phi_{py}} = \frac{k_3'}{2k_3' + k_5[R]} \tag{14}$$

The steady-state treatment of R in the mechanism, eq 5–11, gives a steady-state concentration of R (eq 15) which depends on the yield, ϕ, the absorbed light intensity, I_0, and the rate constant k_5.

$$[R\cdot] \approx (\phi I_0)^{1/2}k_5^{-1/2} \approx (2 \times 10^{-3})k_5^{-1/2} \tag{15}$$

The substitution of eq 15 in eq 14 and the rearrangement of the resulting equation gives eq 16.

$$k_5^{1/2}/k_3' = 8.3 \times 10^2 \tag{16}$$

Hence if reaction 5 is a diffusion-controlled reaction, e.g., $k_5 \approx 5 \times 10^9\ M^{-1}\ s^{-1}$, then the value of $k_5/\epsilon = 1.5 \times 10^5\ cm\ s^{-1}$, obtained in flash photolysis, gives an extinction, $\epsilon \approx 3 \times 10^4\ M^{-1}\ cm^{-1}$, that is in good agreement with those reported for other one-electron-reduced ligand radicals.[13] Moreover, the rate constant for reaction 7 obtained under this approximation is $k_3' \approx 90\ s^{-1}$.

Registry No. Ru(pc)(py)$_2$, 68588-46-9; Ru(pc)(py)CO, 67588-47-0; py, 110-86-1; Cl$^-$, 16887-00-6; CH$_2$Cl$_2$, 75-09-2; CO, 630-08-0; CH$_3$CN, 75-05-8; Ru(pc)(py)CH$_3$CN, 82665-23-4; benzene, 71-43-2.

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Comparative Kinetics of Axial Ligation to Ruthenium and Iron Porphyrin and Phthalocyanine Complexes. Relationship between Spin State and Cis and Trans Effects

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Kinetic data for the dissociative axial substitution reactions of benzyl isocyanide (BzNC) and CO complexes of ruthenium octaethylporphyrin (OEP), tetraphenylporphyrin (TPP), and phthalocyanine (Pc) complexes are reported and compared with corresponding data for iron complexes. The relative lability of BzNC complexes containing 1-methylimidazole (CH$_3$Im) and 4-*tert*-butylpyridine (*t*-Bupy) is RuPc < RuP << FePc < FeP. The porphyrin systems are inherently more labile by 3–5 kcal/mol in ΔG^{*}. In complexes with two weak-field axial ligands, a spin change occurring along the reaction coordinate for ligand dissociation is proposed to account for an additional ~3 kcal/mol lower ΔG^{*} only in the iron porphyrin systems. Trans effects of CO and BzNC are rationalized in terms of spin-state effects in the transition state.

Introduction

Extensive kinetic studies of iron(II) complexes of porphyrins[1–4] and phthalocyanines[5–7] have shown a substantially different lability in dissociative axial ligation of imidazoles, pyridines, carbon monoxide, and isocyanides. In carbonylruthenium porphyrins, RuP(CO)(L), a remarkable lability of nitrogen donors (L) trans to CO is reported.[8,9] A similar labilization is observed in isocyanide derivatives of ruthenium porphyrins.[10] However, the corresponding RuP(CH$_3$Im)$_2$ or RuP(py)$_2$ complexes are very inert.[11]

It has been proposed that spin-state changes and the consequent movement of the iron with respect to the tetradentate ligand plane may be involved in labilization effects in axial ligand substitution reactions in the iron complexes.[5] For hemes, high-spin pentacoordinate complexes can be isolated and studied. No report of pentacoordinate Fe(II) phthalocyanines has appeared although extensive kinetic evidence for pentacoordinate intermediates in the dissociative substitution reactions of six-coordinate FeN$_4$L$_2$ systems exists.[5–7] Discussion of the spin state of such intermediates in FePc complexes has been speculative.[5] A comparative study of the ruthenium complexes of porphyrins and phthalocyanines is of interest since the ruthenium is not expected to give high-spin complexes and the greater size of ruthenium, relative to iron, makes it somewhat too large for the phthalocyanine ring. Thus the ruthenium complexes might be expected to provide insight into spin-state and ring size effects, features given particular importance in hemes and hemoproteins.

Several reports of studies of ruthenium phthalocyanines have appeared during the course of our work.[12–14] Sweigart[15] has reported kinetic comparisons of axial ligand lability in FePc and RuPc complexes of phosphines and phosphites. Herein we describe comparisons of axial ligand lability in isocyanide and carbon monoxide complexes of RuP, RuPc, FeP, and FePc and reconcile enormous differences in axial ligand lability in terms of cis and trans effects.

Experimental Section

Crude RuPc and RuPc(CO) were prepared from phthalonitrile and RuCl$_3$ or Ru$_3$(CO)$_{12}$, respectively, by methods essentially the same as described elsewhere.[12,15] RuPc(CO)(L), L = CH$_3$Im and *t*-Bupy, compounds, were prepared as described by James.[12] RuTPP(C-

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O)(C_2H_5OH) and RuOEP(CO)(C_2H_5OH) were prepared by the method of Eaton.[8]

RuTPP(BzNC)$_2$. BzNC (0.1 g) was added to a chloroform solution of RuTPP(CO)(C_2H_5OH) (0.2 g). The solution was stirred for 10 min, hexane was added, and the precipitate was filtered and washed with hexane and dried in vacuo: yield 0.2 g; ν_{NC} = 2150 cm^{-1}. RuOEP(BzNC)$_2$ was prepared as above; ν_{NC} = 2148 cm^{-1}. These complexes have spectral properties analogous to those of a previously reported *t*-BuNC derivative of ruthenium porphyrins.[9]

RuPc(BzNC)$_2$. RuPc(CO) (0.2 g) and 0.1 g of BzNC were refluxed for 5 h in 50 mL of $CHCl_3$. The solution was then concentrated and precipitation induced by addition of hexane. The solid was washed with hexane and dried in vacuo: yield 0.18 g; ν_{NC} = 2170 cm^{-1}; λ_{max} = 640 nm.

RuPc(BzNC)(CH_3Im). RuPc(BzNC)$_2$ (0.1 g) was refluxed with 0.1 mL of CH_3Im in 50 mL of $CHCl_3$ for 3 h in the dark. The solution was filtered, and the filtrate was concentrated and precipitation induced by addition of hexane: yield 0.08 g; ν_{NC} = 2160 cm^{-1}; λ_{max} = 640 nm.

RuPc(BzNC)(*t*-Bupy) was prepared similarly.

The RuPc derivatives show characteristic NMR spectra[12] consisting of an AA'BB' multiplet at low field due to the Pc ring protons with axial ligand resonances shifted well upfield due to the Pc ring current. The isocyanide derivatives are somewhat less soluble in $CDCl_3$ than corresponding carbonyl derivatives. RuPc(BzNC)$_2$ NMR ($CDCl_3$): δ Pc (AA'BB') 9.23, 7.94; BzNC 2.42 (CH_2) and 4.97, 5.07, and multiplet at 6.7 (aromatic). RuPc(BzNC)(CH_3Im) NMR: Pc (AA'BB') 9.20, 7.92; BzNC 2.42 (CH_2); CH_3Im 2.09 (CH_3), ring resonances not assigned.

All RuPc isocyanide derivatives prepared from "RuPcCO" gave satisfactory elemental analyses (C,H,N). Derivatives prepared from the "RuPc" starting material all gave low C,H,N analyses more consistent with 1.5 ± 0.2 chlorides/ruthenium (based on C,H,N). These derivatives may contain a chlorinated Pc ring.[16] They were found to be spectrally and kinetically indistinguishable from the "pure" materials prepared via the $Ru_3(CO)_{12}$ route.

Kinetics. Reactions were monitored by spectrophotometric methods on a Perkin-Elmer Hitachi microprocessor-controlled UV–vis–near-IR spectrophotometer. The reagent (CH_3Im, *t*-Bupy, or BzNC) was added via syringe to thermostated solutions of the ruthenium complex in 1-cm cuvettes. Reactions were scanned with time, showing clean isosbestic points. The majority of the kinetic data was obtained by monitoring the absorbance at a suitable wavelength with time to take full advantage of the scale expansion features of the Hitachi instrument. For reactions of RuTPP(BzNC)$_2$ with CH_3Im the increase in absorbance at 532 nm or the decrease at 505 nm was monitored, for reactions of RuOEP(BzNC)$_2$ with CH_3Im the increase at 500 nm or the decrease at 558 nm was monitored (the reaction is isosbestic at 478, 540, and 574 nm), for reactions of RuPc(CO)(L) with BzNC the decrease at 642 nm was monitored, for reactions of RuPc(BzNC)$_2$ with L the decrease at 640 nm was monitored, and for reactions of RuPc(BzNC)(L) with BzNC the increase at 642 nm was monitored. All reactions were carried out under pseudo-first-order conditions, [Ru] $\simeq 10^{-5}$ M, with added ligand in large excess (0.01–0.1 M). Rates were independent of the nature or concentration of added ligand. log plots of the absorbance data vs. time were linear over 3 half-lives. Reproducibility of separate runs was typically ±5% or less.

Results and Discussion

Kinetic data for the porphyrin and phthalocyanine complexes for reactions 1–3 are given in Tables I and II.

$$RuN_4(BzNC)_2 + CH_3Im \rightarrow RuN_4(BzNC)(CH_3Im) + BzNC \quad (1)$$

$$RuN_4(L)(BzNC) + BzNC \rightarrow RuN_4(BzNC)_2 + L \quad (2)$$

$$RuN_4L(CO) + 2BzNC \rightarrow RuN_4(BzNC)_2 + CO + L \quad (3)$$

Pseudo-first-order rate constants were found to be independent of the concentration of added ligand in all cases and also independent of the nature of added ligand (CH_3Im and *t*-Bupy) for reaction 1. The observed rates are, therefore, identified with rate-determining dissociation of the leaving group in the dissociative mechanism (D) for which an overwhelming body of evidence now exists.[5-10]

Table I. Kinetic Data for Axial Ligation to Ruthenium Porphyrin and Phthalocyanine Complexes in Toluene[a,b]

complex	*T*, °C	10^3k, s^{-1}	complex	*T*, °C	10^3k, s^{-1}
RuTPP(BzNC)$_2$	60	77.5	RuPc(BzNC)(CH_3Im)	75	2.90
	50	22.4		65	0.87
	45	10.8		55	0.22
	40	5.23		45	0.056
	35	2.65	RuPc(BzNC)(*t*-Bupy)	65	5.9
	25	0.67		60	3.2
	15	0.13		50	0.73
RuOEP(BzNC)$_2$	45	40.0		40	0.15
	35	10.6		30	0.032
	25	2.56	RuPc(CO)(CH_3Im)	70	1.1
	15	0.50		60	0.33
RuPc(BzNC)$_2$	75	6.1		50	0.078
	65	1.7		40	0.022
	55	0.50	RuPc(CO)(*t*-Bupy)	70	8.0
	45	0.095		60	5.5
	35	0.028		50	1.4
				40	0.37
				30	0.077

[a] Leaving group listed last. [b] Estimated error ±5%.

Table II. Activation Parameters for Axial Substitution Reactions in Toluene[a,e]

	$\Delta G^{\ddagger}_{298}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	ref
RuTPP(BzNC)(BzNC)[b]	21.8	26.4	15.3	this work
RuOEP(BzNC)(BzNC)[b]	20.9	26.0	15.4	this work
RuPc(BzNC)(BzNC)[b]	24.7	28.5	12.7	this work
RuPc(BzNC)(CH_3Im)[c]	25.1	28.5	11.2	this work
RuPc(BzNC)(*t*-Bupy)[c]	24.2	30.5	21	this work
RuPc(CO)(CH_3Im)[c]	25.1	27.5	8	this work
RuPc(CO)(*t*-Bupy)[c]	23.6	28.0	15	this work
RuOEP(CO)(*t*-Bupy)[d]	17.3	18.7	4.8	8
RuTPP(CO)(*t*-Bupy)[d]	19.1	21.2	7.0	8
RuTPP(BzNC)(*t*-Bupy)[d]	18.9	22.3	11.5	10
RuTPP(BzNC)(CH_3Im)[d]	19.3	23.2	13	10

[a] Ligand listed last is the leaving group. [b] Reaction with CH_3Im (eq 1). [c] Reaction with BzNC (eq 2 or 3). [d] Ligand exchange in 1,1,2,2-tetrachloroethane solution by NMR line shape. [e] Estimated errors: $\Delta H^{\ddagger}$, ±1.0; $\Delta S^{\ddagger}$, ±3. These correspond to 2–3 standard deviations from the least-squares line. The error in $\Delta G^{\ddagger}$, ±0.1, is based on the error in *k*.

The rate-determining step in reaction 3 is assumed to be replacement of L trans to CO in a dissociative mechanism since CO is otherwise inert. No evidence for the RuN_4(CO)(BzNC) intermediate is observed. The reaction of the carbonyl complex with BzNC thus affords a simple way of determining the lability of ligands trans to CO, in cases where CO is more inert than L.

Cis Effects. Kinetic data are summarized in Table III in the form of $\Delta G^{\ddagger}_{298}$ for ligand dissociation. Overall, the order of lability is RuPc < RuTPP < FePc < FeP. The greater inertness of the ruthenium complexes is a common feature of substitution reactions of transition-metal complexes.[15]

Previous work has shown FePc complexes to be, in general, more inert than corresponding FeP complexes. It has been proposed that the greater lability of the porphyrin complexes might be due to a spin change occurring along the reaction coordinate for ligand dissociation in the porphyrins but not in the phthalocyanines. This suggestion is supported by structural data showing a better fit between low-spin iron and the Pc ring (M–N$_P$ = 1.90 Å, M–N$_{Pc}$ = 2.0 Å).

Structural data for carbonylmetal porphyrins and phthalocyanines (Table IV) show increased metal–nitrogen distances

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(16) The exact nature of the "chlorinated" species is controversial.[12-15] See also: Seddon, K. R. *Coord. Chem. Rev.* **1982**, *41*, 79.

Table III. $\Delta G^{\ddagger}_{298}$ (kcal/mol) for Reactions of Iron and Ruthenium Porphyrin and Phthalocyanine Complexes[a]

reacn	trans group	leaving group	RuTPP	RuPc	FeP	FePc
1	BzNC	BzNC	21.8	24.7		18.4[e]
2	BzNC	CH_3Im	19.3[b]	25.1		19.9[e]
3	BzNC	*t*-Bupy	18.9[b]	24.2		
4	CO	CH_3Im	18.3[j]	25.1	16.9[g]	
5	CO	*t*-Bupy	19.1[b]	23.6		
6	$P(OBu)_3$	$P(OBu)_3$		21.0[d]		15.1[c]
7	$P(OBu)_3$	CH_3Im		21.0[d]		17.0[c]
8	$P(OBu)_3$	py		18.8[d]		15.4[c]
9	CH_3Im	CH_3Im	slow	slow	13.1[h]	21.3[e]
10	CH_3Im	BzNC	slow	slow	17.9[i]	23.1[e]
11	CH_3Im	CO	slow	slow	19.6[g]	19.8[f]

[a] Toluene solution unless stated otherwise. [b] In 1,1,2,2-tetrachloroethane.[8,10] [c] In acetone, 21 °C.[7] [d] Reference 4. [e] Reference 6. [f] Reference 5. [g] For imidazole deuteroheme dimethyl ester carbonyl in benzene, 20 °C.[1] [h] Calculated from data in ref 2 for FeTPP $(CH_3Im)_2$. [i] Chelated protoheme BuNC in benzene, 20 °C.[3] [j] At 352 K for mesoporphyrin dimethyl ester imidazole carbonyl in $CDCl_3$: Faller, J.; Sibert, J. W. *J. Organomet. Chem.* 1971, *31*, C5.

Table IV. Structural Data for Metal Porphyrins and Phthalocyanines (Å)

complex	av $M-N_4$	axial M–N	M–Ct[a]
$FePc(4\text{-}Mepy)_2$[b]	1.932	2.040	0
FePc(DMF)(CO)[c]	1.889	2.07	+0.04
FeTPP(THF)(CO)[d]	1.98		+0.10
FeTPP(py)(CO)[e]	2.02	2.10	+0.02
RuTPP(py)(CO)[f]	2.06	2.193	+0.079
$RuOEP(py)_2$[g]	2.047	2.10	0
OsPc(py)(CO)[h]	2.01	2.209	+0.10
$OsMe_2OEP(py)(CO)$[i]	2.067	2.230	+0.18

[a] Displacement of metal from N_4 plane; + indicates toward the CO ligand. [b] Cariati, F.; Morazzoni, F.; Zocchi, M. *J. Chem. Soc., Dalton Trans.* 1978, 1018. [c] Calderazzo, F.; Pampaloni, G.; Vitali, D.; Pelizzi, G.; Collamati, I.; Fredani, S.; Serra, A. M. *J. Organomet. Chem.* 1980, *191*, 217. [d] Scheidt, W. R.; Haller, K. J.; Fons, M.; Mashiko, T.; Reed, C. A. *Biochemistry* 1981, *20*, 3653. [e] Peng, S.; Ibers, J. A. *J. Am. Chem. Soc.* 1976, *98*, 8032. [f] Little, R. G.; Ibers, J. A. *Ibid.* 1973, *95*, 8583. [g] Hopf, F. R.; O'Brien, T. P.; Scheidt, W. R.; Whitten, D. G. *Ibid.* 1975, *97*, 277. [h] Reference 14. [i] Buchler, J. W.; Lay, K. L.; Smith, P. D.; Scheidt, W. R.; Rupperecht, G. A.; Kenney, J. E. *J. Organomet. Chem.* 1976, *110*, 109.

(both in-plane and axial) in the series Fe < Ru < Os. The phthalocyanine hole size is seen to be smaller than that of the porphyrins. In the carbonyl derivatives, the out-of-plane displacement toward the CO ligand (indicated by +M–Ct) is progressively greater in the series Fe < Ru < Os. The displacement in the iron complexes is probably not significant, however, in the larger ruthenium and osmium derivatives; the larger out-of-plane displacements may result in a ground-state weakening of the trans ligand.

The greater size of ruthenium and the greater d-orbital splittings for second-row transition metals precludes a spin change in the ruthenium complexes. The greater lability of the RuP complexes compared to RuPc must, therefore, be due to an inherently greater labilization by the porphyrin *not* associated with spin effects. This appears as a 3–5 kcal/mol greater $\Delta G^{\ddagger}$ for the phthalocyanine complexes. The difference is greater with σ donors than with π acceptors as leaving groups. The nearly identical rates of CO dissociation from FePc and FeP may be accounted for in terms of the inherently greater transition-state stabilization of the porphyrin system being offset by a ground-state weakening of the Fe–CO bond in the phthalocyanine case. This ground-state weakening has been previously discussed[5] in terms of the phthalocyanine being a better π acceptor than the porphyrin ligand. ν_{CO} values are 1967 and 1990 cm^{-1} for P and Pc, respectively, indicating a greater π back-bonding with FeP.

With the exception of $\Delta G^{\ddagger}$ = 13.1 kcal/mol for the $FeP(CH_3Im)_2$ complex, the relative labilities in FeP and FePc are not particularly remarkable and may be similar to the ruthenium complexes. There are enough gaps in the table to allow some ambiguity. The 5 kcal/mol difference in BzNC dissociation trans to CH_3Im is in the range of labilization effects found in ruthenium complexes. If the trans effects of CO and BzNC are comparable in FeP, as they are in RuP, RuPc,[10] FeTIM, and Fe(14ane) complexes,[17] we may expect CH_3Im lability trans to BzNC to have $\Delta G^{\ddagger} \simeq 16.9$. This would then be 3 kcal/mol less than the corresponding FePc value.

The most remarkable value in the table is the lability of CH_3Im trans to CH_3Im for iron porphyrins, $\Delta G^{\ddagger}$ = 13.1. This value is ~8 kcal/mol less than that for the corresponding FePc complex. While kinetic constants for the corresponding ruthenium systems are not available, both systems undergo substitution reactions only slowly even at elevated temperatures and it seems unlikely that the large differences in labilization for the iron complexes will be observed in the ruthenium systems. The 8 kcal/mol difference in $\Delta G^{\ddagger}$ for FeP and FePc may be attributed to 5 kcal/mol associated with the intrinsically greater lability in FeP and ~3 kcal/mol associated with transition-state stabilization resulting from spin-change effects.

On the basis of recent data on five-coördinate heme derivatives containing strong-field ligands, one does not expect a spin change to occur during axial substitution reactions trans to strong-field ligands. FeP(RNC) and FeP(CO) are low-spin complexes; thus for reactions 1–8 in Table III the intermediate is expected to be low spin. In reactions 10 and 11, where a strong-field ligand is lost trans to CH_3Im, the spin change may come too late along the reaction coordinate to have a large effect. Only in the case when both axial ligands are weak field is a significant effect observed.

Trans Effects. Imidazole labilization in carbonylruthenium porphyrins is often cited as evidence for a large cis-labilization effect of the porphyrin ring. In fact, comparison with the lability of other ligands in ruthenium porphyrins reveals that the "unusual lability" applies only to ligands trans to CO, isocyanides, or other strong trans directors. The effect is better characterized as a trans labilization. This trans effect is particularly remarkable in view of equally dramatic trans-delabilizing effects in $FeN_4(CO)(L)$ and $FeN_4(BzNC)(L)$ systems. In the iron porphyrins, imidazole is 1000 times more inert trans to CO than trans to imidazole.[1,2] A similar trans-delabilizing effect of BzNC and CO is observed in other iron macrocycles.[17,18]

Structural data (Table IV) for metalloporphyrin and phthalocyanine derivatives do not reflect these opposite trans effects. The Ru–N(py) distance is clearly longer trans to CO, and in the FeTPP(py)(CO) complex the Fe–N(py) distance of 2.10 Å is long when compared with that of a low-spin $[FeOEP((3\text{-}Cl)py)_2]^+$ complex,[19] Fe–N(py) = 2.03 Å (the distance in the Fe(II) analogue is not expected to be significantly longer). The explanation for these opposite trans effects must, therefore, be sought in the transition states and whether spin changes occur along the reaction coordinate for ligand dissociation. A reasonable description of structural changes occurring along the reaction coordinate for ligand dissociation can be inferred from X-ray data for $[Fe(OEP)((3\text{-}Cl)py)_2]^+$, which undergoes a temperature-dependent spin change.[19]

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When this ferric heme goes to high spin, an increase in the Fe–N(py) distances from 2.04 to 2.31 Å and an expansion of the porphyrin core by $\sim$0.055 Å are observed. While a spin equilibrium analogous to that observed in this ferric heme is not significant in the ground state of hexacoordinate ferrous porphyrins, a spin change may be anticipated along the reaction coordinate for axial ligand dissociation for iron porphyrins when the trans ligand is a weak-field ligand. The intermediate may resemble those of high-spin pentacoordinate hemes such as that of Fe(TPP)(2-MeIm)[20] with the iron 0.42 Å out-of-plane.

When a strong-field ligand such as CO or BzNC is present, the iron will remain low spin with the intermediate resembling the structures of FeOEP(CS)[21] or FeTPP(NO)[22] with a smaller displacement (0.22 Å) from the N_4 plane and only slight increases in Fe–N_4 distances. Five-coordinate low-spin carbonyl and isocyanide heme derivatives have been observed in capped hemes,[23,24] providing convincing evidence that no spin change is expected for ligand dissociation trans to CO or BzNC. The trans ligand is thus much more inert than in a $FeP(CH_3Im)_2$ complex, where a spin change is anticipated, giving a high-spin $FeP(CH_3Im)$. The FePc system is the only Fe macrocycle investigated to date that gives a more labile CH_3Im in the $FeN_4(CH_3Im)(BzNC)$ than in $FeN_4(CH_3Im)_2$. This also suggests that the $FePc(CH_3Im)$ intermediate is low spin as indicated previously on the basis of the relative lability of CH_3Im in $FeP(CH_3Im)_2$ and $FePc(CH_3Im)_2$.

The spin anomalies present in the iron complexes are not possible in ruthenium systems. All RuN_4L intermediates are expected to remain low spin, and thus, only the natural trans-labilizing effect of π-acceptor ligands is observed.

The proposed spin change along the reaction coordinate presents some theoretical difficulties which have been discussed for electron-transfer and photosubstitution reactions.[25] Spin effects have not been seriously considered for thermal substitution reactions because higher electronic states are generally not thermally accessible, and one presumes that spin-forbidden processes are unimportant.

However, in substitution reactions of hemes and related systems, electronic states other than the ground state are known to be thermally accessible and the rates of intersystem crossing are rapid (despite being doubly spin forbidden). For Fe(II) complexes intersystem crossing rates of $\geq 10^7$ s^{-1} ($^1A \rightleftharpoons {}^5T$) are reported and furthermore the barriers for intersystem crossing seem to be primarily due to nonelectronic factors similar to those involved in ligand dissociation.[25] Estimated probabilities of $^1A \rightleftharpoons {}^5T$ crossing in Fe(II) systems are $\sim 10^{-3}$.[25] One expects greater probabilties for the less spin-forbidden crossing to a triplet state involving population of d_{z^2}. Such a triplet state would have significantly weaker axial bonding but would not require the N_4 core expansion observed when $d_{x^2-y^2}$ is populated. The triplet state involving d_{z^2} population has been proposed as the state responsible for the photolability of hemes.[26]

While alternative explanations may explain the unusual labilization and trans effects described here, it is difficult to account for the *magnitude* ($\sim 10^6$) of these effects without invoking something dramatic like a spin change. Population of d_{z^2} will certainly profoundly assist axial ligand dissociation. Additional evidence for spin effects in thermal substitution reactions comes from studies of CO lability in Fe(14ane) and Fe(15ane) macrocycles.[17]

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Registry No. CO, 630-08-0; BzNC, 10340-91-7; RuPc(CO), 74891-28-4; $RuTPP(BzNC)_2$, 81642-67-3; $RuPc(BzNC)_2$, 83006-01-3; $RuPc(BzNC)(CH_3Im)$, 83006-02-4; RuPc(BzNC)(*t*-Bupy), 83006-03-5; CH_3Im, 616-47-7; *t*-Bupy, 3978-81-2; $RuOEP(BzNC)_2$, 83006-04-6; $RuPc(CO)(CH_3Im)$, 83006-05-7; RuPc(CO)(*t*-Bupy), 67588-49-2; RuPc, 27636-56-2.

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Substituent Effects on the Redox Reactions of Para-Substituted Tetraphenylporphyrin Complexes of Ruthenium(II)

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The electrochemical oxidation and reduction of ((*p*-X)TPP)Ru(CO)(*t*-Bupy) were investigated in CH_2Cl_2–0.1 M TBAP solution. Six different complexes were investigated where X = Et_2N, OMe, Me, Pr, Cl, and CF_3. All of the complexes gave two oxidations and a single reduction process with the exception of ((*p*-Et_2N)TPP)Ru(CO)(*t*-Bupy), which had three oxidations and one reduction. Plots of $E_{1/2}$ vs. 4σ were linear for the reduction and curvilinear for the first and second oxidation. Linear plots could be obtained for oxidations, however, when σ^+ was utilized in place of σ as the substituent constant. The species produced upon the first controlled-potential oxidation were investigated by electronic absorption, ESR, and infrared spectroscopy, and on the basis of this data, the first oxidation was assigned as ring centered in all cases. Unlike previous results with $[((p\text{-X})TPP)Ru(CO)]^+$, a room-temperature ESR spectrum of $[((p\text{-}Et_2N)TPP)Ru(CO)(t\text{-Bupy})]^+$ could be obtained with $g = 2.016$. A mechanism for oxidation of all of the ((*p*-X)TPP)Ru(CO)(*t*-Bupy) complexes is presented, and comparisons are made with previously published data for ((*p*-X)TPP)Ru(CO) complexes in the same solvent.

Introduction

The electrochemical oxidation of ruthenium(II) porphyrins such as (P)Ru(CO), (P)Ru(CO)(L), and $(P)Ru(L)_2$ has been well characterized in nonaqueous media.[1-5] When CO is one of the extraplanar ligands, the site of oxidation is at the porphyrin ring, yielding a cation radical.[1] In contrast the

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