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## Kinetics and Equilibria for Benzyl Isocyanide Binding to Ferrous Phthalocyanine Complexes

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Six-coordinate low-spin ferrous phthalocyanine complexes,  $L_2FePc$ , where  $L = 1$ -methylimidazole, piperidine, or pyridine reversibly bind benzyl isocyanide (RNC) in toluene solution via a dissociative mechanism. The formation constants for the  $LFePc(RNC)$  complexes are a factor of 1000 greater than those for  $FePc(RNC)_2$ . The lability of RNC trans to L increases in the order  $RNC \gg pip > py > CH_3Im$ . Thermodynamically, benzyl isocyanide is bound to the ferrous phthalocyanine in preference to CO by a factor of 1000 and it is a factor of 1000 more inert than CO. The lability and stability of CO and RNC complexes of ferrous phthalocyanine and porphyrin are discussed.

### Introduction

A "heme model" may be defined as any Fe(II) complex containing a planar tetradentate ligand such as a porphyrin, phthalocyanine, Schiff base, bisglyoxime, or macrocycle. These complexes typically add two ligands to axial coordination sites to give low-spin diamagnetic complexes. Their axial ligand substitution reactions are of particular interest since in the case of an iron porphyrin and other metal porphyrins, the axial ligands are unusually labile. Factors giving rise to the unusual lability of axial ligands in metal porphyrins and related complexes, while not well understood, are clearly important to the functioning of heme proteins.

Kinetic studies of several heme models which qualitatively mimic the reversible oxygen-carrying heme proteins in their ability to reversibly bind carbon monoxide<sup>1-3</sup> and alkyl isocyanides<sup>4</sup> have been reported. Kinetic studies of oxygen binding to iron porphyrins have also been reported.<sup>5</sup> While the reversible oxygen-binding properties of the heme group are clearly more pertinent to the function of hemoglobin and myoglobin, the reversible binding of carbon monoxide and alkyl isocyanides, which also bind to the proteins, serve as useful probes for the kinetic and thermodynamic differences between different heme models. The binding of oxygen to simple Fe(II) model systems is often complicated by irreversible oxidation. In addition, oxygen is typically a poorer ligand than CO or RNC in these systems and thus often may not bind under conditions where CO and RNC do.

The axial ligand substitution reactions of heme models in nonaqueous solvents proceed by a dissociative mechanism. This work is an extension of a previous study of the ferrous phthalocyanine system to alkyl isocyanide ligands. The differences in  $\sigma$ - and  $\pi$ -bonding properties of CO and RNC should give some information about the binding properties of the iron complex and how the Lewis acid-base properties of the iron are modified by the in-plane ligand in heme models.

### Experimental Section

The syntheses of the six-coordinate amine complexes,  $L_2FePc$ , have been described previously.<sup>3</sup> The dibenzyl isocyanide complex  $FePc(RNC)_2$  was prepared quantitatively from the  $(pip)_2FePc$  complex in chloroform solution by addition of excess benzyl isocyanide. The diisocyanide complex precipitated upon addition of petroleum ether. Toluene was distilled from  $CaH_2$  prior to use. Pyridine, piperidine, and methylimidazole were distilled from KOH.

**Kinetic Measurements.** Reactions were followed spectrophotometrically using a Cary 14 spectrophotometer. Solutions in 1-cm quartz cells 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. Solutions were thermostated for approximately 15 min prior to the reaction measurements. The slower reactions were followed by periodically scanning the spectrum between 500 and 370 nm and excellent isosbestic points were observed in these cases. 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.

All of the reactions were found to be independent of the concentration of the iron phthalocyanine complex. Concentrations of Fe were typically about  $5 \times 10^{-5}$  M. All reactions were run under pseudo-first-order conditions with the added ligand always in large excess. Typical procedures for the rate determinations for the various reactions investigated are given as follows.

$FePc(RNC)_2 + CH_3Im = (CH_3Im)FePc(RNC) + RNC$ . A toluene solution of the diisocyanide complex was prepared by dissolving the solid  $FePc(RNC)_2$  in toluene. A spectral cell containing 3 mL of the toluene solution was thermostated in the spectrophotometer and the decay of the absorbance at 394 nm following the addition of 0.03 mL of  $CH_3Im$  was monitored.

$CH_3ImFePc(RNC) + RNC = FePc(RNC)_2 + CH_3Im$ . To 3 mL of a toluene solution of  $FePc(RNC)_2$  was added 0.1 mL of a  $10^{-2}$  M methylimidazole solution in toluene. After the mixture stood for a few minutes, the formation of the  $CH_3ImFePc(RNC)$  was essentially complete. The spectrometer was set at 394 nm and the increase in the absorbance following addition of 0.03 mL of neat benzyl isocyanide was monitored.

$LFePcRNC + L = L_2FePc + RNC$ . To 3 mL of a toluene solution of  $FePc(RNC)_2$  was added 1.0 mL of neat ligand  $L =$  pyridine, piperidine, or methylimidazole. The rapid initial reaction to give  $LFePc(RNC)$  was ignored and the slow subsequent reaction was followed by periodically scanning the spectrum between 500 and 370 nm or monitoring the increase in absorbance at 420 nm.

$L_2FePc + RNC \rightarrow LFePc(RNC) \rightarrow FePc(RNC)_2$ . Solutions of the diamine complexes where  $L = CH_3Im$  or  $Im$  were prepared from the solid complexes in toluene. To 3 mL of these solutions was added 0.1 mL of neat benzyl isocyanide. The reaction was followed by monitoring the decrease in absorbance at 420 nm or the increase in absorbance at 394 nm.

**Equilibrium Measurements.** Equilibrium constants were determined from spectral data for toluene solution ( $[Fe] = 5 \times 10^{-5}$  M) containing varying concentrations of added L or RNC as follows.

$L_2FePc + RNC = LFePc(RNC) + L$ . To solutions of the  $L_2FePc$  complexes in toluene containing excess L (typically 1 M) were added varying amounts of a  $2 \times 10^{-2}$  M RNC solution in toluene. Owing to the extreme photosensitivity of the equilibrium<sup>4</sup> and the slow rate of approach to equilibrium, solutions were allowed to equilibrate for 24 h (72 h for  $L =$  methylimidazole) in the dark, prior to transfer to the spectrophotometer in the dark. (The amount of light passing through the solution in recording the visible spectrum was found not to affect the position of the equilibrium.) Spectral data were analyzed at the absorbance maximum of the diamine complexes at 420 nm.

$LFePc(RNC) + RNC = FePc(RNC)_2 + L$ . The equilibrium was conveniently studied by addition of various amounts of ligand L (either neat or in toluene) to a stock solution of the  $FePc(RNC)_2$  complex in toluene containing  $2.06 \times 10^{-2}$  M excess RNC. Solutions were allowed to equilibrate for 5 min in the spectrophotometer prior to running the spectra.

### Results

The binding of alkyl isocyanides to the low-spin ferrous phthalocyanine complexes is described by the reaction scheme

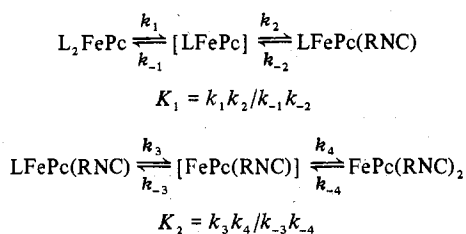
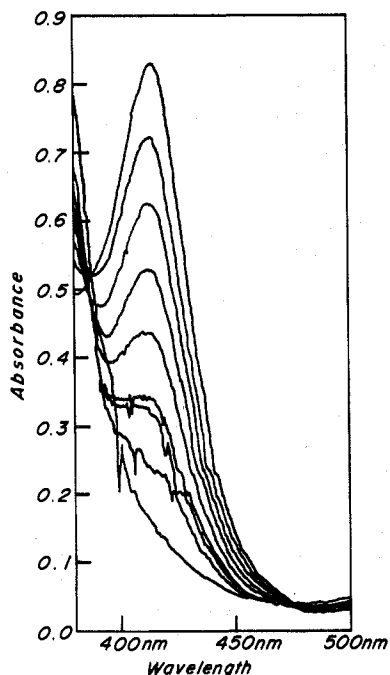


Figure 1. Reaction scheme.

Figure 2. Typical spectral data for the determination of the equilibrium constant for  $(py)_2FePc + RNC = (py)FePc(RNC) + py$  at constant  $[py] = 1.22$  M and varying  $[RNC] = 0.0-0.1$  M.Table I. Equilibrium Constants<sup>a</sup> for the Iron Phthalocyanine System

L	log $K_1$	log $K_2$	log $K_{CO}^b$
Piperidine	+3.5	+0.3	-0.07
Pyridine	+3.5	+0.5	-0.43
Methylimidazole	+2.6	-0.8	-1.52

<sup>a</sup> Obtained by visible spectral titration in toluene solution at 23 °C. Estimated error  $\pm 0.10$  in log  $K$ ; see reaction scheme in Figure 1 for the meaning of  $K_1, K_2$ . <sup>b</sup> Reference 3.

(Figure 1). Both the mono- and the dibenzyl isocyanide complexes may be obtained depending upon the concentration of amine and isocyanide. The two equilibrium constants (Table I) are sufficiently different in magnitude that they may be treated separately. Addition of a small amount of isocyanide ( $10^{-4}$  M) to a toluene solution of the  $L_2FePc$  complex results in formation of the mixed complex  $LFePc(RNC)$ . At much higher concentrations of isocyanide (0.1 M) a new species is formed which we assign to the diisocyanide complex. The three different species have quite distinct visible spectra in the 450–350-nm region (Figures 2, 3). The  $L_2FePc$  complex gives a green solution in toluene and is characterized by an absorbance maximum at 420 nm. The mixed complex  $LFePc(RNC)$  gives a blue solution in toluene and has no maximum at either 420 or 394 nm. The  $FePc(RNC)_2$  complex also gives a blue solution but contains a sharp maximum at 394 nm which distinguishes it readily from the monoisocyanide complex. The marked difference in spectra allows for characterization of the different species in solution. Absorbance changes at  $\sim 420$  nm provide a means of following the

Table II. Temperature Dependence of the Rates of the Reactions

$T, ^\circ C$	$10^2 k_{-4}, s^{-1}$	$k_3, s^{-1}$
5	1.34	$6.3 \times 10^{-4}$
10	2.52	$1.4 \times 10^{-3}$
15	5.15	$3.3 \times 10^{-3}$
20	9.8	
23		$1.02 \times 10^{-2}$
30		$2.9 \times 10^{-2}$

Table III. Temperature Dependence of Reaction Rates

L	15 °C	23 °C	30 °C	40 °C	50 °C
$LFePc(RNC) + L \rightarrow L_2FePc + RNC$ ( $k_{-2}$ )					
$CH_3Im$		$9.2 \times 10^{-5}$	$4.3 \times 10^{-4}$	$2.04 \times 10^{-3}$	
py		$1.98 \times 10^{-4}$	$1.0 \times 10^{-3}$	$4.5 \times 10^{-3}$	
pip		$1.6 \times 10^{-4}$	$5.15 \times 10^{-4}$	$2.5 \times 10^{-3}$	$1.1 \times 10^{-2}$
$L_2FePc + RNC \rightarrow LFePc(RNC) + L$ ( $k_1$ )					
$CH_3Im$	$1.3 \times 10^{-3}$	$3.96 \times 10^{-3}$	$1.95 \times 10^{-2}$		
Im	$5.9 \times 10^{-4}$	$2.4 \times 10^{-3}$	$7.1 \times 10^{-3}$	$3.2 \times 10^{-2}$	

rate of formation or loss of the  $L_2FePc$  species. The reaction  $LFePc(RNC) + RNC = FePc(RNC)_2$  results in only a minor change in the absorbance at 420 nm but a large change in absorbance at 394 nm.

Infrared measurements in chloroform solution for the  $FePc(RNC)_2$  show a sharp maximum at  $2180$   $cm^{-1}$ . On addition of a small amount of an amine ligand, this band disappears and a broad band at  $2160$   $cm^{-1}$  assigned to the overlap of bands due to free RNC and  $LFePc(RNC)$  is observed.

**Kinetic Results.** The kinetic measurements all involve the direct measurement of limiting dissociative rate constants. In all of the reactions, the rate was independent of the concentration of iron complex. The different reactions were carried out under conditions where the rate was also independent of the concentration of added substrate.

$FePc(RNC)_2 + CH_3Im = CH_3ImFePc(RNC) + RNC$ . The reaction of the diisocyanide complex of iron phthalocyanine with amine ligands was found to be independent of the nature or concentration of the added amine under the conditions of the experiments. Methylimidazole was typically used to displace the isocyanide since subsequent further reaction of the  $CH_3ImFePc(RNC)$  is slow. The reaction was studied over the temperature range 5–20 °C. The derived first-order rate constants are given in Table II. The subsequent reaction of the monoisocyanide complex with additional methylimidazole to give the  $(CH_3Im)_2FePc$  complex was not a complicating factor since the rate of dissociation of the isocyanide when trans to methylimidazole is about a factor of  $10^3$  slower than the rate of dissociation of the isocyanide when trans to another isocyanide.

$LFePcRNC + L = L_2FePc + RNC$ . Dissociation of the second isocyanide ligand was studied over the temperature range 23–50 °C owing to the much slower rates. The reactions could be conveniently studied by reaction of the diisocyanide complex with excess amine  $L = CH_3Im, py, pip$ . Since the rate of formation of  $LFePcRNC$  is fast ( $t_{1/2}$  being only a few seconds at 20 °C), upon mixing the solutions and activating the spectrophotometer the solution contains effectively only the  $LFePcRNC$  complex. The rate of reaction of this species with excess amine is readily followed at 420 nm. The formation of  $L_2FePc$  is characterized by an increase in the absorbance at 420 nm. All reactions went to completion at concentrations of added amine of 2.0 M. First-order log plots were obtained and the derived rate constants are given in Table III.

$LFePc(RNC) + RNC = FePc(RNC)_2 + L$ . The reaction of the mixed complex with excess isocyanide was studied for

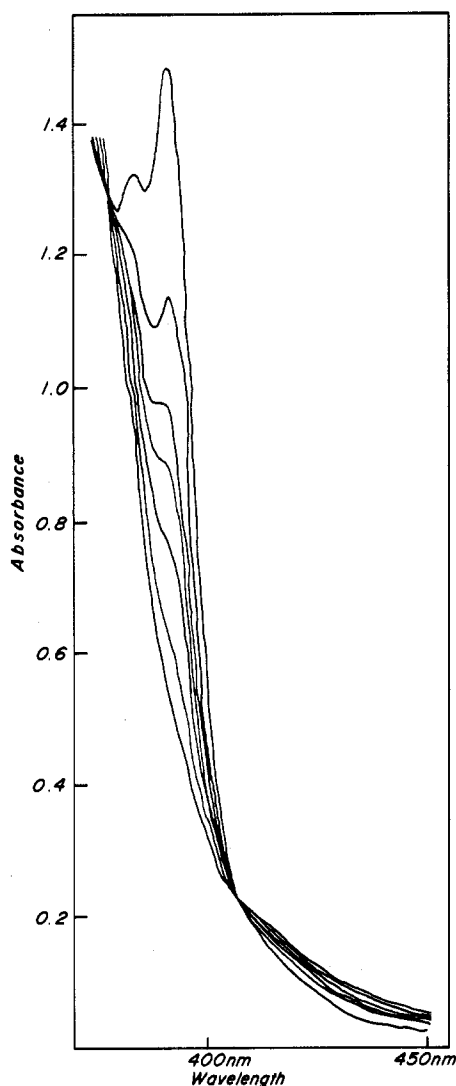


Figure 3. Typical spectral data for the determination of the equilibrium constant for  $(py)FePc(RNC) + RNC = FePc(RNC)_2 + py$  at constant  $[RNC] = 2.06 \times 10^{-2} M$  and varying  $[py] = 0.0-1.2 M$ .

$L =$  methylimidazole, by the addition of a small amount of the amine ligand ( $\sim 10^{-4} M$ ) to a solution of  $FePc(RNC)_2$ . The resulting solution had the characteristic spectrum of the mixed complex with no maximum at 420 or 394 nm. Subsequent addition of excess isocyanide to this solution resulted in a rapid reaction to give the diisocyanide complex as evidenced by the reappearance of the maximum at 394 nm. Excellent first-order kinetic plots were obtained; the rate constants as a function of temperature are given in Table II.

$L_2FePc + RNC = LFePcRNC + L$ . The rate of dissociation of the amine ligand from the bisamine complex was studied by addition of excess RNC to a toluene solution of the  $L_2FePc$  complex. The rate of dissociation of the amines have been reported previously<sup>3</sup> for  $L = pip, py,$  and  $Im$  from studies of the reaction of the amine complexes with carbon monoxide. The rates for  $L = py$  and  $pip$  are too fast for study on a conventional spectrophotometer and therefore were not investigated in this study. The rates of reaction of the imidazole complexes are slower.<sup>3</sup> Since the rate of dissociation of  $L$  from  $LFePcRNC$  was found to be faster than the rates of  $L$  dissociation from  $L_2FePc$ , addition of excess RNC to  $L_2FePc$  results in formation of the  $FePc(RNC)_2$  complex. The reaction of  $LFePc(RNC)$  to give  $FePc(RNC)_2$  does not interfere with the measurement of the rate of dissociation of  $L$  from the diamine complex. This is seen by obtaining  $k$  from two different wavelengths. Analysis of the spectra at 394 nm where

Table IV. Activation Parameters

L off	L trans	$\Delta G^\ddagger,^a$ kcal/mol	$\Delta H^\ddagger,^b$ kcal/mol	$\Delta S^\ddagger,^c$ eu
$CH_3Im$	$CH_3Im$	21.0	28.2	23
$Im$	$Im$	20.6	28.0	24
$CH_3Im$	RNC	19.8	24.9	17
RNC	$CH_3Im$	23.3	29.7	22
RNC	$py$	22.8	29.8	23
RNC	$pip$	22.2	29.5	24
RNC	RNC	18.3	21.4	10

<sup>a</sup> 30 °C. <sup>b</sup> Estimated error  $\pm 1.0$  kcal/mol. <sup>c</sup> Estimated error  $\pm 4$  eu.

the major contribution is from the  $FePc(RNC)_2$  complex gives data in good agreement with analysis of the spectra at 420 nm where the major contribution to the spectral change is due to the reaction  $L_2FePc + RNC = LFePcRNC$ . Excellent isosbestic points further support the validity of the treatment of the data as due to the rate of  $L$  dissociation from  $L_2FePc$  in a slow step. The observed rate constants for the imidazole system are in excellent agreement with previously reported data for  $L = Im$  from studies of the reactions with carbon monoxide. The rate constants obtained from the log plots are given in Table III.

**Activation Parameters.** Activation parameters for the reactions studied were obtained from Arrhenius plots. The data are given in Table IV.

### Discussion

The equilibrium constant for isocyanide binding to ferrous phthalocyanines is approximately  $10^3$  times larger than that for carbon monoxide. Measurements on the binding of benzyl isocyanide to iron porphyrins indicate that this large difference in the affinity for RNC vs. CO is not present in the porphyrin systems.<sup>6</sup> Data for CO and ethyl isocyanide binding to hemoglobin also show that CO is bound in preference to ethyl isocyanide in both hemoglobin and myoglobin.<sup>6</sup>

The large differences in the affinity of iron porphyrins and iron phthalocyanines for CO and RNC may be rationalized in terms of a stronger in-plane ligand field present in the phthalocyanine case.<sup>3,7</sup> This stronger ligand field will result in the metal  $d_{xz}$  and  $d_{yz}$  orbitals, which are involved in back-donation, lying lower in energy in the phthalocyanine case and thus being less available for back-donation to the axial ligands. This may be due to a greater  $\pi$  interaction with the in-plane phthalocyanine than with the porphyrin ligand. It is generally accepted that isocyanides are better  $\sigma$  donors and poorer  $\pi$  acceptors than carbon monoxide. Both the  $\sigma$ -donor orbital and the  $\pi$ -acceptor orbital lie lower in CO than they do in RNC.<sup>8</sup> Thus, the porphyrin system, which is a better axial  $\pi$  donor, binds CO and RNC about equally well while the phthalocyanine system, which is a poorer axial  $\pi$  donor, has a preference for RNC over CO by a factor of  $10^4$ . The greater reluctance of the phthalocyanine complex to back-bond to axial donors is also in agreement with the more difficult oxidation of the ferrous phthalocyanine complexes.

It is clear that the iron porphyrin system is significantly more labile than any of the proposed models with respect to  $L, CO,$  and RNC dissociation. The reason for the unique properties of the iron porphyrins may be due to a low energy barrier for extension of the Fe-L bond in the axial positions. Proceeding along the reaction coordinate may be facilitated by the movement of the iron out of the plane of the porphyrin ring. This distortion has its lowest energy in the case of the porphyrin ligand, presumably due to the resistance of the porphyrin skeleton to radial expansion or contraction and to the matching of the size of the hole and the effective size of the metal.<sup>9</sup> The ability of iron to go high spin in proceeding along the reaction coordinate may provide a major part of the

stabilization of the transition state involving the Fe substantially out of the plane of the porphyrin ring.<sup>3</sup>

The trans effects in these dissociative reactions of tetragonal complexes differ in substance from the more widely investigated trans effects in square-planar complexes<sup>10</sup> since the energy barrier for dissociation of the ligand is independent of the nature of the entering group. The trans effect would be expected to closely parallel the trans influences in this case.

With respect to dissociation of isocyanide trans to amine ligands, the effects are similar to those observed for CO dissociation. The order of RNC lability trans to the various amines studied is  $\text{pip} > \text{py} > \text{CH}_3\text{Im}$ . The ligand exerting the largest trans effect on isocyanide dissociation is the isocyanide ligand itself. The rate of dissociation of RNC trans to RNC is a factor of  $10^4$  times faster than when RNC is trans to the amine ligands studied. The observed trans effect is consistent with the principle of antisymbiosis<sup>11</sup> and may be explained in terms of the two isocyanide ligands sharing  $\sigma$  and  $\pi$  orbitals on the metal. Attempts to detect either the  $\text{FePc}(\text{CO})_2$  or  $\text{FePc}(\text{RNC})(\text{CO})$  at room temperature up to 760 Torr of CO have been unsuccessful. It is well-known that strong  $\pi$ -acceptor ligands destabilize each other in mutually trans positions.

The kinetic data obtained in the 1-methylimidazole system allow one to evaluate the mutual trans effects of the trans ligands on each other since both  $\text{CH}_3\text{Im}$  and RNC dissociation from  $\text{FePc}(\text{RNC})(\text{CH}_3\text{Im})$  may be measured. It is seen that the isocyanide ligand is less labile in the mixed complex while  $\text{CH}_3\text{Im}$  is more labile in the mixed complex. In the absence of steric interaction between the axial ligands and planar ligand, the iron may move out of the plane slightly in the direction of the preferred ligand. Thus we predict that in the  $\text{FePc}(\text{RNC})(\text{CH}_3\text{Im})$  the iron may lie out of the plane toward the isocyanide ligand. Such a movement would be in the direction of the reaction coordinate for dissociation of  $\text{CH}_3\text{Im}$  but opposite to the direction of the reaction coordinate for RNC dissociation.

It is of interest that the trans effects observed in the phthalocyanine system are similar to those reported by Basolo

et al.<sup>5</sup> for oxygen dissociation from iron porphyrin-oxygen complexes. In addition the relative labilities of the amines, piperidine, imidazole, and pyridine are similar in the two systems. These features appear to be transferable from one heme model to another and even to cobalt porphyrins.<sup>12</sup> The absolute features of a given heme model, i.e. how well it will bind CO or RNC and how labile these ligands will be, appear to be complicated functions of the in-plane ligand and its effect on the  $\sigma$  and  $\pi$  bonding to the axial ligands. In view of the number of factors involved in the lability of axial ligands in these systems and the large cis and trans effects observed, a large body of data will be required before a direct relationship between the structure of the macrocyclic tetradentate ligand and the lability of axial ligands coordinated to its Fe(II) complex becomes clear.

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**Registry No.**  $\text{FePc}(\text{RNC})_2$ , 53596-02-4;  $\text{CH}_3\text{ImFePc}(\text{RNC})$ , 62006-60-4;  $\text{pyFePc}(\text{RNC})$ , 62006-61-5;  $\text{pipFePc}(\text{RNC})$ , 62006-62-6;  $\text{ImFePc}(\text{RNC})$ , 62006-63-7;  $(\text{CH}_3\text{Im})_2\text{FePc}$ , 55925-76-3;  $(\text{Im})_2\text{FePc}$ , 16702-09-3;  $(\text{py})_2\text{FePc}$ , 15650-77-8;  $(\text{pip})_2\text{FePc}$ , 25232-79-5.

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## Preparation, Characterization, and Reactions of the Thiocarbonyl Complexes Dicarbonyl( $\eta^5$ -cyclopentadienyl)(thiocarbonyl)ruthenium(1+) and Dicarbonylbis( $\eta^5$ -cyclopentadienyl)di- $\mu$ -thiocarbonyl-diruthenium

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The reaction of  $\text{CpRu}(\text{CO})_2^-$  successively with  $\text{CS}_2$ ,  $\text{CH}_3\text{I}$ , and  $\text{CF}_3\text{SO}_3\text{H}$  yields the cationic thiocarbonyl complex  $\text{CpRu}(\text{CO})_2(\text{CS})^+$ . This complex reacts with  $\text{N}_3^-$  and  $\text{N}_2\text{H}_4$  to give  $\text{CpRu}(\text{CO})_2\text{NCS}$  and with  $\text{NCO}^-$  to yield  $\text{CpRu}(\text{CO})_2\text{CN}$ . With  $\text{NaH}$ ,  $\text{CpRu}(\text{CO})_2(\text{CS})^+$  is reduced to a mixture of the dimeric complexes  $[\text{CpRu}(\text{CO})(\text{CS})]_2$  (major product) and  $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{CS})$ . In both dimers the CS groups are in the bridging positions, and there is no evidence for nonbridged structures unlike  $[\text{CpRu}(\text{CO})_2]_2$  which exists partially in a nonbridged form. Infrared and proton NMR studies indicate that both  $[\text{CpRu}(\text{CO})(\text{CS})]_2$  and  $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{CS})$  exist in cis and trans forms which interconvert too rapidly to be separated. The presence of the bridging CS groups does, however, slow the rate of isomerization. Qualitative studies indicate that this rate decreases in the order  $[\text{CpRu}(\text{CO})_2]_2 > \text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{CS}) > [\text{CpRu}(\text{CO})(\text{CS})]_2$ . Mechanisms for these isomerizations are discussed. The preference of CS for a bridging over a terminal position in these molecules is rationalized in terms of the weakness of the  $\text{C}\equiv\text{S}$   $\pi$  bonds which lose little  $\pi$ -bond stabilization in moving from a terminal ( $\text{C}\equiv\text{S}$ ) to a bridging ( $>\text{C}=\text{S}$ ) position. These arguments also suggest that CO should have a lower preference for a bridging position than CS.

#### Introduction

One of the earliest reported<sup>1</sup> examples of a thiocarbonyl-containing complex was the cationic species  $\text{CpFe}(\text{CO})_2(\text{CS})^+$ , where  $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ . Subsequent investigation<sup>2</sup> revealed that

the thiocarbonyl carbon is usually the preferred site of attack when  $\text{CpFe}(\text{CO})_2(\text{CS})^+$  is exposed to nucleophiles. Recently it was found that interaction of  $\text{CpFe}(\text{CO})_2(\text{CS})^+$  with sodium hydride generates the novel thiocarbonyl-bridged dimer