dophosphine **8** and Me_3SiCl. The mixture was then heated at 85 °C in an oil bath for 18 h. Gas evolution was observed during this time. A ^{31}P NMR spectrum of the mixture showed the major product to be the phsophinimine **11** along with small amounts of the dimers **10a** and **10b**. Solvent removal left a viscous liquid from which **11** was distilled as a colorless liquid (ca. 20% yield, bp 75-76 °C (0.20 mm)). Anal. Calcd: C, 38.92; H, 9.55. Found: C, 38.36; H, 9.60. The solid remaining in the distillation flask was shown by ^{31}P NMR to contain the dimers **10a** and **10b**.

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Registry No. **1**, 76946-89-9; **2**, 76946-90-2; **3**, 76946-91-3; **4**, 76173-65-4; **5**, 76946-92-4; **6**, 76946-93-5; **7**, 76946-94-6; **8**, 76946-95-7; **10a**, 76946-96-8; **10b**, 76946-97-9; **11**, 76946-98-0; $(Me_3Si)_2NPCl_2$, 54036-90-7; Me_3SiCH_2MgCl, 13170-43-9; *t*-BuLi, 109-72-8; MeOH, 67-56-1; Me_3SiN_3, 4648-54-8; Me_3SiCl, 75-77-4; $(Me_3Si)_2NH$, 999-97-3; PCl_3, 7719-12-2; $LiN(SiMe_3)_2$, 4039-32-1.

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Axial Ligand Substitution Reactions of Ruthenium(II) Phthalocyanine

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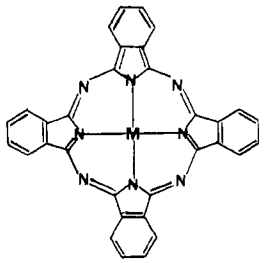
The synthesis and characterization of bisadducts of ruthenium(II) phthalocyanine, $RuPcL_2$, and chlorinated phthalocyanine analogues, $RuPc(Cl)L_2$, are reported. Axial donor ligands include *N*-methylimidazole, pyridine, tri-*n*-butylphosphine, and tri-*n*-butyl phosphite. Kinetic and thermodynamic studies of axial ligand substitution show that the reaction mechanism is dissociative (D) and that the five-coordinate intermediate, RuPcL, possesses little or no ability to discriminate between nucleophiles. The $RuPcL_2$ complexes differ from the iron analogues in that the former are much more inert, and the importance of M→L π-back-bonding is much more important for ruthenium. Trans-group and leaving-group effects are reported: *N*-methylimidazole (MeIm) greatly deactivates the trans ligand in RuPc(MeIm)(L). The reaction $RuPc(P(OBu)_3)_2$ + MeIm ⇌ $RuPc[P(OBu)_3][MeIm]$ + $P(OBu)_3$ is a novel example of one for which the limiting forward and reverse rate constants are identical.

Introduction

Metal phthalocyanines, M(Pc), have been extensively studied for many years and have found various important commercial applications as pigments, catalysts, and electrical materials.[1]



M(Pc)

In the many metal phthalocyanine catalyzed autoxidation reactions it is known[2] that the thermodynamics and dynamics of substrate binding to the catalyst are crucial factors, and frequently close correlations exist between reactivity and dioxygen affinity or M(III)/M(II) reduction potentials. The structural similarity between the phthalocyanine macrocyclic ring and synthetic or naturally occurring porphyrins provides additional impetus for investigations. Phthalocyanine complexes of Fe^{2+} and Co^{2+} readily bind one or two axial ligands and under suitable conditions bind dioxygen. Indeed, Antonini et al.[3] have shown that iron and cobalt tetrasulfonated phthalocyanine will combine with globin in a 1:1 molar ratio to yield proteins that reversibly bind dioxygen, although the O_2-off rate is much slower than in oxyhemoglobin. These metal phthalocyanines were also found to displace the iron protoporphyrin from hemoglobin and methemoglobin, suggesting that both types of complexes bind at the same site.

In order to understand better the catalytic properties of metallophthalocyanines and the reasons for the seemingly unique behavior of analogous porphyrin complexes, it is necessary to know the thermodynamic and kinetic factors controlling axial ligand substitution. We recently reported[4] a detailed kinetic study of reaction 1, in which the trans group

$$(T)FePc(L) + X \rightarrow (T)FePc(X) + L \qquad (1)$$

(T), leaving group (L), and nucleophile (X) include a variety of nitrogen and phosphorus donor ligands. The activation parameters and rate behavior showed conclusively that reaction 1 follows a simple dissociative (D) mechanism.

$$(T)FePc(L) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (T)FePc + L$$
$$(T)FePc + X \xrightarrow{k_3} (T)FePc(X) \qquad (2)$$

Six-coordinate iron porphyrin complexes follow a similar mechanism, but the axial ligand lability as measured by k_1 is less for the iron phthalocyanines by a factor of 10^3 or more. For reaction 1 the ratio k_3/k_2 is always close to unity, implying that the five-coordinate intermediate (T)FePc is a very reactive species with little ability to discriminate between nucleophiles. In sharp contrast to this, five-coordinate iron porphyrins are relatively stable and can have large discrimination ratios. These fundamental differences are probably due to the ease of spin-state conversion and metal movement out of the mean macrocyclic plane found with metalloporphyrins. The larger

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0020-1669/81/1320-1683$01.25/0

ligand field and superior π-accepting properties of the phthalocyanine ring make spin-state change energetically difficult. Therefore the (T)FePc intermediate is likely to be low spin with little out-of-plane metal displacement, and thus is nondiscriminating.

In this paper we report the synthesis, characterization, and axial ligand substitution dynamics of several ruthenium(II) phthalocyanine adducts. Relatively little basic chemistry is known about RuPc complexes. Several observations suggest that additional investigations would be worthwhile: RuPc is more effective than FePc as a catalyst in some hydrocarbon autoxidation reactions, and the well-known π-donating ability of Ru(II) (in contrast to Fe(II)) may produce fundamental differences between the RuPc and FePc adducts. In particular, one goal was to see if Ru(II) mimics Fe(II) in the large decrease in axial lability observed whenever imidazole is the trans group in (T)FePc(L). Deactivation by imidazole seems to occur also with iron(II) porphyrins and is clearly relevant to hemoprotein-mediated reactions.

There have been several recent reports concerning the synthesis of RuPc adducts. James et al.[5] prepared $RuPcL_2$ and RuPc(CO)L (L = pyridine, imidazole, DMF, Me_2SO) from crude RuPc, which was made from $RuCl_3 \cdot 3H_2O$, *o*-cyanobenzamide, and naphthalene. Tsutsui et al.[6] prepared RuPc(CO)py in much better yield by condensing $RuCl_3 \cdot 3H_2O$ or $Ru_3(CO)_{12}$ with phthalonitrile. Several workers claim[7] that $RuCl_3 \cdot 3H_2O$ and phthalonitrile react to give RuPc(Cl), which contains Ru(III) and Cl^- as the counterion. However, Boucher et al.[8] claim that ring chlorination occurs during synthesis and that RuPc(Cl) contains Ru(II). Herein we report spectroscopic and dynamic data for the bisadducts of both RuPc and RuPc(Cl).

Experimental Section

Solvents and ligands were purified and dried by standard methods. Electronic spectra were recorded on a Gilford 250 spectrophotometer equipped with a wavelength-scanning accessory. ^1H and ^{13}C FT NMR spectra were recorded on a Bruker WP-60, and FD mass spectra, on a ZAB-2F spectrometer.

Ruthenium Phthalocyanine (RuPc) and $RuPcL_2$. Crude RuPc was prepared by a modification of a previously reported procedure.[6] Phthalonitrile (0.5 g) and $Ru_3(CO)_{12}$ (0.093 g) were heated in air at 200 °C for 4 h. The resultant black solid was ground to a powder and stirred in benzene for 1 h to remove excess phthalonitrile. The crude product of RuPc or RuPcCO was used without further purification for the synthesis of the bisadducts.

The crude RuPc was added to excess ligand L, where L was tri-*n*-butylphosphine (PBu_3) or tri-*n*-butyl phosphite ($P(OBu)_3$). the mixture was heated under argon for 2 h at a temperature near the boiling point and then cooled and dissolved in benzene. The resulting deep blue solution was chromatographed over alumina with benzene solvent. The first blue eluate, present in large quantity, was rotary evaporated until near dryness. The solid was dissolved in anhydrous ethyl ether, and the mixture was filtered to remove insoluble impurities and then rotary evaporated again. Acetone was added to the PBu_3 adduct, and methanol, to the $P(OBu)_3$ adduct. When the solution was cooled to 0 °C, deep blue crystals formed, which were filtered and washed thoroughly with the appropriate cold solvent and then vacuum dried for 4 h at room temperature. The yields were approximately 30% based on the starting material, $Ru_3(CO)_{12}$. Elemental C, H, N analyses by Baron Consulting Co., Orange, Conn., were excellent for the bisadduct formulation $RuPcL_2$.

RuPc(Cl) and RuPc(Cl)L_2. Phthalonitrile and $RuCl_3 \cdot 3H_2O$ in a 5:1 weight ratio were heated for 4 h. experiments were done under air, argon, and CO and at temperatures ranging from 170 to 250 °C. In all cases the resulting black solid was stirred in benzene, filtered, and dried. This crude "RuPc" was used directly to synthesize the adducts with PBu_3, $P(OBu)_3$, pyridine (py), and *N*-methylimidazole (MeIm) by the procedure presented above, except that methylene chloride instead of benzene was used to elute the product. Analytical data for C, H, N, and Cl were excellent for the formulation RuPc(Cl)L_2 where the phthalocyanine ring is presumably monochlorinated.

$FePcL_2$. These complexes were prepared as described previously.[4]

Kinetic Studies. The dynamics of axial ligand substitution in the bisadducts were followed on a Gilford 250 spectrophotometer or a Dionex stopped-flow spectrometer. The solvent, toluene, was freshly distilled from CaH_2 and dried over molecular sieves. The temperature was maintained with a Gilford Thermoset controller and except for activation parameter determinations was 25.0 ± 0.1 °C for most experiments. The nucleophile concentration and in most cases the leaving-group concentration was kept in pseudo-first-order excess over the total metal concentration which was about 5×10^{-5} M. Rate constants were evaluated from ln $(A - A_\infty)$ vs. time plots and from standard least-squares fitting programs. Activation parameters were calculated from a least-squares fit to the Eyring equation using rate data obtained over the temperature range 15–40 °C.

Some reactions that were excessively slow at room temperature were followed qualitatively by refluxing the reactants in toluene and periodically removing aliquots and recording the visible spectra.

Equilibrium Studies. Equilibrium constants for several of the substitution reactions were obtained by making static absorbance measurements on reaction mixtures that were equilibrated at 25 °C long enough to ensure that equilibrium had been attained. Solutions were prepared that had various leaving-group to nucleophile concentration ratios ([L])/([X]) and a fixed total metal complex concentration. Absorbance measurements were fit to eq 3 by using a least-squares program. In eq 3 A is the absorbance, A_0 and A_∞ are the absorbances of pure reactants and products, and K is the equilibrium constant. A typical plot is given in Figure 1. Thermodynamic functions were obtained by measuring A and A_0 over the temperature range 15–50 °C and fitting the data to the standard van't Hoff equation. The cuvette temperature was controlled to ±0.1 °C with a Gilford Thermoset attachment.

$$A = \frac{1}{K}(A_0 - A)\left(\frac{[L]}{[X]}\right) + A_\infty \qquad (3)$$

Mixed-ligand complexes RuPcLL′ were generated in situ by adding a known amount of excess L′ to a solution of $RuPcL_2$ and equilibrating until spectral measurements showed that equilibrium had been attained and that the conversion to RuPcLL′ was essentially 100%. The minimum time allowed for equilibration was 1 h at room temperature.

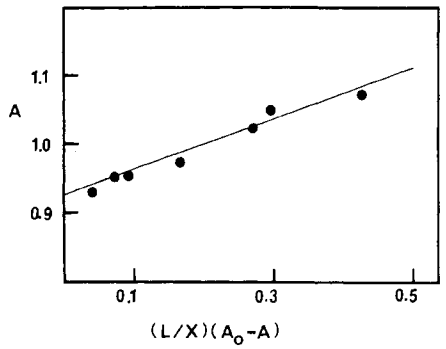

Figure 1. Equilibrium constant plot of eq 3 for the reaction RuPc[$P(OBu)_3$]$_2$ + MeIm ⇌ RuPc[$P(OBu)_3$][MeIm] + $P(OBu)_3$.

Table I. Electronic Spectra of Six-Coordinate Ruthenium Phthalocyanine Adducts[a]

complex	λ_{max} ($10^{-4}\epsilon$, M^{-1} cm^{-1})
RuPc[$P(OBu)_3$]$_2$	402 (1.0), 566 (2.1), 638 (7.7)
RuPc(PBu_3)$_2$	361 (3.3), 435 (1.5), 572 (2.3), 631 (4.6)
RuPc(Cl)(py)$_2$	375 (2.6), 567 (2.9), 622 (8.4)
RuPc(Cl)(MeIm)$_2$	384 (2.7), 423 (0.9), 569 (2.6), 622 (7.9)

[a] Solvent toluene; 25 °C.

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Table II. ^{1}H NMR Spectra of Six-Coordinate Iron and Ruthenium Phthalocyanine Adducts[a]

complex	phthalocyanine[b]	axial ligand[c]
$FePc[P(OBu)_3]_2$	9.07, 7.64	1.19 (1), 0.29 (3.5)
$RuPc[P(OBu)_3]_2$	9.20, 7.85	1.06 (1), 0.29 (3.5)
$RuPc(Cl)[P(OBu)_3]_2$	9.15, 7.88	1.06 (1), 0.28 (3.5)
$FePc(PBu_3)_2$	9.26, 7.89	0.13 (2.5), −1.11 (1), −2.08 (1)
$RuPc(PBu_3)_2$	9.13, 7.87	0.10 (2.5), −1.22 (1), −2.04 (1)
$RuPc(Cl)(PBu_3)_2$	9.12, 7.78	0.11 (2.5), −1.21 (1), −2.07 (1)
$RuPc(Cl)(py)_2$	9.10, 7.89	6.04 (1), 5.23 (2), 2.44 (2)
$RuPc(Cl)(MeIm)_2$	9.04, 7.81	4.68 (1), 2.41 (1), 2.16 (3), 2.03 (1)

[a] $CDCl_3$ solvent; δ scale relative to Me_4Si. [b] Each resonance consists of a pair of doublets (AA′BB′). [c] Relative areas in parentheses.

Table III. $^{13}C\{^1H\}$ NMR Spectra of Six-Coordinate Iron and Ruthenium Phthalocyanine Adducts[a]

complex	phthalocyanine	axial ligand
$FePc(PBu_3)_2$	147.3, 142.6, 127.8, 121.4	24.4, 23.1, 17.7, 13.0
$RuPc(PBu_3)_2$	143.7, 141.6, 128.1, 121.9	24.4, 22.9, 17.0, 13.0
$FePc[P(OBu)_3]_2$	147.8, 142.2, 127.4, 121.9	62.6, 31.7, 18.2, 13.5
$RuPc[P(OBu)_3]_2$	143.8, 141.3, 127.5, 121.3	61.8, 31.5, 18.0, 13.3
$RuPc(Cl)[P(OBu)_3]_2$	143.8, 141.2, 127.5, 121.4	61.8, 31.5, 18.0, 13.3

[a] $CDCl_3$ solvent; shifts in ppm relative to Me_4Si.

The mixed complexes were then used in the kinetic experiments.

Results and Discussion

$RuPcL_2$ and $RuPc(Cl)L_2$ Complexes. Electronic spectra, ^{1}H NMR, and $^{13}C\{^1H\}$ NMR spectra are given in Tables I, II, and III, respectively. The PBu_3 and $P(OBu)_3$ bisadducts $RuPcL_2$, prepared by the $Ru_3(CO)_{12}$ route to RuPc, were well characterized by analysis and NMR chemical shifts and band areas. The FD mass spectrum of $RuPc[P(OBu)_3]_2$ at 80 °C and 10–20 mA emitter currents consists of a parent cluster at m/e = 1114. Very little dissociation of the axial ligands occurred under these conditions. ^{1}H NMR spectra of $FePcL_2$ and $RuPcL_2$ contain the usual[9] two AA′BB′ phthalocyanine resonances at low field. The axial ligand chemical shifts are considerably shielded by the phthalocyanine ring.

Synthesis of ruthenium phthalocyanine from $RuCl_3 \cdot 3H_2O$ consistently produced bisadducts that gave poor analysis for $RuPcL_2$ ($C_{32}H_{16}N_8RuL_2$) but good ones for the formulation $RuPc(Cl)L_2$ ($C_{32}H_{15}N_8ClRuL_2$). The product obtained by heating $RuCl_3 \cdot 3H_2O$ and phthalonitrile has caused considerable confusion.[6-8] Reported products include RuPc, (Cl)RuPc, and RuPc(Cl), where the second contains Ru(III) and coordinated chloride and the third contains a chlorinated phthalocyanine ring. FePc is known to react with HCl to form a complex that was initially thought to be $(Cl)Fe^{III}Pc$ but now[10] is beleived to contain a Fe(II)–Cl bond with one protonated aza nitrogen on the phthalocyanine ring. Consistent with this is the observation that adding excess base (py, MeIm, etc.) to FePc·HCl produces $FePcL_2$ with no halogen remaining. Nevertheless, it is possible to oxidize FePc to $(Cl)Fe^{III}Pc$ by stirring FePc in a chlorinated solvent such as chlorobenzene.[11] Chlorination of the phthalocyanine ring is well-known,[12] particularly with the important pigment CuPc. Boucher et al.[8] suggest that the RuPc(Cl) made by the $RuCl_3 \cdot 3H_2O$ method contains a chlorinated phthalocyanine ring. Tsutsui et al.,[6] however, made RuPc(CO)(py) by the $RuCl_3 \cdot 3H_2O$/phthalonitrile method using a CO atmosphere and reported little or no chloride incorporation. We found 1 mol of chlorine in all the compounds made from $RuCl_3 \cdot 3H_2O$, whether the reaction was performed under air, CO, or argon.

In agreement with Boucher et al.[8] we found that the chloride was not removed by the addition of base to RuPc(Cl). This argues against the kind of HCl adduct formed by FePc. Kinetic studies described below show that oxidation to Ru(III) does not occur. An FD mass spectrum of $RuPc(Cl)[P(OBu)_3]_2$ shows the major ion cluster at m/e = 1149, precisely where expected for $C_{32}H_{15}N_8ClRu[P(OBu)_3]_2$. This shows that the chloride is not present as ionic Cl^-. A chlorinated phthalocyanine ring seems to be the logical formulation, and Boucher et al.[8] present ^{1}H NMR data for $RuPc(Cl)(py)_2$ that is said to clearly differentiate between a monochlorinated and nonchlorinated ring. We found, however, that both the ^{1}H and ^{13}C NMR spectra of $RuPc(Cl)L_2$ and the $RuPcL_2$ analogues were virtually identical (see Tables II and III). The electronic spectra were identical also. One would expect the AA′BB′ phthalocyanine ring pattern in the ^{1}H NMR spectra to be disrupted upon monochlorination at the α or β position on one of the benzene rings. It is even more surprising to find identical ^{13}C NMR spectra. We are unable at this time to provide a satisfactory explanation of these peculiar results.

Ligand Substitution Reactions. Equilibrium and kinetic data obtained for axial ligand substitution in $RuPc(Cl)L_2$ were, within experimental error, identical with the results for the $RuPcL_2$ analogues, showing that the chlorinated complexes almost certainly do not contain Ru(III). Since $RuPcL_2$ and $RuPc(Cl)L_2$ are so similar in behavior, the discussion below is limited to the nonchlorinated system.

Addition of PBu_3, MeIm, or py to $RuPc[P(OBu)_3]_2$ produced the mixed complex $RuPc(L)[P(OBu)_3]$. Replacement of the second $P(OBu)_3$ either is very slow or does not occur for thermodynamic reasons. For this reason it was possible to make kinetic and thermodynamic measurements without interference from a second $P(OBu)_3$ substitution step. It was also possible to prepare the mixed complexes in situ and study their conversion back to $RuPc[P(OBu)_3]_2$ by adding excess $P(OBu)_3$.

All of the kinetic and thermodynamic results are consistent with the following scheme (Table IV):

$$\begin{aligned} RuPcL_2 &\underset{k_2}{\overset{k_1}{\rightleftharpoons}} RuPcL + L \\ RuPcL + X &\underset{k_4}{\overset{k_3}{\rightleftharpoons}} RuPcLX \end{aligned} \qquad (4)$$

The equilibrium constants $K = k_1k_3/k_2k_4$ were determined from static absorbance measurements of solutions of $RuPcL_2$ containing various ratios of [L]/[X]. With X = MeIm and py the equilibrium constants were also determined by starting with a solution of the mixed complex RuPcLX prepared in situ and again varying the concentration ratio [L]/[X]. The values of K calculated for the forward and reverse reactions were in excellent agreement, proving the reversibility of reaction 4. A typical plot of equation 3, which yields K from the slope, is given in Figure 1. The temperature dependence of K for reaction 5 was obtained from experiments performed

$$RuPc[P(OBu)_3]_2 + MeIm \underset{}{\overset{K}{\rightleftharpoons}} RuPc[P(OBu)_3](MeIm) + P(OBu)_3 \qquad (5)$$

in 5° steps over the range 15–50 °C. The equilibrium constant was found to be almost temperature independent: $\Delta H^\circ = -0.5$

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Table IV. Kinetic and Thermodynamic Data[a] for the Reaction (T)RuPc(L) + X → L

trans group (T)	leaving group (L)	[L], M	nucleophile (X)	[X], M	K^b	k_1, s^{-1}	k_3/k_2
$P(OBu)_3$	$P(OBu)_3$	0–0.0985	MeIm	0.0126–0.1006	2.6 ± 0.3	0.0025 ± 0.0003	2.7 ± 0.5
$P(OBu)_3$	$P(OBu)_3$	0–0.0432	py	0.3076–0.5560	0.047 ± 0.005	0.0023 ± 0.0003	2.4 ± 0.5
$P(OBu)_3$	$P(OBu)_3$	0–0.0963	PBu_3	0.0642–0.1010	6.0 ± 1.0	0.0028 ± 0.0003	1.6 ± 0.4
$P(OBu)_3$	MeIm	0.0108–0.1077	$P(OBu)_3$	0.0126–0.1269	0.41 ± 0.13	0.0026 ± 0.0003	0.4 ± 0.1
$P(OBu)_3$	py	0.0118	$P(OBu)_3$	0.0135–0.1454	21.3 ± 2.3	0.115 ± 0.015	0.4 ± 0.1
PBu_3	$P(OBu)_3$	0	PBu_3	0.0474		0.0002[c]	

[a] Solvent toluene; 25 °C. [b] Equilibrium constant; determined by static experiments. [c] From a single experiment.

± 0.5 kcal; ΔS° = 0.6 ± 3 cal/(deg mol).

For the mechanism in scheme 4 the observed pseudo-first-order rate constant, k_{obsd}, is given by eq 6. For the

$$k_{obsd} = \frac{k_1k_3[X] + k_2k_4[L]}{k_3[X] + k_2[L]} \quad (6)$$

reaction of $RuPc[P(OBu)_3]_2$ with MeIm, k_{obsd} was found to be independent of either the X or L concentration. The reaction was studied with a variety of [L]/[X] ratios, with both $RuPcL_2$ and RuPcLX as the reactant, and k_{obsd} was always 0.0025 ± 0.0003 s^{-1} at 25 °C. Direct measurement of k_1 when [L] ≈ 0 in the forward direction and of k_4 when [X] ≈ 0 in the reverse direction showed that k_1 and k_4 are equal within experimental error. Under these conditions eq 6 simplifies to $k_{obsd} = k_1 = k_4$ regardless of the [L]/[X] ratio. This situation is highly unusual, and we know of no other reaction involving a net chemical change for which the forward and reverse rate constants are identical. Had the kinetics of reaction 5 been studied in the forward direction only, the invariance of k_{obsd} would have suggested a very large discrimination ability, defined as k_3/k_2, for the intermediate species RuPcL. The ratio k_3/k_2 was calculated to be 2.7 from knowledge of the equilibrium constant K. A related, and more useful, way to treat the kinetic data is to write k_{obsd} as the sum $k_f + k_r$, which separates the forward and reverse contributions to the approach to equilibrium (eq 7 and 8). Figure 2 shows k_{obsd} and k_f as

$$k_{obsd} = k_f + k_r = \frac{k_1k_3[X]}{k_3[X] + k_2[L]} + \frac{k_2k_4[L]}{k_3[X] + k_2[L]} \quad (7)$$

$$k_f = \frac{k_1k_3[X]/[L]}{k_2 + k_3[X]/[L]} = \frac{k_{obsd}}{1 + ([L]/[X])(1/K)} \quad (8)$$

a function of [X]/[L] for reaction 5. Equation 8 and K, measured independently as described above, were used to compute values of k_f. A reciprocal plot of $1/k_f$ vs. [L]/[X] yields the limiting forward rate constant k_1 and the discrimination ratio k_3/k_2. A relative deviation least-squares program was used for this and related plots for k_r.

The activation parameters for the dissociation of $P(OBu)_3$ from $RuPc[P(OBu)_3]_2$ (k_1) were calculated from rate measurements over the temperature range 15–40 °C for reaction 5. The results are: $\Delta H^\ddagger$ = 27.8 ± 1.4 kcal; $\Delta S^\ddagger$ = 23 ± 4 cal/(deg mol).

The reaction of $RuPc[P(OBu)_3]_2$ and py was studied in both directions. For this case $k_4 > k_1$, and, for the conditions used, the reverse reaction went essentially to completion; therefore, $k_{obsd} = k_r$. A reciprocal plot of $1/k_r$ vs. $[py]/[P(OBu)_3]$ gave k_3/k_2 = 2.4 ± 0.5. These results, along with a direct measure of k_1 (forward reaction, $[P(OBu)_3] \approx 0$), allowed the equilibrium constant to be calculated as 0.048. This value is in excellent agreement with K calculated from static experiments (Table IV).

The reaction of $RuPc[P(OBu)_3]_2$ with PBu_3 proceeds in two steps with the second $P(OBu)_3$ replacement being slower than the first. The limiting rate constant (k_1) for the second step was estimated as 2.1 × 10^{-4} s^{-1} at 25 °C, which is more than 10 times slower than k_1 for the first substitution.

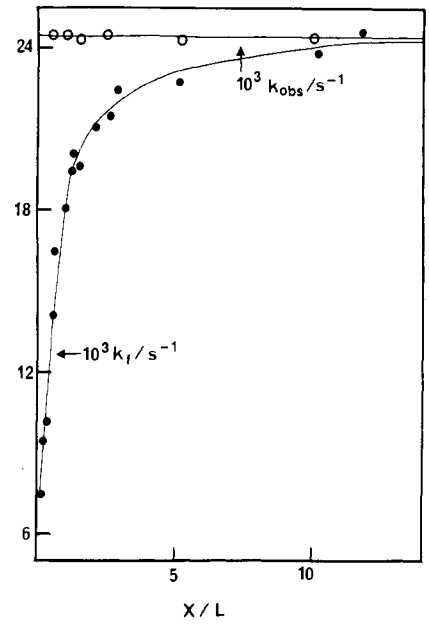

Figure 2. Plot of observed rate constants and calculated forward rate constants (eq 8) for the reaction $RuPc[P(OBu)_3]_2$ + MeIm ⇌ $RuPc[P(OBu)_3][MeIm]$ + $P(OBu)_3$.

Several reactions that were extremely slow were followed qualitatively by refluxing the reaction mixture in toluene. Reactions 9–11 occur in the presence of excess nucleophile but

$$RuPc(py)_2 + 2P(OBu)_3 \rightarrow RuPc[P(OBu)_3]_2 + 2py \quad (9)$$

$$RuPc(py)_2 + 2MeIm \rightarrow RuPc(MeIm)_2 + 2py \quad (10)$$

$$RuPc(MeIm)_2 + 2P(OBu)_3 \rightarrow RuP_2[P(OBu)_3]_2 + 2MeIm \quad (11)$$

are at least several orders of magnitude slower than those listed in Table IV.

The activation parameters for reaction 5, the invariance of k_1 for the reaction of $RuPc[P(OBu)_3]_2$ with different nucleophiles, and the data treatment discussed above show conclusively that axial ligand substitution in $RuPcL_2$ occurs by a simple dissociative (D) mechanism. The same mechanism holds for the iron phthalocyanines.[4] As with analogous $FePcL_2$ complexes, the ability of the five-coordinate intermediate to discriminate between nucleophiles is very low. The discrimination ratios k_3/k_2 for the $FePcL_2$ reactions are all close to unity, and Table IV shows that k_3/k_2 for the $RuPcL_2$ reactions, though somewhat greater, are not very far from unity. This suggests that RuPcL is unstable and very reactive, in sharp contrast to five-coordinate iron(II) porphyrin complexes. As discussed previously[4] this is likely due to the higher ligand field in phthalocyanine complexes so that, as for the porphyrins, a high-spin state is energetically inaccessible.

Table V shows that $FePcL_2$ complexes are much more labile than $RuPcL_2$ analogues. The ratio $k_1(Fe)/k_1(Ru)$ is much larger when the π-acceptor ligand $P(OBu)_3$ is the leaving group

Table V. Comparison of Axial Ligand Labilities of Iron[a] and Ruthenium Phthalocyanine Adducts[b]

trans group	leaving group	k_1(Fe)/k_1(Ru)
$P(OBu)_3$	$P(OBu)_3$	20 000
$P(OBu)_3$	MeIm	890
$P(OBu)_3$	py	260
PBu_3	$P(OBu)_3$	100 000

[a] Data for iron complexes from ref 4. [b] k_1(Fe) at 21 °C in acetone; k_1(Ru) at 25 °C in toluene.

than when the leaving group is MeIm or py. This probably is due to the well-known[13] superior π-back-bonding ability of Ru(II), leading to increased Ru–$P(OBu)_3$ bond strength. This π-back-bonding ability of Ru(II) probably also accounts for the following leaving-group effect differences with $P(OBu)_3$ as the trans group. Fe: py > MeIm < $P(OBu)_3$ (14:1:11). Ru: py > MeIm > $P(OBu)_3$ (50:1:0.5).

The trans effect for both $FePcL_2$ and $RuPcL_2$ follows the order $P(OBu)_3$ > PBu_3 > py, MeIm. This ability of MeIm to inactivate trans ligands is probably also present in iron porphyrin systems[14] and obviously plays an important biological role. Interestingly, in other iron macrocyclic complexes MeIm seems to be a trans activator.[15] Unfortunately the present results with $RuPcL_2$ complexes cannot be compared with those of analogous ruthenium(II) porphyrin complexes except to state that the latter also seem[16] to substitute axial ligands via a dissociative mechanism. We are currently investigating the dynamics of some ruthenium porphyrin complexes.

In summary, the phthalocyanine complexes of iron and ruthenium differ greatly in axial lability and the importance of M→L π bonding but possess the same reaction mechanism, reaction-intermediate discrimination ratios, and trans-effect series. Although the dynamics of axial ligand substitution in phthalocyanine complexes differ from that found with metalloporphyrins in very fundamental ways, it is just such differences that can illuminate the mechanistic details of metalloporphyrin chemistry.

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Registry No. $RuPc[P(OBu)_3]_2$, 76986-82-8; $RuPc(PBu_3)_2$, 76986-81-7; $RuPc(Cl)(py)_2$, 76986-80-6; $RuPc(Cl)(MeIm)_2$, 76986-79-3; $RuPc(Cl)[P(OBu)_3]_2$, 76986-78-2; $RuPc(Cl)(PBu_3)_2$, 76986-77-1; $FePc[P(OBu)_3]_2$, 61005-31-0; $FePc(PBu_3)_2$, 61005-30-9; $RuPc[P(OBu)_3](MeIm)$, 76986-76-0; $RuPc[P(OBu)_3](py)$, 76986-75-9; $RuPc(PBu_3)[P(OBu)_3]$, 76986-74-8; MeIm, 616-47-7; py, 110-86-1; PBu_3, 998-40-3; $P(OBu)_3$, 102-85-2; $Ru_3(CO)_{12}$, 15243-33-1; RuPc, 27636-56-2.

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Transition-Metal Tetrahydroborate Complexes as Catalysts. 1. Nonempirical Determination of Static, Dynamic, and Chemical Properties of the Model Compounds $NaBH_4$ and AlH_2BH_4

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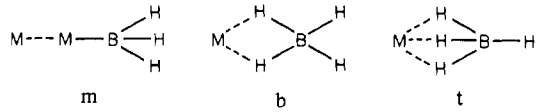
Ab initio computations have been performed on the compounds $NaBH_4$ and AlH_2BH_4 in order to achieve a better understanding of the peculiar characteristics of the M–BH_4 bond. Our results suggest a tridentate coordination for the sodium ion and a bidentate coordination for the aluminum compound. The dynamics of the hydrogen-interchange process has also been analyzed, and a Berry pseudorotation step has been excluded because of its high activation energy. Since BH_4^- is isoelectronic with CH_4, the present results can also give better insight into the structure of intermediate complexes in the saturated hydrocarbon activation process.

Introduction

The tetrahydroborate ion, BH_4^-, is one of the most useful and extensively used reagents, both in organic synthesis[2] and in inorganic or organometallic chemistry.

Among its chemical properties, the BH_4^- ion shows the tendency to reduce metal carbonyls to clusters with bridging hydride ligands[3] and, more generally, to form unusual covalent complexes with several transition metals.[4] The coordination always occurs through bridging hydrogen atoms, as exemplified by[4] the following (m = monodentate, b = bidentate, t = tridentate):



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