

(Scheme III) involves attack of protic electrophiles at the Re center, generating a square-pyramidal hydride intermediate that undergoes rapid reductive elimination of methane to produce a 16e intermediate which reacts stereospecifically with  $X^-$ . These authors have argued that the lifetime of the hydride intermediate is short, i.e. reductive elimination is fast, so that no racemization by pseudorotation (or an equivalent process) occurs and retention of configuration prevails.

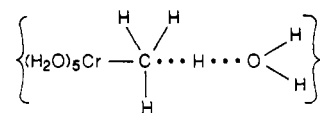
Contrary to the statement made in ref 17, a rate law as in eq 13 is in accord with this mechanism provided that (i) the reductive elimination is the rate-determining step a, which is plausible since this step involves the cleavage of covalent bonds whereas step b involves only rapid addition of  $X^-$  to a cationic 16e fragment, and (ii) steady-state conditions apply for intermediate II.<sup>18</sup>

$(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_3)$  reacts in acids with relatively nonnucleophilic counterions such as  $\text{CF}_3\text{SO}_3^-$  with production of  $\text{CH}_4$ ,<sup>18</sup> whereas **1** does not react at all in 1 M  $\text{HClO}_4$  or  $\text{H}_2\text{SO}_4$ . Therefore, we feel that the chemistry of **1** with protic electrophiles  $\text{HX}$  does not support a mechanism where reductive elimination of  $\text{CH}_4$  is the rate-determining step.

An alternative mechanism involves the protonation of **1** at a secondary amine nitrogen after one  $\text{Re-N}_{\text{amine}}$  bond has been cleaved (Scheme III). The 16e intermediate IV may then react with addition of the nucleophile  $X^-$  with concomitant release of  $\text{CH}_3^-$ , which is rapidly protonated, and rapid re-formation of the  $\text{Re-N}_{\text{amine}}$  bond. The  $\text{Re-N}_{\text{amine}}$  bond trans to the CO ligand in **1** is the weakest; it is the bond *cis* to the  $\text{Re-CH}_3$  group. The incoming  $\text{Cl}^-$  may exert a *cis*-labeling effect on the methyl group, which is then a good leaving group, and the rearrangement of the chloro ligand in addition to the formation of the third  $\text{Re-N}_{\text{amine}}$  bond yields a formal substitution reaction with retention of configuration at the Re center and retention of the chelate ring conformations. In this context it is interesting to note that chromium(III)-alkyl complexes, e.g.  $[(\text{H}_2\text{O})_5\text{Cr}(\text{CH}_3)]^{2+}$ , are hydrolyzed in acidic solutions affording  $\text{Cr}(\text{OH})_6^{3+}$  and methane.<sup>36</sup> The rate law is of the form

$$-d[\text{Cr}^{\text{III}}\text{-CH}_3]/dt = (k_{\text{H}_2\text{O}} + k_{\text{H}_3\text{O}^+}[\text{H}^+])[\text{Cr}^{\text{III}}\text{-CH}_3] \quad (17)$$

which differs from the rate law in eq 13. A mechanism involving the transition state



has been proposed for the  $k_{\text{H}_3\text{O}^+}$  pathways. In this instance electrophilic attack at the coordinated methyl group occurs. This mechanism cannot be operative in the reaction of **1** with  $\text{HX}$  in aqueous solution since it does not show a first-order dependence on [nucleophile] as in eq 13.

An interesting difference in reactivity between  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CH}_3)(\text{PPh}_3)$  and **1** is manifested by the observation that the former reacts with  $\text{I}_2$  affording  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)\text{I}$  and probably  $\text{CH}_3\text{I}$ , whereas the latter forms **7** and  $\text{HI}$ . For the formation of the former, electrophilic attack of halogens at the Re center with a square pyramidal intermediate,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})(\text{CH}_3)\text{X}]$ , and reductive elimination of  $\text{CH}_3\text{X}$  has been proposed.<sup>18</sup> It is suggestive that in **1** the Re center is again not available for this kind of electrophilic attack and alternative reaction paths prevail. The origin of this reactivity difference may be steric hindrance (seven-coordinate intermediates are more crowded than "five"-coordinate  $\eta^5\text{-C}_5\text{H}_5\text{ReABCD}$  species), but we feel that complexes of the type  $[\text{LRe}(\text{NO})(\text{CO})(\text{CH}_3)]^+$  are electron poorer than their organometallic counterparts. Thus this study nicely demonstrates how the reactivity of rhenium-carbon bonds are varied by the nature of the coligands.

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## Ligand Substitution Studies of Aquo(phosphine)ruthenium(II) Complexes

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Ligand substitutions for a series of complexes of the form  $\text{cis-}[\text{Ru}^{\text{II}}(\text{OH}_2)(\text{bpy})_2(\text{PR}_3)]^{2+}$  (where  $\text{bpy} = 2,2'$ -bipyridine and  $\text{PR}_3 =$  tertiary phosphine ligand) have been examined in nonaqueous solution. The second-order rate constants for the substitution of the water ligand by acetonitrile, 4-acetylpyridine, and chloride depend on the steric and electronic nature of the coordinated phosphine ligand. By use of tris(para-substituted phenyl)phosphines, the electronic effect of the coordinated ligand on the rate constant for substitution is investigated while a constant steric environment is maintained. The natural logarithms of the second-order rate constants for the substitution of water by acetonitrile decrease as a linear function of the Hammett parameters of the para substituents in the following order:  $\text{N}(\text{CH}_3)_2 > \text{OCH}_3 > \text{CH}_3 > \text{H} > \text{F} > \text{CF}_3$ . Similarly, by use of various trialkylphosphines, the steric effect of the ligand can be examined while the  $E_{1/2}$  values of the  $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$  couples remain constant. In this case, increases in the ligand cone angles result in a linear increase in the natural logarithms of the second-order rate constants for the substitution of water by acetonitrile.

### Introduction

Recently, we investigated high-valent oxometal complexes as stoichiometric oxidants, where we reported the isolation of stable oxoruthenium(IV) complexes that utilize a tertiary phosphine ligand in a position *cis* to the oxo ligand.<sup>1-3</sup> These complexes

are active stoichiometric oxidants, where the coordinated phosphine ligand affects both the rate of oxidation of substrates and the resulting product distributions.<sup>4-6</sup> In addition, we also reported the aerobic oxidation of cyclohexene catalyzed by an aquo(phosphine)ruthenium(II) complex.<sup>7</sup> The first step in the catalytic

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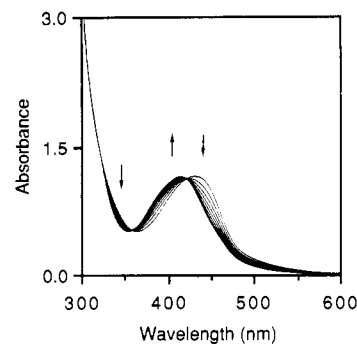
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cycle may be the generation of a five-coordinate ruthenium(II) complex from the loss of a water ligand, in a noncoordinating solvent. In order to further investigate this mechanism, we report here the effects of the ligand coordination environment on the rate of substitution of the aquo ligand in aquo(phosphine)ruthenium(II) complexes.

Ligand substitution on ruthenium complexes has been the subject of a number of investigations, where the majority of these studies were conducted in aqueous solutions.<sup>8-48</sup> However, due



**Figure 1.** Spectral changes observed in the reaction of acetonitrile (0.2 M) with  $[\text{Ru}^{\text{II}}(\text{OH}_2)(\text{bpy})_2(\text{P}(m\text{-C}_6\text{H}_4\text{CH}_3)_3)](\text{ClO}_4)_2$  ( $1.7 \times 10^{-4}$  M) in *o*-dichlorobenzene at 25 °C. Spectra were recorded at 2-min intervals.

to the presence of a tertiary phosphine ligand, aquo(phosphine)ruthenium(II) complexes are soluble in nonpolar, noncoordinating solvents such as *o*-dichlorobenzene. Thus, the rate of ligand exchange can be measured in a solvent that will not complicate the ligand-exchange kinetics by acting as a ligand. In addition, tertiary phosphine ligands have proved to be ideal for this study, due to the wide range of well-characterized steric<sup>49-69</sup>

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and electronic<sup>70-75</sup> properties associated with these ligands, which can be examined individually, with little ambiguity. For the systematic kinetic study of ligand substitution on aquo(phosphine)ruthenium(II) complexes in *o*-dichlorobenzene, a number of complexes with various tertiary phosphine ligands were synthesized, where the steric and electronic effects of the coordinated phosphine ligand were quantified by cone angles and  $E_{1/2}$  values of the ruthenium(III/II) redox couples, respectively.

### Experimental Section

**Materials.** All chemicals used in preparations were of reagent grade and were used without further purification, unless otherwise noted. Acetonitrile and 4-acetylpyridine (Aldrich) were fractionally distilled, and *o*-dichlorobenzene was vacuum-distilled over barium oxide prior to use. Tetrabutylammonium chloride was precipitated from acetone with ether and recrystallized from toluene in an inert-atmosphere glovebox. Elemental analyses were performed by Atlantic Micro Labs, Norcross, GA.

**Caution!** While we have used perchlorate as a counterion with a number of ruthenium(II) complexes without incident, perchlorate salts of metal complexes with organic ligands are potentially explosive. Care should be exercised in using a spatula or stirring rod to mechanically agitate any solid perchlorate. These complexes, as well as any other perchlorate salt, should only be handled in small quantities.<sup>76,77</sup>

The complexes  $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{Cl})(\text{PR}_3)](\text{ClO}_4)$  were prepared by modifications of published procedures.<sup>2,78</sup> The complexes  $[\text{Ru}^{\text{II}}(\text{OH}_2)(\text{bpy})_2(\text{PR}_3)](\text{ClO}_4)_2$  (where  $\text{PR}_3 = \text{PEt}_3$ ,  $\text{P}(i\text{-Pr})_3$ ,  $\text{P}(n\text{-Bu})_3$ ,  $\text{PCy}_3$ ,  $\text{PBz}_3$ ,  $\text{PPh}_3$ ,  $\text{P}(p\text{-C}_6\text{H}_4\text{CF}_3)_3$ )<sup>79</sup> have been reported earlier.<sup>2</sup>

$[\text{Ru}^{\text{II}}(\text{OH}_2)(\text{bpy})_2(\text{P}(p\text{-C}_6\text{H}_4\text{CH}_3)_3)](\text{ClO}_4)_2$ . A 100-mg sample of  $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{Cl})(\text{P}(p\text{-C}_6\text{H}_4\text{CH}_3)_3)](\text{ClO}_4)$  was reacted with 1.2 equiv of  $\text{AgClO}_4$  in 250 mL of distilled water. The solution was purged with nitrogen and then heated at reflux for 1 h. After the solution was cooled to room temperature,  $\text{AgCl}$  was filtered off, and the filtrate was chilled

**Table I.** Second-Order Rate Constants for the Exchange of Water Ligands with Incoming Ligands (Y), for the Complexes  $[\text{Ru}^{\text{II}}(\text{OH}_2)(\text{bpy})_2(\text{L})]^{2+}$ , at 25 °C: Electronic Effects of Phosphine Ligands on the Rate Constants for Ligand Substitution in *o*-Dichlorobenzene Solution<sup>a</sup>

L <sup>b</sup>	Y	$E_{1/2}$ , <sup>c</sup> V	$10^3 k_2$ , M <sup>-1</sup> s <sup>-1</sup>
$\text{P}(p\text{-C}_6\text{H}_4\text{CF}_3)_3$	$\text{CH}_3\text{CN}$	1.45	0.50
$\text{P}(p\text{-C}_6\text{H}_4\text{F})_3$	$\text{CH}_3\text{CN}$	1.38	2.1
$\text{PPh}_3$	$\text{CH}_3\text{CN}$	1.32	6.0
$\text{P}(p\text{-C}_6\text{H}_4\text{CH}_3)_3$	$\text{CH}_3\text{CN}$	1.30	10
$\text{P}(m\text{-C}_6\text{H}_4\text{CH}_3)_3$	$\text{CH}_3\text{CN}$	1.30	11
$\text{P}(p\text{-C}_6\text{H}_4\text{OCH}_3)_3$	$\text{CH}_3\text{CN}$	1.29	11
$\text{P}(p\text{-C}_6\text{H}_4\text{N}(\text{CH}_3)_2)_3$	$\text{CH}_3\text{CN}$	1.03	110
$\text{PPh}_3$	4-Ac <sup>d</sup>	1.32	1.8
$\text{P}(p\text{-C}_6\text{H}_4\text{CH}_3)_3$	4-Ac <sup>d</sup>	1.30	3.0
$\text{P}(m\text{-C}_6\text{H}_4\text{CH}_3)_3$	4-Ac <sup>d</sup>	1.30	2.9
$\text{P}(p\text{-C}_6\text{H}_4\text{N}(\text{CH}_3)_2)_3$	4-Ac <sup>d</sup>	1.03	33
$\text{P}(p\text{-C}_6\text{H}_4\text{CF}_3)_3$	$\text{Cl}^-$	1.45	0.86
$\text{PPh}_3$	$\text{Cl}^-$	1.32	7.1
$\text{P}(p\text{-C}_6\text{H}_4\text{N}(\text{CH}_3)_2)_3$	$\text{Cl}^-$	1.03	100

<sup>a</sup>The cone angles of the coordinated phosphine ligands are all 141°. <sup>b</sup>See ref 79 for an explanation of phosphine ligand abbreviations. <sup>c</sup> $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$ , measured in  $\text{CH}_2\text{Cl}_2$ , vs SSCE reference electrode. <sup>d</sup>4-Ac<sup>d</sup> = 4-acetylpyridine.

to precipitate any unreacted starting material, which was then removed by gravity filtration. The product was precipitated by the addition of excess sodium perchlorate and the solid collected by vacuum filtration, washed with cold water, and air-dried; yield 82 mg (75%). Anal. Calcd for  $\text{RuC}_{41}\text{H}_{39}\text{Cl}_2\text{N}_4\text{O}_9\text{P}\cdot 1.5\text{H}_2\text{O}$ : C, 51.20; H, 4.40. Found: C, 51.12; H, 4.32.

$[\text{Ru}^{\text{II}}(\text{OH}_2)(\text{bpy})_2(\text{P}(m\text{-C}_6\text{H}_4\text{CH}_3)_3)](\text{ClO}_4)_2$ . This complex was synthesized from the analogous chloro(phosphine)ruthenium(II) complex by the method described above, resulting in a 67% yield. Anal. Calcd for  $\text{RuC}_{41}\text{H}_{39}\text{Cl}_2\text{N}_4\text{O}_9\text{P}\cdot \text{H}_2\text{O}$ : C, 51.69; H, 4.34. Found: C, 51.60; H, 4.38.

$[\text{Ru}^{\text{II}}(\text{OH}_2)(\text{bpy})_2(\text{P}(p\text{-C}_6\text{H}_4\text{OCH}_3)_3)](\text{ClO}_4)_2$ . This complex was prepared by the same method as described above, resulting in a 65% yield. Anal. Calcd for  $\text{RuC}_{41}\text{H}_{39}\text{Cl}_2\text{N}_4\text{O}_{12}\text{P}\cdot \text{H}_2\text{O}$ : C, 49.21; H, 4.13. Found: C, 49.03; H, 4.33.

$[\text{Ru}^{\text{II}}(\text{OH}_2)(\text{bpy})_2(\text{P}(p\text{-C}_6\text{H}_4\text{F})_3)](\text{ClO}_4)_2$ . This complex was prepared by the same method as described above, resulting in a 59% yield. Anal. Calcd for  $\text{RuC}_{38}\text{H}_{30}\text{Cl}_2\text{F}_3\text{N}_4\text{O}_9\text{P}\cdot \text{H}_2\text{O}$ : C, 47.32; H, 3.34. Found: C, 47.32; H, 3.31.

$[\text{Ru}^{\text{II}}(\text{OH}_2)(\text{bpy})_2(\text{P}(p\text{-C}_6\text{H}_4\text{N}(\text{CH}_3)_2)_3)](\text{ClO}_4)_2$ . This complex was prepared by the same method as described above, resulting in a 71% yield. Anal. Calcd for  $\text{RuC}_{44}\text{H}_{48}\text{Cl}_2\text{N}_7\text{O}_9\text{P}\cdot \text{H}_2\text{O}$ : C, 49.96; H, 4.95. Found: C, 49.87; H, 4.84.

$[\text{Ru}^{\text{II}}(\text{OH}_2)(\text{bpy})_2(\text{PPh}_2(o\text{-C}_6\text{H}_4\text{CH}_3))](\text{ClO}_4)_2$ . This complex was prepared by the same method as described above, resulting in a 48% yield. Anal. Calcd for  $\text{RuC}_{39}\text{H}_{35}\text{Cl}_2\text{N}_4\text{O}_9\text{P}\cdot \text{H}_2\text{O}$ : C, 50.66; H, 4.03. Found: C, 50.41; H, 3.83.

$[\text{Ru}^{\text{II}}(\text{OH}_2)(\text{bpy})_2(\text{P}(i\text{-Bu})_3)](\text{ClO}_4)_2$ . This complex was prepared by the same method as described above, resulting in a 32% yield. Anal. Calcd for  $\text{RuC}_{32}\text{H}_{45}\text{Cl}_2\text{N}_4\text{O}_9\text{P}\cdot \text{H}_2\text{O}$ : C, 45.18; H, 5.57. Found: C, 45.21; H, 5.50.

**Measurements.** UV-visible spectra were recorded by using a Bausch and Lomb Spectronic 2000 spectrophotometer. Electrochemical measurements were made versus a saturated sodium chloride calomel reference electrode (SSCE) using an IBM EC/225 voltammetric analyzer. A platinum disk working electrode was used along with a platinum wire common electrode. Measurements in acetonitrile solution were made with 0.1 M tetraethylammonium perchlorate (TEAP) as the supporting electrolyte. In methylene chloride, measurements were made with 0.1 M tetrabutylammonium tetrafluoroborate as the supporting electrolyte. Electrochemical experiments were conducted with ferrocene added as an internal standard.<sup>80</sup> Kinetic studies were determined spectrophotometrically using Beckman DU spectrophotometers that were retrofitted with Gilford accessories. The cell blocks in the spectrophotometers were maintained at constant temperature by the circulation of water from thermostated water baths.

**Kinetics Procedure.** The reaction kinetics for acetonitrile or chloride substitution were monitored spectrophotometrically at the wavelength maximum of the MLCT band of the initial aquo(phosphine)ruthenium(II) complex, while for 4-acetylpyridine as the entering group the growth

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- (79) Abbreviations used in the text for phosphine substituents: Et = ethyl, Pr = propyl, Bu = butyl, Cy = cyclohexyl, Bz = benzyl, Ph = phenyl,  $p\text{-C}_6\text{H}_4\text{CF}_3$  = *p*-(trifluoromethyl)phenyl,  $p\text{-C}_6\text{H}_4\text{CH}_3$  = *p*-tolyl,  $m\text{-C}_6\text{H}_4\text{CH}_3$  = *m*-tolyl,  $o\text{-C}_6\text{H}_4\text{CH}_3$  = *o*-tolyl,  $p\text{-C}_6\text{H}_4\text{OCH}_3$  = *p*-methoxyphenyl,  $p\text{-C}_6\text{H}_4\text{F}$  = *p*-fluorophenyl,  $p\text{-C}_6\text{H}_4\text{N}(\text{CH}_3)_2$  = *p*-(dimethylamino)phenyl.

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**Table II.** Second-Order Rate Constants for the Exchange of Water Ligands with Incoming Ligands (Y), for the Complexes  $[\text{Ru}^{\text{II}}(\text{OH}_2)(\text{bpy})_2(\text{L})]^{2+}$ , at 25 °C: Steric Effects of Phosphine Ligands on the Rate Constants for Ligand Substitution in *o*-Dichlorobenzene Solution

$\text{L}^a$	Y	$E_{1/2}^b$ , V	cone angle, <sup>c</sup> deg	$10^3 k_2$ , $\text{M}^{-1} \text{s}^{-1}$
PEt <sub>3</sub>	CH <sub>3</sub> CN	1.16	132	0.84
P( <i>n</i> -Pr) <sub>3</sub>	CH <sub>3</sub> CN	1.18	132	1.0
P( <i>n</i> -Bu) <sub>3</sub>	CH <sub>3</sub> CN	1.18	140 <sup>d</sup>	2.9
P( <i>i</i> -Pr) <sub>3</sub>	CH <sub>3</sub> CN	1.17	160	180
P( <i>i</i> -Bu) <sub>3</sub>	CH <sub>3</sub> CN	1.18	143	290
PCy <sub>3</sub>	CH <sub>3</sub> CN	1.22	170	620
PBz <sub>3</sub>	CH <sub>3</sub> CN	1.28	165	160
PPh <sub>3</sub>	CH <sub>3</sub> CN	1.32	141 <sup>e</sup>	6.0
PPh <sub>2</sub> ( <i>o</i> -C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> )	CH <sub>3</sub> CN	1.32	161	380
P( <i>n</i> -Bu) <sub>3</sub>	4-Acapy <sup>f</sup>	1.18	140	0.61
P( <i>i</i> -Pr) <sub>3</sub>	4-Acapy	1.17	160	26
P( <i>n</i> -Bu) <sub>3</sub>	Cl <sup>-</sup>	1.18	140	6.4
P( <i>i</i> -Pr) <sub>3</sub>	Cl <sup>-</sup>	1.17	160	260

<sup>a</sup>See ref 79 for an explanation of phosphine ligand abbreviations. <sup>b</sup> $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$ , measured in CH<sub>2</sub>Cl<sub>2</sub>, vs SSCE reference electrode. <sup>c</sup>See ref 49. <sup>d</sup>See ref 63c. <sup>e</sup>See ref 67. <sup>f</sup>4-Acapy = 4-acetylpyridine.

**Table III.** Activation Parameters for the Reactions of  $[\text{Ru}^{\text{II}}(\text{OH}_2)(\text{bpy})_2(\text{L})]^{2+}$  with Acetonitrile in *o*-Dichlorobenzene

$\text{L}^a$	$\Delta H^\ddagger$ , kcal/mol	$\Delta S^\ddagger$ , eu
PEt <sub>3</sub>	14.7 ± 1.2	-23.4 ± 3.7
P( <i>i</i> -Pr) <sub>3</sub>	11.1 ± 1.1	-24.6 ± 3.7
PPh <sub>3</sub>	14.8 ± 1.0	-19.1 ± 3.3
P( <i>p</i> -C <sub>6</sub> H <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub> ) <sub>3</sub>	14.3 ± 0.9	-15.2 ± 3.1
P( <i>p</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub> ) <sub>3</sub>	20.3 ± 1.2	-6.0 ± 4.2

<sup>a</sup>See ref 79 for an explanation of phosphine ligand abbreviations.

of the product was monitored at the wavelength maximum for these complexes. Rate measurements were made under pseudo-first-order conditions, where the incoming ligand was in excess. In a typical kinetics experiment, the reaction was initiated by adding 2 mL of the solution containing the metal complex to 1 mL of one of six solutions of varying concentrations of incoming ligand (typically 0.2–2.0 M). Both solutions were thermally equilibrated and then mixed quickly in the cell with a disposable pipet, and the absorbance versus time curve was then recorded with use of the chart drive as a time base. The spectra corresponding to the substitution reactions were found to proceed isobestically in each case. The beginning and final spectra matched those of the reactant and product, respectively.

For substitution of water by acetonitrile or 4-acetylpyridine plots of  $\ln [(A_0 - A_{\text{eq}})/(A_t - A_{\text{eq}})]$  versus time were linear and the pseudo-first-order rate constants were calculated by using a least-squares treatment of the rate data according to eq 1, where  $A_{\text{eq}}$  is the final absorbance at the completion of the substitution,  $A_0$  is the initial absorbance,  $A_t$  is the absorbance measured at time  $t$ , and  $k_{\text{obs}}$  is the pseudo-first-order rate constant. These observed rate constants were then plotted versus sub-

$$-\ln [A_t - A_{\text{eq}}] = k_{\text{obs}} t - \ln [A_0 - A_{\text{eq}}] \quad (1)$$

strate concentration to obtain the second-order rate constants. For the substitution of water by chloride, it was necessary to plot  $1/[k_{\text{obs}}]$  vs  $1/[\text{Cl}^-]$  to give  $k$ , the first-order rate constant for ligand substitution, as the reciprocal of the  $y$  intercept due to the large association constant,  $K_a$ , for this reaction. The precision of the measurements for all rate constants was within 10% at a 95% confidence limit.

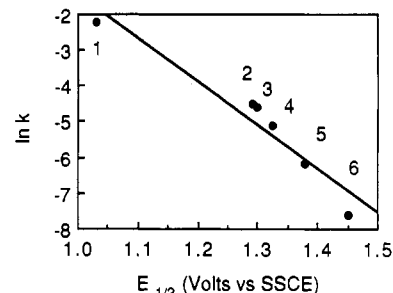
## Results

**Kinetic Studies.** The substitution of the aquo ligand by acetonitrile for  $[\text{Ru}^{\text{II}}(\text{OH}_2)(\text{bpy})_2(\text{PR}_3)]^{2+}$  complexes in methylene chloride, water, and *o*-dichlorobenzene displayed well-behaved second-order kinetics. A typical UV-visible spectrum for the reaction of an aquo(phosphine)ruthenium(II) complex with acetonitrile is illustrated in Figure 1. The results of the kinetic studies for the substitution of the aquo ligand by acetonitrile, 4-acetylpyridine, and chloride are listed in Tables I and II. The effects of solvent on the rate constants for ligand substitution are listed in Table IV. By use of a variety of phosphine ligands in these complexes, certain trends are isolated in the substitution

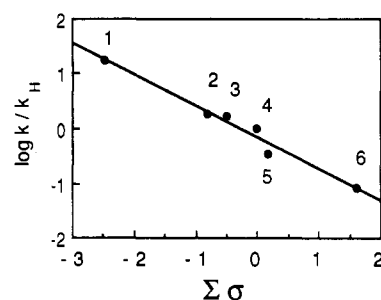
**Table IV.** Second-Order Rate Constants for the Exchange of Water Ligands with Incoming Ligands (Y), for the Complexes  $[\text{Ru}^{\text{II}}(\text{OH}_2)(\text{bpy})_2(\text{L})]^{2+}$ , at 25 °C: Effects of Solvent on the Rate Constants for Ligand Substitution

$\text{L}^a$	Y	solvent	cone angle, deg	$E_{1/2}^b$ , V	$10^3 k_2$ , $\text{M}^{-1} \text{s}^{-1}$
PPh <sub>3</sub>	CH <sub>3</sub> CN	<i>o</i> -DCB <sup>c</sup>	141 <sup>d</sup>	1.32	6.0
PPh <sub>3</sub>	CH <sub>3</sub> CN	CH <sub>2</sub> Cl <sub>2</sub>	141	1.32	15
PPh <sub>3</sub>	CH <sub>3</sub> CN	H <sub>2</sub> O	141	1.32	1.1
PEt <sub>3</sub>	CH <sub>3</sub> CN	<i>o</i> -DCB	132 <sup>e</sup>	1.16	0.84
PEt <sub>3</sub>	CH <sub>3</sub> CN	CH <sub>2</sub> Cl <sub>2</sub>	132	1.16	1.3
PEt <sub>3</sub>	CH <sub>3</sub> CN	H <sub>2</sub> O	132	1.16	0.20

<sup>a</sup>See ref 79 for an explanation of phosphine ligand abbreviations. <sup>b</sup> $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$ , measured in CH<sub>2</sub>Cl<sub>2</sub>, vs SSCE reference electrode. <sup>c</sup>*o*-DCB = *o*-dichlorobenzene. <sup>d</sup>See ref 67. <sup>e</sup>See ref 49.



**Figure 2.** Plot of the natural logarithm of the rate constant for the substitution of the aquo ligand by acetonitrile on  $[\text{Ru}^{\text{II}}(\text{OH}_2)(\text{bpy})_2(\text{PR}_3)]^{2+}$  complexes as a function of the observed  $E_{1/2}$  values for the ruthenium(III/II) redox couple for these complexes. The phosphine ligands used in these complexes were (1) P(*p*-C<sub>6</sub>H<sub>4</sub>N(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>, (2) P(*p*-C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>)<sub>3</sub>, (3) P(*p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)<sub>3</sub>, (4) PPh<sub>3</sub>, (5) P(*p*-C<sub>6</sub>H<sub>4</sub>F)<sub>3</sub>, and (6) P(*p*-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>)<sub>3</sub>. The  $E_{1/2}$  values were measured by cyclic voltammetry of the respective complexes in methylene chloride (vs SSCE) with 0.1 M tetrabutylammonium tetrafluoroborate as the supporting electrolyte. The ligand substitution reactions were carried out in *o*-dichlorobenzene at 25 °C.



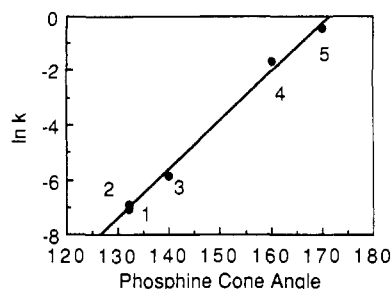
**Figure 3.** Plot of  $\log(k/k_{\text{H}})$  as a function of the Hammett substituent constants for the substitution of the aquo ligand by acetonitrile on  $[\text{Ru}^{\text{II}}(\text{OH}_2)(\text{bpy})_2(\text{P}(\text{p}-\text{C}_6\text{H}_4\text{X})_3)]^{2+}$  complexes in *o*-dichlorobenzene at 25 °C. The data is plotted by X substituents as (1) N(CH<sub>3</sub>)<sub>2</sub>, (2) OCH<sub>3</sub>, (3) CH<sub>3</sub>, (4) H, (5) F, and (6) CF<sub>3</sub>.  $\Sigma\sigma = 3\sigma$ , where the values for  $\sigma$  taken from ref 83 ( $\sigma$  parameters: -N(CH<sub>3</sub>)<sub>2</sub>, -0.830; -OCH<sub>3</sub>, -0.268; -CH<sub>3</sub>, -0.170; -H, 0; -F, 0.062; -CF<sub>3</sub>, 0.540).

kinetics. Tris(*para*-substituted phenyl)phosphines, P(C<sub>6</sub>H<sub>4</sub>X)<sub>3</sub>, were employed to study the electron-donating–electron-withdrawing properties of the coordinated ligands on the rate of substitution, while a constant cone angle was maintained. The  $E_{1/2}$  values of the ruthenium(III/II) couples, as measured by cyclic voltammetry, decreased by 400 mV for X = CF<sub>3</sub> ( $E_{1/2} = 1.45$  V) to X = N(CH<sub>3</sub>)<sub>2</sub> ( $E_{1/2} = 1.03$  V), accompanied by a corresponding increase of 220 in rate constants (Table I). Also, a plot of  $\ln k$  vs  $E_{1/2}$  values for the ruthenium(II) complexes displayed a linear relationship ( $r^2 = 0.93$ ), with a slope of -12, and is shown in Figure 2. A plot of  $\log(k_{\text{X}}/k_{\text{H}})$  vs  $\Sigma\sigma$  ( $\sigma$  = Hammett substituent constant)<sup>81–84</sup> for the phosphine ligands also yielded a linear fit

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**Figure 4.** Plot of the natural logarithm of the rate constant for ligand substitution as a function of steric bulk of the phosphine ligand, described by cone angles, for the substitution of the aquo ligand by acetonitrile on  $[\text{Ru}^{\text{II}}(\text{OH}_2)(\text{bpy})_2(\text{PR}_3)_2]^{2+}$  complexes in *o*-dichlorobenzene at 25 °C. The phosphine ligands utilized for this plot were (1)  $\text{PEt}_3$ , (2)  $\text{P}(n\text{-Pr})_3$ , (3)  $\text{P}(n\text{-Bu})_3$ , (4)  $\text{P}(i\text{-Pr})_3$ , and (5)  $\text{P}(\text{Cy})_3$ . The cone angle values for points 1, 2, 4, and 5 were taken from ref 49c, and the value for point 3 was taken from ref 63c.

( $r^2 = 0.98$ ), with a slope of  $-0.57$  (Figure 3).

Trialkylphosphine ligands were used to study the effect of steric bulk on the rate of ligand substitution in this system. For those complexes with the same ruthenium(III/II) potential, Tolman cone angles<sup>49</sup> were used to quantify the relative steric influence of the phosphine ligands. Ruthenium(II) complexes utilizing the series of ligands  $\text{PEt}_3$ ,  $\text{P}(n\text{-Pr})_3$ ,  $\text{P}(i\text{-Pr})_3$ ,  $\text{P}(n\text{-Bu})_3$ , and  $\text{PCy}_3$  all displayed the same  $E_{1/2}$  values for the ruthenium(III/II) couple, as measured by cyclic voltammetry. A plot of  $\ln k$  vs cone angle of the coordinated phosphine ligand displays a positive linear relationship ( $r^2 = 0.99$ ), with a slope of 0.18 (Figure 4). Although Tolman lists the cone angle for  $\text{P}(n\text{-Bu})_3$  as 132° (which is the same value given for  $\text{PEt}_3$  and  $\text{P}(n\text{-Pr})_3$ ), a value of 140°, as suggested by Mosbo,<sup>63c</sup> provided a better correlation for these data. The cone angle listed for  $\text{P}(i\text{-Bu})_3$  (143°) also did not fit in this scheme, where the rate constant for ligand substitution on this complex was approximately 10 times larger than that predicted by this treatment, from Tolman's cone angle. From the experimental results, a cone angle of 164° for  $\text{P}(i\text{-Bu})_3$  would better fit the observed data. Also, rate enhancements based on the size of the phosphine ligand were not limited to trialkylphosphine complexes. The (ortho-substituted phenyl)phosphine ligand  $\text{PPh}_2(o\text{-C}_6\text{H}_4\text{CH}_3)$  has a cone angle 20° larger (161°) than the cone angle for  $\text{PPh}_3$  (141°),<sup>85</sup> while the aquo(phosphine)ruthenium(II) complex with this substituted ligand has a ruthenium(III/II) redox potential matching that observed for the triphenylphosphine complex. The second-order rate constant associated with the substitution of the aquo ligand for the  $\text{PPh}_2(o\text{-C}_6\text{H}_4\text{CH}_3)$  complex is over 60 times larger than the rate constant for the  $\text{PPh}_3$  complex, again demonstrating the steric effect of these ligands on the rate constants for substitution (Table II). The plot of  $\ln k$  versus the cone angle for these two complexes yields a slope of 0.20, closely matching the slope found for the plot by using the aquo(trialkylphosphine)ruthenium(II) complexes.

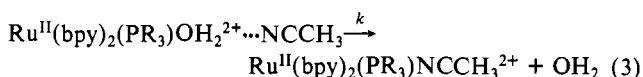
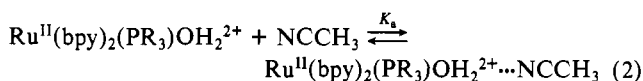
The incoming ligand was varied for the aquo substitution reactions in order to test the mechanism of substitution. The rate constants collected for 4-acetylpyridine as the entering group are given in Tables I and II, and these values are slightly smaller than the analogous rate constants observed with acetonitrile as the entering ligand. The rate constant data for the replacement of water by chloride were determined by using tetrabutylammonium chloride in *o*-dichlorobenzene, and the results are listed in Tables I and II. These rate constants are slightly larger than those observed for substitution using acetonitrile. In addition, the nonlinear relationship for  $k_{\text{obs}}$  versus  $[\text{Cl}^-]$  is consistent with a substantially large association between the ruthenium complex and  $\text{Cl}^-$  prior to ligand exchange. In a nonaqueous solvent such as *o*-dichlorobenzene ion-pairing is expected to be high, yielding large values for the association constants,  $K_a$ , resulting in rate

saturation at high  $[\text{Cl}^-]$  values.

**Activation Parameters.** Activation parameters<sup>86</sup> were determined from the slopes and intercepts of plots of  $\ln(k/T)$  versus  $1/T$ , over the temperature range 15–50 °C, for a number of representative reactions. The results obtained are given in Table III.

### Discussion

The rate constant data collected for these reactions are indicative of a dissociative-interchange ( $I_d$ ) mechanism, which is the expected mechanism of ligand substitution on ruthenium(II).<sup>85</sup> In an  $I_d$  mechanism, the main contribution to the activation energy of the reaction is the energy required to break the bond to the leaving group. However, before the bond can be fully broken, the metal center begins to form a bond with a ligand from its outer coordination sphere. So, although the nature of an  $I_d$  reaction is dissociative, a dependence on the concentration of the incoming ligand is observed, making this type of reaction "accidentally bimolecular".<sup>87</sup> Equations 2 and 3 illustrate the  $I_d$  mechanism



for the reaction of an aquo(phosphine)ruthenium(II) complex with acetonitrile. The pseudo-first-order rate constant of the reaction,  $k_{\text{obs}}$ , is given by eq 4, where  $K_a$  is the association constant described

$$k_{\text{obs}} = kK_a[\text{Y}]/(1 + K_a[\text{Y}]) \quad (4)$$

in eq 2 and Y is the incoming ligand. The linear plots of the pseudo-first-order rate constants versus the incoming ligand concentration,  $[\text{NCCH}_3]$  or  $[4\text{-Acpy}]$ , suggest that the association constants,  $K_a$ , for these reactions are small ( $<10$ ). The lack of a strictly first-order dependence of the pseudo-first-order rate constants on the concentration of  $\text{Cl}^-$  in the substitution of water by chloride indicates that the  $K_a$  values for these reactions are large (300–4000). The relative insensitivity of the magnitude of the second-order rate constants,  $k$ , for the substitution reactions, to the nature of the entering ligands ( $\text{Y} = \text{NCCH}_3$ , 4-Acpy, and  $\text{Cl}^-$ ) is consistent with an  $I_d$  mechanism for ligand substitution.

The electronic influence of the phosphine ligand on the ruthenium center, as it affects the rate of ligand substitution, was studied by utilizing tris(para-substituted phenyl)phosphines in positions cis to the aquo ligand on the octahedral complexes. These ligands have the same cone angle of 141°, indicating similar steric properties, but transfer distinctly different electronic effects to the metal center, as measured electrochemically by the potential of the ruthenium(III/II) redox couple (Table I). The natural logarithm of the rate constant for ligand substitution varies as a negative linear function of the  $E_{1/2}$  values of the complexes as plotted in Figure 2. If these redox potentials are taken as a measure of the relative amount of electron density at the metal center, then as the amount of electron density at the metal center is increased, substitution of the aquo ligand is enhanced, consistent with a dissociative mechanism. In addition, a negative linear correlation between  $\log(k_X/k_H)$  and  $\sum\sigma$  for the corresponding phosphine ligand substituents was observed for these complexes. The Hammett equation is given as

$$\log(k/k_0) = \rho\sigma$$

where  $k_0$  is the rate constant when  $\text{X} = \text{H}$ ,  $k$  is the rate constant for the X group,  $\rho$  is a constant for a reaction under a given set of conditions, and  $\sigma$  (Hammett substituent constant) is a constant for the X group.<sup>81–84</sup> By use of the Hammett equation in this system, a  $\rho$  value of  $-0.57$  was calculated, for *o*-dichlorobenzene as the solvent, at 25 °C. The negative sign of  $\rho$  indicates the

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(85) A cone angle of 141° for  $\text{PPh}_3$  was determined through a variable-temperature NMR study of (phosphino)chromium complexes.<sup>67</sup>

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development of positive charge in the transition state for these ligand substitution reactions. The increasing positive charge at the metal center during the breaking of the ruthenium–oxygen bond is destabilized by electron-withdrawing substituents, which therefore inhibits the dissociation of the aquo ligand. Thus, if ligand dissociation is the rate-determining step of the reaction, a corresponding reduction in the rate constant for ligand substitution for these complexes should be observed.

A plot of the  $E_{1/2}$  values of the ruthenium(III/II) redox couples obtained for the aquo(phosphine)ruthenium(II) complexes in  $\text{CH}_2\text{Cl}_2$  vs  $\sum\sigma$  is also linear ( $r^2 = 0.93$ ) and gave a  $\rho$  value of +0.10. The positive sign of the  $\rho$  value is consistent with the expectation that electron-donating groups stabilize, and electron-withdrawing groups destabilize, ruthenium(III), relative to the analogous unsubstituted complexes. The magnitude of  $\rho$  for this correlation indicates that the substituents on the phosphine ligands have a moderate effect on the resulting  $E_{1/2}$  values, compared to other systems. Larger values of  $\rho$  have been obtained for the plot of  $E_{1/2}$  against  $\sum\sigma$  for III/II redox couples of ruthenium with acetylacetonate ( $\rho = 0.38$ – $0.50$ )<sup>88,89</sup> and nitrosoarene ( $\rho = 1.05$ )<sup>90</sup> ligands. The  $\rho$  values obtained from a Hammett correlation with  $E_{1/2}$  values for triazene 1-oxide complexes of ruthenium ( $\rho = 0.10$ – $0.18$ )<sup>91</sup> closely match those found in this study. Finally, our observed  $\rho$  values are larger than those found for metal-centered redox reactions of substituted tetraphenylporphyrin complexes ( $\rho = 0.02$ – $0.08$ )<sup>92</sup> where the ligand substituents are located further from the metal center and thus have a smaller effect on the  $E_{1/2}$  values of the metal complexes.

Trialkylphosphine ligands were utilized in this study in order to investigate the role of the steric influence of the phosphine ligand on the aquo substitution kinetics. A plot of  $\ln k$  vs ligand cone

angle is given in Figure 4 and illustrates the linear rate constant enhancement promoted by the increasing phosphine ligand size. An increase in cone angle from 132 to 170° for the change from  $\text{PEt}_3$  to  $\text{PCy}_3$  corresponds to an increase in rate constant for ligand substitution by a factor of 750. This change is 3 times as large as the maximum variation in rate constants found for the substituted triphenylphosphine ligands, which suggests that the steric bulk of the coordinated phosphines has a much greater overall effect on the rate constant for aquo substitution for these complexes than the electronic properties of the phosphine ligands. These results are consistent with a dissociative type of mechanism, where the bulky cis-coordinated phosphine sterically destabilizes the ruthenium–aquo bond. The rate-controlling dissociation of the aquo ligand relieves the steric crowding at the metal center caused by the larger phosphine ligands and results in a corresponding increase in the rate of ligand substitution.

The activation parameters were determined for representative reactions involving the substitution of the aquo ligand by acetonitrile (Table III). The enthalpies and entropies of activation vary only over a small range, and as expected, the increase in the lability of the aquo ligand is followed by the lowering of the  $\Delta H^\ddagger$  values for the corresponding reactions. The negative  $\Delta S^\ddagger$  values found for these reactions in *o*-dichlorobenzene are consistent with negative activation entropies reported in previous studies of dissociative ligand substitution on ruthenium in nonaqueous solvents.<sup>19</sup> The negative values obtained for  $\Delta S^\ddagger$  also suggest that the loss of the aquo ligand leads to a square-pyramidal type of five-coordinate intermediate in the transition state.<sup>93</sup> A positive value for  $\Delta S^\ddagger$  would indicate the formation of a trigonal-bipyramidal intermediate in ligand substitution by the  $I_d$  mechanism on octahedral metal species.<sup>93</sup>

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## Nickel(II) and Nickel(III) Bis(dipeptide) Complexes of $\alpha$ -Aminoisobutyric Acid

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Nickel(II) forms bis complexes with Aib<sub>2</sub> (the dipeptide of  $\alpha$ -aminoisobutyric acid) that change from a high-spin form,  $\text{Ni}^{\text{II}}(\text{H}_1\text{Aib}_2)(\text{Aib}_2)^-$ , to a low-spin form,  $\text{Ni}^{\text{II}}(\text{H}_1\text{Aib}_2)_2^{2-}$ , with loss of a proton ( $\text{p}K_a = 10.0$  at 25 °C) and the formation of a second N(peptide)–Ni(II) bond. Other dipeptides form tetragonally compressed six-coordinate bis complexes, but change of spin with pH is observed only when Aib is in the second residue. This is attributed to the electron-donating effect of the  $\alpha$ -carbon methyl groups on the ligand field strength. A low-spin six-coordinate Ni(II) complex is proposed. Oxidation of the orange low-spin Ni(II) complex gives a dark olive green tetragonally compressed  $\text{Ni}^{\text{III}}(\text{H}_1\text{Aib}_2)_2^-$  complex that is very stable in neutral and basic solutions. The standard reduction potential for the Ni(III,II) couple is only 0.34 V (vs NHE). A self-exchange rate constant of 48  $\text{M}^{-1} \text{s}^{-1}$  (25.0 °C,  $I = 0.1$ ) is determined for  $\text{Ni}^{\text{III,II}}(\text{H}_1\text{Aib}_2)_2^{2-}$ . This is 500 times larger than values found for outer-sphere electron-transfer reactions of Ni(III,II)–tripeptide complexes. Acid reacts with  $\text{Ni}^{\text{III}}(\text{H}_1\text{Aib}_2)_2^-$  in a three-step process to give two other Ni(III) complexes before decomposition to Ni(II) occurs. The last reaction ( $k_{\text{obsd}} = 0.002 \text{ s}^{-1}$ ) is independent of pH and is 100 times slower than the corresponding reaction of the bis(diglycinato)nickel(III) complex.

### Introduction

Nickel(II) forms pale blue high-spin complexes in the presence of excess glycylglycine (GG). Potentiometric titrations<sup>1,2</sup> show

that the predominant species at pH 11 is  $\text{Ni}^{\text{II}}(\text{H}_{-1}\text{G}_2)_2^{2-}$ , where  $\text{H}_{-1}$  refers to the number of deprotonated peptide nitrogens. This agrees with an X-ray crystal structure<sup>3</sup> for  $\text{Ni}^{\text{II}}(\text{H}_{-1}\text{G}_2)_2^{2-}$  where Ni(II) is surrounded by two mutually perpendicular glycylglycine

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