transfer products in relatively high yield. The bimolecular rate constant for quenching is essentially diffusion controlled, and the reaction parameters suggest that nuclear tunneling may be involved in the quenching reaction. The high yield of electron-transfer products observed on flash photolysis suggests that an excited state of the Co(II) complex which has a coordinated radical–anion is not a distinct intermediate in these quenching reactions.

The products of the quenching reaction, the Ru(III) and Co(II) complexes, rapidly revert to the initial reactants, the Ru(II) and Co(III) complexes. The rate constant for the back-reaction is approximately an order of magnitude smaller than the diffusion-corrected calculated rate constant, but within the expected agreement for a reaction between 2+ and 3+ reactants. The agreement suggests that the nonadiabaticities associated with spin multiplicities and mixed d–$\pi^*$ pathways have only a slight retarding effect on the rate of these redox reactions.

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**Registry No.** $Ru(bpy)_3^{2+}$, 15158-62-0; $Co(bpy)_3^{3+}$, 19052-39-2; $Co(phen)_3^{3+}$, 18581-79-8; $Ru(bpy)_3^{3+}$, 18955-01-6; $Co(bpy)_3^{2+}$, 15878-95-2; $Co(phen)_3^{2+}$, 16788-34-4.

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Contribution from the National Chemical Research Laboratory,
South African Council for Scientific and Industrial Research, Pretoria 0001, Republic of South Africa

# Kinetics and Mechanism of the Reactions of (1,5-Cyclooctadiene)chloro(picoline)iridium(I) with 2,2′-Bipyridyl and 1,10-Phenanthroline

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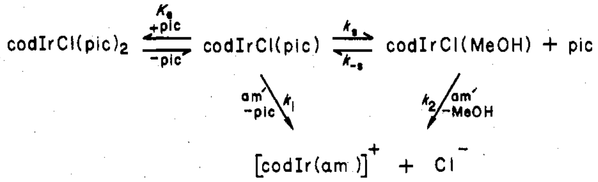
The reactions codIrClY + am′ → codIr(am′)$^+$ + Cl$^-$ + Y {where Y = 2-picoline (pic) or methanol and am′ = 2,2′-bipyridyl (bpy) or 1,10-phenanthroline (phen)} have been studied in methanol spectrophotometrically by a stopped-flow technique. On addition of pic to the reaction solution, it was found that the five-coordinate complex codIrCl(pic)$_2$ was generated. It was also found that the solvo species codIrCl(MeOH) was in a steady state during the reaction. All the data comply with the reaction scheme



from which the rate law

$$k_{obsd} = k_1[am']/(1 + K_e[pic]) + k_sk_2[am']/(k_{-s}[pic] + k_2[am'] + k_2K_e[am'][pic] + k_{-s}K_e[pic]^2)$$

could be derived. When am′ = phen, the contribution of the first term is negligible. Since codIrCl(MeOH) can be generated by dissolving the dimer [codIrCl]$_2$ in methanol, its reaction with am′ could also be studied and thus all the rate and equilibrium constants could be determined.

## Introduction

Square-planar substitution reactions of low-spin d$^8$ metal complexes of the form

$$ML_3X + Y \rightarrow ML_3Y + X \qquad (1)$$

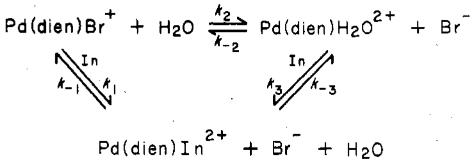
have generally been found[1] to conform to the classic two-term rate law

$$k_{obsd} = k_s + k_y[Y] \qquad (2)$$

where $k_s$ and $k_y$ represent the reactions via a solvent path and direct path, respectively, and [Y] represents the concentration of the incoming nucleophile.

A number of kinetic studies have since shown that the classic rate law 2 could simply be classed as a limiting case of a more general rate law.

The most general case was found for the reaction of Pd(dien)Br$^+$ with inosine[2] in aqueous solution (dien = diethylenetriamine). The proposed mechanism was



giving a rate law of the form

$$k_{obsd} = k_1[In] + k_{-1}[Br^-] + \frac{k_2k_3[In] + k_{-2}k_{-3}[Br^-]}{k_{-2}[Br^-] + k_3[In]} \qquad (3)$$

If the reactions to give the final products are irreversible, i.e., $k_{-1}$ and $k_{-3}$ are zero, and if $k_3[In] \gg k_{-2}[Br^-]$, rate law 3 simplifies to the classical two-term rate law. However, here $k_3[In] \approx k_{-2}[Br^-]$ and the Pd(dien)H$_2$O$^{2+}$ species is in a steady state.

Kennedy, Gosling, and Tobe[3] have recently studied the kinetics of the reaction of Pt(Me$_2$S)Cl$_3^-$ with a series of amines in methanol to yield Pt(Me$_2$S)(am)Cl$_2$ + Cl$^-$ and found that

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(1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed., Wiley, New York, 1967, Chapter 5.

(2) J. Y. Seguin and M. Zador, *Inorg. Chim. Acta*, **20**, 203 (1976).

(3) B. P. Kennedy, R. Gosling, and M. L. Tobe, *Inorg. Chem.*, **16**, 1745 (1977).

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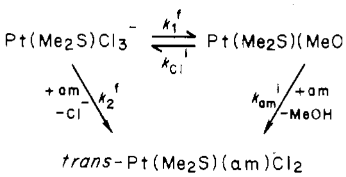
competition for the solvo complex $Pt(Me_2S)(MeOH)Cl_2$ exists between the outgoing and incoming ligands.



Consequently the more complete rate law

$$k_{\text{obsd}} = \frac{k_1{}^{\text{f}} k_{\text{am}}{}^{\text{i}}[\text{am}]}{k_{\text{Cl}}{}^{\text{i}}[\text{Cl}^-] + k_{\text{am}}{}^{\text{i}}[\text{am}]} + k_2{}^{\text{f}}[\text{am}] \qquad (4)$$

was observed.

Here we have a case where the substrates are not in equilibrium with the product but a steady state still exists so that if $k_{\text{Cl}}{}^{\text{i}}[\text{Cl}^-] \ll k_{\text{am}}{}^{\text{i}}[\text{am}]$, rate law 4 will simplify to the form of the classic two-term rate law.

A study of the kinetics of the reaction of (1,5-cyclooctadiene)(tricyclohexylphosphine)chlororhodium(I) with various nucleophiles by de Waal and Robb[4] gave a reaction scheme and rate law of the same form as eq 4.

This phenomenon was only observed for the above systems where plots of $k_{\text{obsd}}$ vs. incoming nucleophile concentration, [Y], were found to deviate from linearity, curving down to a zero intercept at low [Y]. This deviation was interpreted as being due to competition for the intermediate solvo species between the incoming nucleophile Y and the outgoing nucleophile X, at low [Y]. In traditional square-planar kinetics $k_{-\text{s}}[\text{X}] \ll k_{\text{y}}[\text{Y}]$ and therefore this phenomenon is not observed.

We have found a further example of this type of behavior in the reactions

$$\text{codIrClY} + \text{am}' \xrightarrow[\text{N}_2]{\text{methanol}} \text{codIr(am}')^+ + \text{Cl}^- + \text{Y} \qquad (5)$$

where cod = 1,5-cyclooctadiene, Y = 2-picoline (pic) or methanol, and am′ = 2,2′-bipyridyl (bpy) or 1,10-phenanthroline (phen).

Addition of pic to the reaction solution, in order to study the reaction quantitatively, further complicated the system. The data are reported here.

## Experimental Section

**Materials.** Analytical grade methanol (Merck) and dichloromethane (Merck) were used for the kinetic experiments.

2,2′-Bipyridyl, 1,10-phenanthroline, and 2-picoline were obtained from Merck and used without further purification. The dimer $[\text{codIrCl}]_2$[5a] was prepared by standard methods and recrystallized from dichloromethane–ethanol. The monomer codIrCl(pic)[5b] was prepared by following the method for the preparation of similar rhodium complexes and recrystallized from dichloromethane–methanol. Microanalysis Calcd for codIrCl(pic): C, 39.2; H, 4.5; N, 3.3; Cl, 8.3. Found: C, 38.8; H, 4.5; N, 3.4; Cl, 8.6.

The products of the reaction, $\text{codIr(bpy)}^+$ and $\text{codIr(phen)}^+$ were prepared[6] as the chloride and perchlorate salts by standard methods.

**Kinetics.** The kinetic data were obtained with a conventional Durrum D110 stopped-flow spectrophotometer at a constant temperature. Pseudo-first-order conditions were maintained by ensuring that the concentrations of the incoming and outgoing ligands were in general at least a factor of 25 greater than that of the starting complex. The entire study was carried out under a nitrogen atmosphere as the reactants and products were found to be dioxygen sensitive. The reactions were followed at λ 560 nm, which corresponds to studying the rate of formation of product. The final UV–vis spectra of the reaction solutions were compared with those obtained from the prepared products and found to be identical.

**Table I.** Absorption Maxima and Extinction Coefficients in Parentheses for All Species in Methanolic Solution

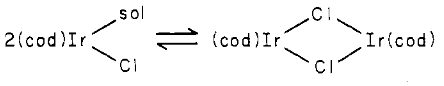
| species | λ (ε) |
|---|---|
| $[\text{codIrCl}]_2$-$[\text{codIrCl(MeOH)}]$[a] | 440 (1524), 390 (2166), 350 (1906) |
| $[\text{codIrCl}]_2$[b] | 452 (3940), 392 (2820), 365 (2960) |
| codIrCl(pic) | 453 (280), 440 sh[e] (240), 402 (940), 390 sh (789) |
| $\text{codIrCl}_2{}^-$[c] | 440, 394, 360 sh |
| $\text{codIrCl(pic)}_2$[d] | 463 (271), 453 sh (268), 408 (847), 400 sh (790) |
| $\text{codIr(phen)}^+\text{ClO}_4{}^-$ | 565 (686), 420 (1220), 365 sh (2828) |
| $\text{codIr(bpy)}^+\text{ClO}_4{}^-$ | 565 (677), 440 (1003), 370 sh (2012) |

[a] λ (nm) and ε ($\text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}$) determined at $[\text{codIrCl}]_2 = 5 \times 10^{-4}$ M in MeOH–4% $CH_2Cl_2$ solution. [b] In benzene. [c] Spectrum obtained by addition of excess LiCl to $[\text{codIrCl}]_2$ in MeOH–4% $CH_2Cl_2$ is apparently not that of 100% $\text{codIrCl}_2{}^-$. [d] Prepared in situ by addition of excess pic to codIrCl(pic). [e] sh = shoulder.

For reaction 5 (when Y = methanol) the dimer was dissolved in methanol–4% dichloromethane as the dimer is insoluble in methanol. This yielded predominantly codIrCl(MeOH) in solution (see later).

## Results and Discussion

**Establishment of All Possible Species in Solution.** The spectra of $[\text{codIrCl}]_2$ in methanol–4% dichloromethane and benzene differ drastically not so much in $\lambda_{\text{max}}$ but in relative peak intensities (Table I). This is most probably due to the fact that the equilibrium



(6)

exists in solution (sol = solvent) and that the equilibrium favors the left in polar solvents and the right in nonpolar solvents. This was also found to be the case for $[\text{codRhCl}]_2$.[7] In studying the kinetics of the solution reactions of codIrCl(pic), one would then have to keep in mind that if this complex solvolyzes to codIrCl(sol), the dimer species will therefore also be present in solution. Furthermore, if one wants to determine the effect of the first outgoing ligand (which would be either $Cl^-$ or pic) on the rate of the reaction, addition of $Cl^-$ or pic to the reaction solution would be necessary. This can once again create new species in solution and further complicate the system. Hence we studied the change in the UV–vis spectra of codIrCl(pic) and $[\text{codIrCl}]_2$ in solution on addition of $Cl^-$ and pic in the presence and absence of dioxygen.

As the dimer is insoluble in methanol, the solutions were made up by dissolving the complex in a small amount of dichloromethane and then adding methanol to give a methanol–4% dichloromethane solution. A benzene solution of the dimer was also made up. Spectra of the above two solutions showed that the former decayed very fast in the presence of dioxygen whereas the latter was quite stable, suggesting that the solvo species codIrCl(sol) is the dioxygen-sensitive one. The spectrum of the dioxygen-free solution of $[\text{codIrCl}]_2$ in methanol–4% dichloromethane showed UV–vis peaks at λ 440, 390, and 350 nm {which should be that of codIrCl(MeOH)} while that of codIrCl(pic) showed peaks at λ 453 and 402 nm and shoulders at λ 440 and 390 nm. Addition of a stoichiometric amount of pic to a methanol–4% dichloromethane solution of $[\text{codIrCl}]_2$ causes the codIrCl(MeOH) peaks at λ 440, 390, and 350 nm to disappear and the codIrCl(pic) peaks at λ 453 and 402 nm to appear. The equilibrium

$$\text{codIrCl(pic)} \rightleftharpoons \text{codIrCl(MeOH)} + \text{pic} \qquad (7)$$

therefore seems to lie far to the left. Similarly, if $Cl^-$ is added

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(4) D. J. A. de Waal and W. Robb, *Inorg. Chim. Acta*, **26**, 91 (1978).

(5) (a) G. Winkhaus and H. Singer, *Chem. Ber.*, **99**, 3610 (1966); (b) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).

(6) G. Mestroni and A. Camus, *J. Organomet. Chem.*, **73**, 119 (1974).

(7) W. Robb and C. G. Nicholson, *S. Afr. J. Chem.*, **30**, 213, 221 (1977).

**Table II.** Kinetic Data ($k_{obsd}$ in $s^{-1}$) for the Reaction codIrCl(pic) + bpy in Methanol at 20 °C

| | added [pic], M | | | | |
|---|---|---|---|---|---|
| [bpy], M | 0 | 0.0104 | 0.0218 | 0.0366 | 0.0505 |
| 0.005[a] | 1.78 | | | | |
| 0.0125[a] | 2.26 | 0.53 | 0.31 | 0.17 | 0.11 |
| 0.025 | 2.50 | 0.77 | 0.45 | 0.29 | 0.20 |
| 0.05 | 2.69 | 1.09 | 0.67 | 0.44 | 0.33 |
| 0.1 | 2.86 | 1.40 | 0.99 | 0.67 | 0.52 |
| 0.2 | 3.07 | 1.77 | 1.36 | 0.97 | 0.77 |
| 0.4 | 3.47 | 2.10 | 1.67 | 1.36 | 1.16 |

[a] These data were not used in the calculation of rate and equilibrium constants (see text).

to a methanolic solution of $[codIrCl]_2$, the codIrCl(MeOH) peaks at λ 390 and 350 nm are replaced by a peak at λ 394 nm and a shoulder at λ 360 nm while the λ 440 nm peak decreases in intensity. This is most probably due to the equilibrium

$$Cl^- + codIrCl(MeOH) \rightleftharpoons codIrCl_2^- + MeOH \quad (8)$$

Addition of pic to a methanolic solution of codIrCl(pic) changed the UV–vis spectrum from $\lambda_{max}$ 402 nm to $\lambda_{max}$ 408 nm. The two most likely species to be formed are $codIr(pic)_2^+$ or $codIrCl(pic)_2$ or both, i.e.

$$codIrCl(pic)_2 \rightleftharpoons codIr(pic)_2^+ + Cl^- \quad (9)$$

We, however, believe that the five-coordinate complex predominates in methanolic solution because of the following:

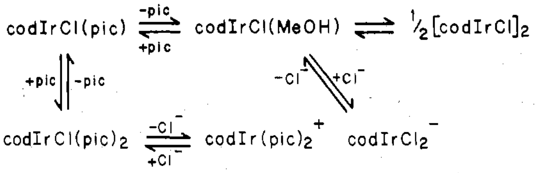
(i) Conductivity measurements showed no significant increase in conductivity when pic was added to a methanolic solution of codIrCl(pic).

(ii) $codIr(phen)^+$ and $codIr(bpy)^+$ form five-coordinate complexes with halides.[6]

(iii) As will be seen later, the presence of a five-coordinate complex is in agreement with the kinetic data.

(iv) Further addition of $Cl^-$ to this solution did once again change the UV–vis spectrum slightly but did not regenerate the codIrCl(pic) spectrum. (Similar effects were found when $Cl^-$ was added first followed by pic.)

It is thus evident that dissolution of codIrCl(pic) in methanol in the presence of $Cl^-$ and pic will cause the following set of equilibria to be established:



(10)

The $\lambda_{max}$ and extinction coefficients of these different species are given in Table I.

**Kinetics.** The rate of reaction 5 (when Y = pic) was found to be first order in complex concentration and very much dependent on pic and chelating amine concentrations. The reaction rate was, however, quite insensitive toward addition of chloride. It can therefore be assumed that, most probably because equilibria 7–9 lie very far to the left, the species $[codIrCl]_2$, $codIrCl_2^-$, and $codIr(pic)_2^+$ do not make a significant contribution to the overall reaction. Tables II and III contain the kinetic data for reaction 5 (Y = pic), Table IV shows the temperature dependence, Table VI contains the rate and equilibrium constants, and Table VII gives thermodynamic parameters.

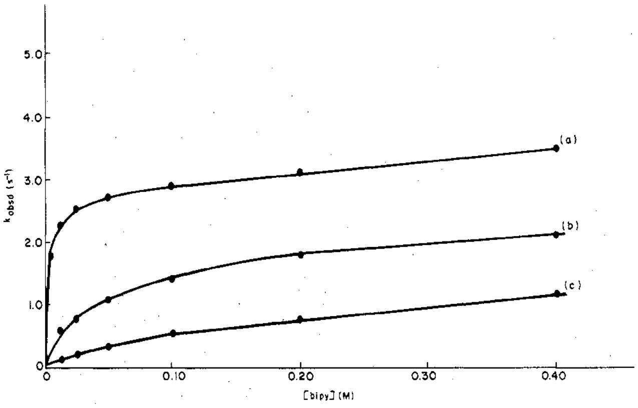
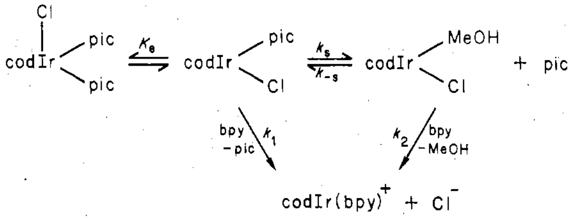


**Figure 1.** Plots of $k_{obsd}$ against bpy concentrations at various added pic concentrations: (a) [pic] = 0; (b) [pic] = 0.0104 M; (c) [pic] = 0.0505 M (t = 20 °C, [codIrCl(pic)] = 0.0005 M).

Reaction 5 (when Y = methanol) was studied by addition of phen or bpy to a methanol–4% dichloromethane solution of the dimer. The results are given in Table V.

**(a) Reaction of codIrCl(pic) + bpy.** A plot of $k_{obsd}$ vs. [bpy] for reaction 5 (Y = pic, am′ = bpy) when no pic was added showed two distinct regions. At high [bpy] a straight-line plot was obtained while at low [bpy] the plot curved toward zero (Figure 1a).

As the pic concentration was increased, the distinction between the two parts of the plot became less well defined, approaching a straight line through the origin (Figure 1b,c). This is exactly what de Waal[4] and Tobe[3] found in their work and can be explained by a competition between the outgoing and incoming ligands for the solvo species. Applying this principle to our data and keeping in mind that $codIrCl(pic)_2$ is most probably formed on addition of pic, reaction scheme 11 can be envisaged.



(11)

**Table III.** Kinetic Data ($k_{obsd}$ in $s^{-1}$) for the Reaction codIrCl(pic) + phen in Methanol at 20 °C

| | added [pic], M | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| [phen], M | 0 | 0.0087 | 0.0156 | 0.0248 | 0.0272 | 0.0279 | 0.0394 | 0.0397 |
| 0.005[a] | 1.49 | | | | | | | |
| 0.0125[a] | 2.16 | 0.45 | 0.30 | 0.14 | 0.14 | | 0.10 | 0.11 |
| 0.025 | 2.33 | 0.54 | 0.45 | 0.29 | 0.23 | 0.35 | 0.18 | 0.16 |
| 0.05 | 2.45 | 0.80 | 0.65 | 0.58 | 0.38 | 0.50 | 0.28 | 0.28 |
| 0.1 | 2.63 | 1.07 | 0.85 | 0.63 | 0.50 | 0.67 | 0.39 | 0.39 |
| 0.2 | 2.76 | 1.41 | 1.01 | 0.80 | 0.75 | 0.87 | 0.55 | 0.51 |
| 0.3 | 2.75 | | | | | | | |
| 0.4 | 2.75 | 1.63 | 1.41 | 0.93 | 0.91 | 1.07 | 0.73 | 0.71 |
| 0.5 | 2.74 | | | | | 1.16 | | |

[a] These data were not used in the calculation of rate and equilibrium constants (see text).

**Table IV**

(i) Temperature Dependence of $k_{obsd}$ for the Reaction codIrCl(pic) + bpy ([pic] = 0) in Methanol

| | $t$, °C | | |
|---|---|---|---|
| [bpy], M | 10.0 | 15.0 | 25.0 |
| 0.0125 | 1.24 | 1.58 | 2.89 |
| 0.025 | 1.31 | 1.81 | 3.14 |
| 0.05 | 1.39 | 1.92 | 3.38 |
| 0.1 | 1.54 | 2.04 | 3.63 |
| 0.2 | 1.73 | 2.12 | 3.81 |
| 0.4 | 1.85 | 2.47 | 4.23 |

(ii) Temperature Dependence of $k_{obsd}$ for the Reaction codIrCl(pic) + phen ([pic] = 0) in Methanol

| | $t$, °C | | |
|---|---|---|---|
| [phen], M | 9.7 | 15.0 | 25.0 |
| 0.0125 | 1.04 | 1.33 | 2.57 |
| 0.025 | 1.12 | 1.57 | 3.08 |
| 0.05 | 1.24 | 1.65 | 3.36 |
| 0.1 | 1.29 | 1.72 | 3.48 |
| 0.2 | 1.42 | 1.78 | 3.77 |
| 0.4 | 1.40 | 1.87 | 3.89 |

**Table V**

(i) $k_{obsd}$ Values for the Reaction $[codIrCl]_2$ + bpy at Different Temperatures in Methanol

| | $t$, °C | | | | |
|---|---|---|---|---|---|
| [bpy], M | 9.8 | 10.0 | 11.8 | 15.0 | 20.0 |
| 0.005 | | 116.0 | | | |
| 0.01 | 225.0 | 212.0 | 247.5 | 293.6 | |
| 0.0125 | 287.6 | 239.0 | 298.7 | 355.4 | 417.0 |
| 0.015 | 331.6 | | | 396.0 | |
| 0.0175 | 362.8 | | 382.9 | 462.0 | |
| 0.02 | | 354.0 | | | |
| 0.025 | | 461.0 | | | |

(ii) $k_{obsd}$ Values for the Reaction $[codIrCl]_2$ + phen at Different Temperatures in Methanol

| | $t$, °C | | |
|---|---|---|---|
| [phen], M | 9.7 | 15.0 | 20.0 |
| 0.01 | 79.3 | 101.5 | 142.0 |
| 0.0125 | 101.5 | 115.5 | 164.0 |
| 0.015 | 111.8 | 128.3 | |
| 0.0175 | 128.8 | 175.4 | |
| 0.02 | | | 249.0 |
| 0.025 | | | 260.0 |

The $codIrCl(pic)_2$ complex is coordinately saturated and is therefore inert toward nucleophilic attack.[8]

Treating codIrCl(MeOH) as being in a steady state, rate law 12 can be derived.

$$k_{obsd} = \frac{k_1[bpy]}{1 + K_e[pic]} + \frac{k_s k_2[bpy]}{k_{-s}[pic] + k_2[bpy] + k_2K_e[bpy][pic] + k_{-s}K_e[pic]^2} \qquad (12)$$

From this it can be seen that the basic form of the two-term rate law is still present since at low [pic] and high [bpy] the $k_{-s}$[pic], $k_{-s}K_e[pic]^2$, and $k_2K_e$[bpy][pic] terms can be neglected relative to the $k_2$[bpy] term, and $1 \gg K_e[pic]$, so that eq 12 simplifies to the classical two-term rate law which is represented by the straight-line portion of Figure 1a. At higher [pic], competition between the forward reaction ($k_2$[bpy]) and the back-reaction ($k_{-s}$[pic]) results in a curved plot, Figure 1b. At very high [pic], equilibrium 7 lies far to the left, making the contribution of the codIrCl(MeOH) species to the overall reaction very small and thus the plot (Figure 1c) approaches a straight line described by $k_{obsd} = k_1[bpy]/(1 + K_e[pic])$.

The different constants in eq 12 were evaluated as follows: First $k_1$ was obtained from the slope of the straight-line part of the plot of $k_{obsd}$ vs. [bpy] at added [pic] = 0. Extrapolation of the straight-line portion of the plot to intersect the $y$ axis yielded $k_s$. For the calculation of the constants $k_{-s}$, $k_2$, and $K_e$, rate law 12 was rewritten as

$$k_{obsd}' = k_{obsd} - \frac{k_1[bpy]}{1 + K_e[pic]} = \frac{k_2k_s[bpy]}{k_{-s}[pic] + k_2[bpy] + k_2K_e[bpy][pic] + k_{-s}K_e[pic]^2} \qquad (13)$$

where $K_e$ is estimated between 0 and 100 $M^{-1}$; see text. Plots of $k_{obsd}'$ vs. [bpy] yielded sharply limiting curves. It can be seen that for the case when added [pic] = 0 and [bpy] is high, eq 13 simplifies to $k_{obsd}' = k_s$, the solvolysis rate constant, given by the limiting value of the above-mentioned plot.

A better way to treat the kinetic data is to invert eq 13 to give

$$\frac{1}{k_{obsd}'} = \frac{k_{-s}[pic]}{k_2k_s[bpy]} + \frac{1}{k_s} + \frac{K_e[pic]}{k_s} + \frac{k_{-s}K_e[pic]^2}{k_2k_s[bpy]} \qquad (14)$$

Plots of $1/k_{obsd}'$ vs. 1/[bpy] for each [pic] should yield a series of straight lines with slopes and intercepts both dependent on [pic]. Plotting these intercepts ($1/k_s + K_e[pic]/k_s$) against [pic] should give linear graphs with an intercept $1/k_s$ and a slope $K_e/k_s$, and $K_e$ could therefore be calculated. However, since $K_e$ is not originally known, the value had to be estimated and an arbitrary range of 0–100 $M^{-1}$ was chosen. For this range straight lines were obtained for the above-mentioned $1/k_{obsd}'$ vs. 1/[bpy] and intercept vs. [pic] plots. The estimated $K_e$ value was varied in an iterative process until correspondence with the calculated $K_e$ value was reached ($K_e$ estimated at 30 $M^{-1}$, $K_e$ calculated at 31 $M^{-1}$).

$K_e$ was also determined spectrophotometrically and a value of 47.5 ± 15 $M^{-1}$ was found, which corresponds, within experimental error, with that obtained kinetically. The large error can most probably be attributed to the presence of some $codIr(pic)_2^+$ when $codIrCl(pic)_2$ is generated in situ. This may also account for the deviation from linearity in the $1/k_{obsd}'$ vs. 1/[bpy] plot at high [pic] and low [bpy]. Since the contribution of the $codIr(pic)_2^+$ species to the overall reactivity is not considered in rate law 14, these data have not been used in the calculations of rate and equilibrium constants.

A plot of the slopes of the $1/k_{obsd}'$ vs. 1/[bpy] graphs, ($k_{-s}[pic]/k_2k_s + k_{-s}K_e[pic]^2/k_2k_s$) vs. [pic] yielded a straight line at low [pic] but became parabolic at high [pic] as predicted by the $k_{-s}K_e[pic]^2/k_2k_s$ term. From the slope, $k_{-s}/k_2k_s$, of the linear portion of the graph, the ratio $k_{-s}/k_2$ could be calculated.

**(b) Reaction of codIrCl(pic) + phen.** A key point in the proposed rate law is that $k_s$, $k_{-s}$, and $K_e$ should be independent of the nature and reactivity of the incoming nucleophile. Thus the study of the reaction of codIrCl(pic) with another amine, phen, was undertaken. The reaction with phen was slower than the reaction with bpy and was found to proceed totally via the solvent path (i.e., $k_1$ is very small). A possible explanation for this could be the relative rigidity of the phen molecule compared to that of the bpy molecule. All the rate and equilibrium constants for this system were determined as for the bpy system by using only eq 14, since $k_{obsd} = k_{obsd}'$. The constants $k_s$ and $K_e$ were found to agree, within experimental error, with those obtained for the reaction with bpy (see Table

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[8] W. J. Louw and J. E. Singleton, *Inorg. Chim. Acta*, **27**, 21 (1978).

**Table VI.** Rate and Equilibrium Constants for the Reaction codIrCl(pic) + am′ in Methanol

| am′ | $t$, °C | $k_s$, s$^{-1}$ | $k_1$, s$^{-1}$ M$^{-1}$ | $10^{-4}k_2$, s$^{-1}$ M$^{-1}$ | $10^{-5}k_{-s}$, s$^{-1}$ M$^{-1}$ | $K_e$, M$^{-1}$ | $10^5K_s$, M |
|---|---|---|---|---|---|---|---|
| bpy | 9.8 | | | 2.15 ± 0.11 | | | |
| | 10.0 | 1.48 ± 0.04 | 0.98 ± 0.33 | 1.92 ± 0.05 | | | |
| | 11.8 | | | 2.29 ± 0.08 | | | |
| | 15.0 | 1.90 ± 0.03 | 1.49 ± 0.23 | 2.70 ± 0.08 | | | |
| | 20.0 | 2.70 ± 0.01 | 2.03 ± 0.03 | 3.33[a] | 1.66 ± 0.08 | 31 ± 6[c] | 1.63 ± 0.08 |
| | 25.0 | 3.37 ± 0.05 | 2.43 ± 0.21 | 4.25[b] | | | |
| phen | 9.7 | 1.38 ± 0.04 | | 0.48 ± 0.06 | | | |
| | 15.0 | 1.83 ± 0.02 | | 0.635 ± 0.23 | | | |
| | 20.0 | 2.75 ± 0.03 | | 0.845 ± 0.14 | 0.67 ± 0.18 | 63 ± 13[c] | 4.13 ± 1.15 |
| | 25.0 | 3.83 ± 0.06 | | 1.09[b] | | | |

[a] Slope of line drawn through one point and intercept (see text). [b] Calculated from the Arrhenius plot. [c] The spectrophotometrically determined value at 20.0 °C for $K_e$ is 47.5 ± 15.

**Table VII.** Thermodynamic Parameters for the Reaction codIrCl(pic) + am′ in Methanol at 25 °C

| am′ | | $E_a$, kJ | $\Delta H^\ddagger$, kJ | $\Delta G^\ddagger$, kJ | $\Delta S^\ddagger$, J mol$^{-1}$ deg$^{-1}$ |
|---|---|---|---|---|---|
| bpy | $k_s$ | 40 ± 2 | 37 ± 2 | 71 | −113 ± 8 |
| | $k_1$ | 43 ± 5 | 40 ± 5 | 72 | −106 ± 16 |
| | $k_2$ | 34 ± 4 | 31 ± 4 | 47 | −54 ± 14 |
| phen | $k_s$ | 48 ± 3 | 45 ± 3 | 71 | −85 ± 10 |
| | $k_2$ | 38 ± 2 | 35 ± 2 | 51 | −51 ± 6 |

VI). This therefore substantiates the validity of the proposed reaction scheme 11.

**(c) Reaction of [codIrCl]$_2$ with bpy and phen.** The ratio $k_{-s}/k_2$ and hence $K_s$ (=$k_s/k_{-s}$) can be resolved by studying the reaction of the dimer with bpy and phen. As discussed previously, equilibrium 6 in methanol lies almost totally to the left, and it is therefore possible to determine $k_2$ by reacting bpy and phen with the "dimer" solution, provided that the dimer reactivity is not orders of magnitude faster than that of codIrCl(MeOH). If the dimer reactivity is faster and equilibrium 6 is fast, the reaction will be dependent on complex concentration. This was not found in our experiments. However, a further small optical density change after the first reaction was observed, which we attributed to a small amount of dimer. Thus a plot of $k_{obsd}$ vs. [am′] should yield a straight line through the origin with a slope of $k_2$. Difficulties were encountered in the determination of $k_2$ for the system [codIrCl]$_2$ + bpy because the reaction at 20 °C proved to be too fast for the stopped-flow spectrophotomete at higher [bpy]. The reaction was repeated at 9.8 °C and the expected straight-line plot through the origin was obtained. Temperature was varied so that a plot of log $k_2$ vs $1/T$ could be made and the $k_2$ values at 20 and 25 °C determined. The reaction of the "dimer" solution with phen gave a straight-line graph with an intercept when $k_{obsd}$ vs. [phen] was plotted. This small intercept was thought to be due to the presence of an equilibrium in the reaction. Although this reaction was a little slower than the reaction with bpy, the same technique had to be used in order to obtain $k_2$ at 20 and 25 °C. These $k_2$ values, which contained quite large standard errors due to the fast rate of the reactions, were used to calculate $k_{-s}$ and $K_s$ for the bpy and phen systems. Taking these large errors into account as well as the fact that third-order data are used, fair agreement seems to exist between the $k_{-s}$ and $K_s$ values found for the two systems (Table VI). This further supports the postulations of equilibrium 6 and reaction scheme 11.

**(d) General Conclusions.** The very low $K_s$ values obtained agree with the assumption that equilibrium 7 lies far over to the codIrCl(pic) species. The $K_e$ values found are of the same magnitude as those determined for the formation constants of codIrXphen (X = I).[8] The fact that $k_2$ is orders of magnitude greater than $k_s$/[sol] and $k_1$ shows why in most square-planar substitution reactions only rate law 2 is observed. Considering the thermodynamic parameters calculated for $k_s$, $k_1$, and $k_2$, it can be seen that the $\Delta H^\ddagger$ values are low whereas the $\Delta S^\ddagger$ values are standard negative for square-planar substitution reactions. Thus it would seem that the reactions are fast because of the low activation energies needed. If the bpy system studied here is compared with the reaction codRhCl(pip) + bpy (pip = piperidine),[7] it is striking to note that the $k_1$ ($k_y$) values are almost the same whereas the $k_s$ value for the Ir system is 2 orders of magnitude greater than that for the Rh system. The reason for this must be attributed to differences in enthalpy as the $\Delta S^\ddagger$ values are approximately the same. Finally, it is interesting to note that for the reaction codMClL + ligand (M = Ir, Rh; L = amine, phosphine) the first outgoing ligand depends on the nature of L. When L = amine, the first leaving group is the amine, whereas when L = phosphine, chloride was found to be the first leaving group.[4]

**Registry No.** codIrCl(pic), 64121-29-5; bpy, 366-18-7; phen, 66-71-7; codIr(phen)$^+$ClO$_4^-$, 41392-67-0; codIr(bpy)$^+$ClO$_4^-$, 41444-85-3; [codIrCl]$_2$, 12112-67-3; codIrCl(MeOH), 71565-61-2; codIrCl(pic)$_2$, 71565-62-3; codIrCl$_2^-$, 71565-63-4.