Reactions of Cobalt(II) Schiff's Base Complexes with Organic Halides. Atom-Transfer Mechanisms

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Abstract: Five-coordinate cobalt(II) Schiff's base complexes of the type Co(saloph)B (where saloph = *N,N'*-bis(salicylidene)-*o*-phenylenediamino and B = pyridine, imidazole, triphenylphosphine, etc.) were found to react with *p*-cyanobenzyl halides (RX) according to the stoichiometry $2Co(saloph)B + RX + B \rightarrow Co(saloph)BR + Co(saloph)B_2^+ + X^-$. These reactions obeyed the rate law $-d[Co(saloph)B]/dt = 2k[Co(saloph)B][RX]$, with values of k (for RX = p-$CNC_6H_4CH_2Br$) in CH_2Cl_2 at 25° ranging from $1.3 \times 10^{-3}\ M^{-1}\ sec^{-1}$ for B = 3-chloropyridine to $0.9\ M^{-1}\ sec^{-1}$ for B = trimethylphosphine. The results are interpreted in terms of the stepwise atom-transfer mechanism $Co(saloph)B + RX \rightarrow Co(saloph)BX + R\cdot$ (rate determining), followed by $Co(saloph)B + R \rightarrow Co(saloph)BR$; $Co(saloph)BX + B \rightarrow Co(saloph)B_2^+ + X^-$. Trends in the kinetic data, notably the dependence of k on the properties of B, are discussed. Equilibrium measurements on the association reactions, $Co(saloph) + B \rightleftarrows Co(saloph)B$, also are reported.

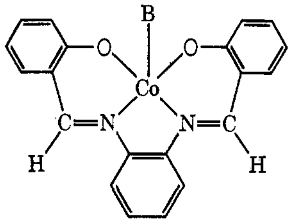
Previous work in this laboratory has demonstrated that the reductions of organic halides (RX) by certain low-spin cobalt(II) complexes (L_5Co^{II}, notably $Co(CN)_5^{3-}$ and $Co(DH)_2B$, where DH_2 = dimethylglyoxime and B is an axial ligand, *e.g.*, pyridine or triphenylphosphine) proceed according to the mechanism and stoichiometry depicted by eq 1-3.[2-4] These reactions were found to yield relatively stable organocobalt products, $L_5Co^{III}R$.

$$L_5Co^{II} + RX \longrightarrow L_5Co^{III}X + R\cdot \qquad \text{(rate determining)} \tag{1}$$

$$L_5Co^{II} + R\cdot \longrightarrow L_5Co^{III}R \tag{2}$$

$$2L_5Co^{II} + RX \longrightarrow L_5Co^{III}X + L_5Co^{III}R \tag{3}$$

In the present paper we describe related studies on the reactions with organic halides of another family of cobalt(II) complexes, namely the Schiff's base complexes, Co(saloph)B (**1**), where saloph = *N,N'*-bis(salicylidene)-*o*-phenylenediamino, and B is an amine or phosphine ligand.[5]



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The objectives of this investigation included the extension of the study of such reactions to cobalt(II) complexes of weaker field ligands than those previously examined, as well as the systematic investigation of the dependence of reactivity on the axial ligand, B, which was subjected to considerable variation. Examination of the stoichiometry and kinetics of the reactions yielded results which are interpreted in terms of a mechanistic scheme closely related to the one cited earlier, namely that depicted by

$$Co(saloph)B + RX \xrightarrow{k} Co(saloph)BX + R\cdot \qquad \text{(rate determining)} \tag{4}$$

$$Co(saloph)B + R \longrightarrow Co(saloph)BR \tag{5}$$

$$Co(saloph)BX + B \longrightarrow Co(saloph)B_2^+ + X^- \tag{6}$$

$$2Co(saloph)B + RX + B \longrightarrow Co(saloph)BR + Co(saloph)B_2^+ + X^- \tag{7}$$

In contrast to the reactions described in this paper, we have recently demonstrated that certain *six-coordinate* cobalt(II) Schiff's base complexes react with nitrobenzyl halides by electron-transfer, rather than atom-transfer (*i.e.*, halogen abstraction), mechanisms.[8] These reactions, which are described elsewhere, exhibit distinctive kinetic and stoichiometric characteristics on the basis of which the two types of mechanism can be distinguished.[8]

Experimental Section

Materials. [Co(saloph)] was prepared by a modification of the method of West.[9] Reaction of 1.58 g (5 mmol) of *N,N'*-bis(salicylidene)-*o*-phenylenediamine[10] with 1.25 g (5 mmol) of $Co(CH_3COO)_2 \cdot 4H_2O$ in 400 ml of boiling methanol yielded 1.21 g (65%) of violet-brown needles of Co(saloph) which were washed with methanol and diethyl ether. *Anal.* Calcd for $C_{20}H_{14}O_2N_2Co$: C, 64.35; H, 3.78; N, 7.51. Found: C, 64.26; H, 3.70; N, 7.57.

[Co(saloph)(imidazole)] deposited as shiny black crystals (0.018 g, 0.041 mmol) from a solution of Co(saloph) (0.0832 g, 0.22 mmol) and imidazole (0.56 g, 8.2 mmol) in 5 ml of CH_2Cl_2. The product was collected on a paper filter, washed with methanol (slightly soluble), water, and acetone, and dried *in vacuo*. *Anal.* Calcd for $C_{23}H_{18}O_2N_4Co$: C, 62.59; H, 4.11; N, 12.70. Found: C, 62.55; H, 4.14; N, 12.75.

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(1) Address correspondence to this author.

(2) J. Halpern and J. P. Maher, *J. Amer. Chem. Soc.*, **86**, 2311 (1964); **87**, 5361 (1965).

(3) P. W. Schneider, P. F. Phelan, and J. Halpern, *ibid.*, **91**, 77 (1969). It should be noted that the values of k cited in this earlier paper correspond to $2k$ as defined in the present one.

(4) P. B. Chock and J. Halpern, *ibid.*, **91**, 582 (1969).

(5) While the structures of the Co(saloph)B complexes are not known with certainty, it seems likely, in view of the known structures of several closely related compounds,[6,7] that the coordination of cobalt(II) is approximately square pyramidal, the quadridentate saloph ligand being essentially planar and the ligand B occupying an axial position.

(6) D. Hall and H. Moore, *Proc. Chem. Soc., London*, 256 (1960).

(7) F. J. Llewellyn and T. N. Waters, *J. Chem. Soc.*, 2639 (1960); D. Hall and T. N. Waters, *ibid.*, 2644 (1960); A. Earnshaw, P. C. Hewlett, E. A. King, and L. F. Larkworthy, *ibid.*, 241 (1968). The last paper also discusses the magnetic properties of cobalt(II) Schiff's base compounds which are complex and not well understood. We have found that five-coordinate complexes of the type Co(saloph)B commonly exhibit temperature-dependent magnetic moments, characteristic of high-spin–low-spin equilibria with values in the range 2–3.5 BM at room temperature, which approach the limiting low-spin value of ~1.9 BM at low temperatures.

(8) L. G. Marzilli, P. A. Marzilli, and J. Halpern, *J. Amer. Chem. Soc.*, **92**, 5752 (1970).

(9) B. O. West, *J. Chem. Soc.*, 395 (1954).

(10) P. Pfeiffer, T. Hesse, H. Pfitzner, W. Scholl, and H. Thielert, *J. Prakt. Chem.*, **149**, 217 (1937).

[Co(saloph)I]. Co(saloph) (0.74 g, 2.0 mmol) and iodine (0.27 g, 1.0 mmol) were weighed into a 125-ml stoppered flask and, after flushing with nitrogen, 100 ml of CH_2Cl_2 was added. The reaction mixture was stirred and warmed (*ca.* 35°) for 1.5 days, following which the product, a brownish-black powder, was collected and washed with CH_2Cl_2 (*ca.* 400 ml) until the washings were nearly colorless; yield, 0.79 g (79%). The product was dried *in vacuo* at 78° for 6 hr, then at room temperature for 16 hr. *Anal.* Calcd for $C_{20}H_{14}IN_2O_2$: C, 48.02; H, 2.82; N, 5.60. Found: C, 47.80; H, 2.66; N, 5.53.

[Co(saloph)(*n*-Bu$_3$P)$_2$]I. A suspension of [Co(saloph)I] (0.20 g, 0.40 mmol) in 20 ml of methanol was treated with tri-*n*-butylphosphine (*n*-Bu_3P, 0.325 g, 1.61 mmol). The wine-red solution which formed immediately was filtered and then water was added dropwise until dark red-violet crystals formed. After successive washings with water containing a few drops of methanol, then water, and finally diethyl ether, the product was dried *in vacuo* at 78° for 4.5 hr and at 21° for 13 hr; yield, 0.216 g (59%). *Anal.* Calcd for $C_{44}H_{68}IN_2O_2P_2Co$: C, 58.40; H, 7.58; N, 3.10. Found: C, 58.33; H, 7.43; N, 3.06.

[Co(saloph)(py)$_2$]I·H$_2$O. To a suspension of Co(saloph) (0.98 g, 3.0 mmol) and *p*-nitrobenzyl iodide (0.87 g, 3.3 mmol) in 20 ml of deoxygenated $CHCl_3$ was added 0.53 ml (6.6 mmol) of pyridine (py). The resulting mixture was shaken (under N_2) for 1 hr and then concentrated to near dryness. Deoxygenated tetrahydrofuran was added slowly, resulting in the formation of a dark red-brown precipitate which was collected on a glass filter, washed thoroughly with tetrahydrofuran, and dried under nitrogen; yield, 0.81 g (80%). The crude product (0.35 g) was recrystallized from methanol (40 ml) by addition of sodium iodide, yielding small violet-red crystals (0.25 g) which were washed with a small amount of ice-cold methanol. *Anal.* Calcd for $C_{30}H_{26}N_4O_3ICo$: C, 53.27; H, 3.87; N, 8.29. Found: C, 53.63; H, 3.60; N, 8.25.

[Co(saloph)(1-MeIMD)$_2$]ClO$_4$. To a suspension of Co(saloph) (0.37 g, 1.0 mmol) and *p*-nitrobenzyl bromide (0.12 g, 0.55 mmol) in 10 ml of chloroform was added 1.64 g (2.0 mmol) of 1-methylimidazole (1-MeIMD). The resulting solution was shaken periodically for 1.3 hr and then concentrated to *ca.* 4 ml in a stream of nitrogen. Dropwise addition of tetrahydrofuran resulted in the formation of a red precipitate of [Co(saloph)(1-MeIMD)$_2$]Br which was collected on a glass filter and washed with tetrahydrofuran and diethyl ether; yield, 0.295 g (96%). The bromide salt was converted to the corresponding perchlorate by dissolving it in hot water, filtering to separate some insoluble brown residue, and treating the filtrate with a methanolic solution of lithium perchlorate (excess). Slow crystallization of the product yielded iridescent garnet-red hexagonal plates which were collected and washed with water, dried on the filter, then washed with diethyl ether, and dried *in vacuo* for 36 hr (yield, 46%). *Anal.* Calcd for $C_{28}H_{26}O_6N_6ClCo$: C, 52.80; H, 4.11; N, 13.20. Found: C, 52.84; H, 4.06; N, 13.34.

[Co(saloph)(py)(*p*-CH$_2$C$_6$H$_4$CN)]·H$_2$O. To a suspension of Co(saloph) (0.75 g, 2.0 mmol) and *p*-cyanobenzyl iodide (0.54 g, 2.2 mmol) in 25 ml of deoxygenated chloroform was added, by means of a syringe, 0.35 ml (4.4 mmol) of pyridine. The resulting solution was allowed to stand for 1 hr, then concentrated in a stream of nitrogen, and treated with tetrahydrofuran to precipitate the [Co(saloph)(py)$_2$]I salt, which was separated by filtration. The filtrate was concentrated further and deoxygenated hexane was added to precipitate a microcrystalline purple-black powder which was washed well with water and dried under nitrogen; yield, 0.55 g (94%). This crude material (0.30 g) was recrystallized from aqueous pyridine to yield 0.17 g of the final product, a black granular powder which was washed and dried as above. *Anal.* Calcd for $C_{33}H_{27}O_2N_4Co$: C, 67.57; H, 4.64; N, 9.55. Found: C, 67.85; H, 4.29; N, 9.47.

Axial Ligands. Triphenylphosphine (Matheson Coleman and Bell) was recrystallized twice from ethanol. 1-Methylimidazole (Aldrich) was fractionally distilled (5 Torr) and the middle cut recrystallized twice in a cold room (−10°), recovering only about half the material each time; mp *ca.* −4°. The following ligands were obtained from the sources cited and used without further purification: 3-chloropyridine ($n^{20}D$ 1.5311), 3,4-lutidine ($n^{20}D$ 1.5110), and tri-*n*-butylphosphine, ($n^{20}D$ 1.4610), Aldrich; benzylamine, Matheson Coleman and Bell; pyridine, A. R., Mallinckrodt; methyldiphenylphosphine and dimethylphosphine, Strem Chemicals; trimethylphosphine and triethylphosphine, Orgmet, Inc.

Organic Halides. *p*-Cyanobenzyl chloride was prepared according to Barkenbus and Holtzclaw[11] by the reaction of 4-methylbenzenecarbonitrile with chlorine, and recrystallized from ethanol as small white needles, mp 77–78.5° (lit.[11] 77–78°). *p*-Cyanobenzyl bromide was prepared by the analogous reaction with bromine according to the method of Case.[12] Recrystallization from ethanol in the presence of charcoal yielded long white needles, mp 113–115° (lit.[12] 115–116°). *p*-Cyanobenzyl iodide was prepared from the corresponding chloride by reaction with potassium iodide in ethanol.[13] Recrystallization from ethanol yielded fluffy white needles, mp 143–145° (lit.[13] 143–144°).

Baker Analyzed grade methylene chloride, used as solvent, was dried over Linde Type 4A molecular sieves.

Equilibrium Measurements. Equilibrium quotients for the formation of Co(saloph)B by association of Co(saloph) with the various axial ligands (B) in solution were determined spectrophotometrically, as described later, using a Cary 14 spectrophotometer.

Kinetic Measurements. All kinetic measurements were performed in CH_2Cl_2 at 25.0 ± 0.1° under a nitrogen atmosphere.

Stock solutions of Co(saloph) in CH_2Cl_2 were stable indefinitely in the absence of added axial ligands (B). The reaction solutions were prepared by adding the organic halide to a CH_2Cl_2 solution of Co(saloph) (generally 1×10^{-4}–8×10^{-4} *M*) in a volumetic flask by means of a syringe. This solution was placed in a 1-cm spectrophotometer cell sealed with a rubber serum cap and purged with nitrogen. In the case of liquid axial ligands (B), the reaction was initiated by injecting the axial ligand with a microliter syringe. In the case of solid axial ligands, *e.g.*, triphenylphosphine, the Co(saloph) solution was injected into a serum-cap-sealed, nitrogen-filled flask containing weighed amounts of the axial ligand and organic halide. Appropriate volume change corrections were made in computing final concentrations.

The reactions were followed spectrophotometrically in a Cary 14 spectrophotometer equipped with a thermostated cell compartment. Absorbance increases in the 450–550-nm spectral region were measured to monitor the reactions of the amine complexes, and in the 500–650-nm region for the phosphine complexes.

Results and Discussion

The present systems differ in the following important respects from the related systems examined earlier involving the reactions of $Co(CN)_5^{3-}$ [2,4] and of Co(DH)$_2$B[3] with organic halides.

1. The reactions of Co(saloph)B are considerably slower than those of the other cobalt(II) complexes, *e.g.*, the rate constant of the reaction of Co(DH)$_2$PPh$_3$ with *p*-CNC$_6$H$_4$CH$_2$Br (0.22 M^{-1} sec^{-1} in benzene)[14] is about 75 times that of Co(saloph)PPh$_3$ (2.9×10^{-3} M^{-1} sec^{-1} in CH_2Cl_2).

2. Dissociation of the five-coordinate Co(saloph)B complexes (into Co(saloph) and B) is considerably more extensive than that of the other five-coordinate cobalt(II) complexes. To suppress this dissociation it was necessary to study the reactions of Co(saloph)B with organic halides in the presence of appreciable excesses of B.

Because of the combination of the above two features, interference from the quaternization reaction of the organic halides (*i.e.*, $RX + B \rightarrow RB^+ + X^-$) was much more severe than in the other systems and precluded, for example, the study of the reactions of methyl or benzyl halides. To minimize this interference it was necessary to use substituted benzyl halides, with substituents which enhanced the rate of the desired reaction with Co(saloph)B and lowered the rate of the competing quaternization reactions. The choice of *p*-cyanobenzyl halides for this study was dictated by these considerations and accomplished the objective of eliminating the interference from quaternization. The use of nitro-

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(11) C. Barkenbus and J. B. Holtzclaw, *J. Amer. Chem. Soc.*, **47**, 2189 (1925).

(12) F. H. Case, *ibid.*, 47, 1143 (1925).

(13) M. Freund and H. H. Reitz, *Chem. Ber.*, **39**, 2219 (1906).

(14) Solvent effects on the rates of reaction of Co(DH)$_2$(PPh$_3$) and related complexes with benzyl halides have previously been found to be small.[3]

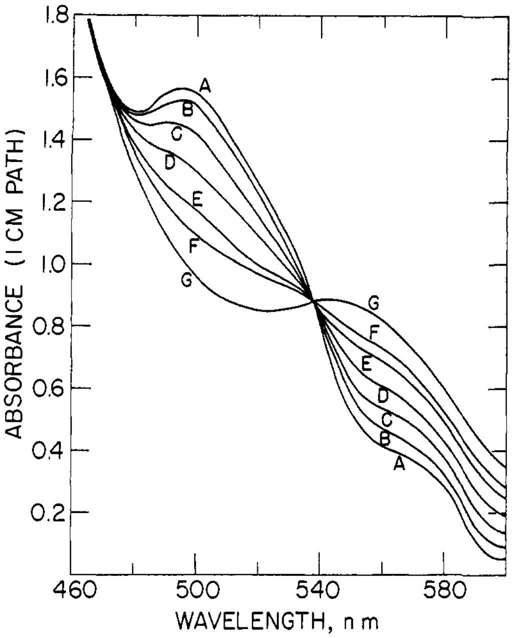

Figure 1. Spectral changes accompanying the addition of pyridine to a CH_2Cl_2 solution containing 4.23×10^{-4} *M* Co(saloph). Pyridine added (*M*): A, 0.0 [spectrum of Co(saloph)]; B, 9.54×10^{-4}; C, 2.39×10^{-3}; D, 4.77×10^{-3}; E, 9.54×10^{-3}; F, 1.43×10^{-2}; G, $\gtrsim 0.1$ [spectrum of Co(saloph)(py)].

benzyl halides in these particular studies was generally precluded because of their tendency to react by the alternative electron-transfer mechanism cited earlier.[8]

3. Halide complexes of (saloph)cobalt(III) of the types Co(saloph)X and Co(saloph)BX (X = halide) are much more labile than the corresponding halide derivatives in the other systems examined (*i.e.*, $Co(CN)_5X^{3-}$ and $Co(DH)_2BX$) and are unstable, in the presence of excess B, with respect to halide displacement to form $Co(saloph)B_2^+$ (eq 6). This was confirmed in representative cases by preparing such complexes (*e.g.*, Co(saloph)I) as described earlier and demonstrating spectrophotometrically their instantaneous conversion in solution to the corresponding $Co(saloph)B_2^+$ complexes (*e.g.*, $Co(saloph)(n\text{-}Bu_3P)_2^+$) on addition of B. The overall stoichiometry (eq 7) thus differs from that of the earlier reactions (eq 3), although the proposed mechanisms are closely related.

Equilibrium Measurements. To determine the extent of dissociation of the Co(saloph)B complexes in solution and the concentrations of excess B necessary to suppress this dissociation, the equilibrium quotients (K_f) of the Co(saloph)B formation reactions (eq 8) were determined for the various axial ligands.

$$\text{Co(saloph)} + \text{B} \longrightarrow \text{Co(saloph)B} \qquad (8)$$

The spectral changes accompanying the addition of various concentrations of pyridine to a methylene chloride solution of Co(saloph) are depicted in Figures 1 and 2. The spectral changes, including the occurrence of two isosbestic points at 537 and *ca.* 470 nm, fully support the formation of a 1:1 complex in accord with eq 8. Values of K_f determined from the measured absorbancies (A) by means of eq 9 (where A_0 is the absorbance of Co(saloph) and A_∞ the absorbance of Co(saloph)B) were found to be independent of the wavelength. For B = pyridine, $K_f = 200 \pm 20\ M^{-1}$, so that dissociation of Co(saloph)(py) is sufficiently small (<5%) to be neglected for the purposes of the kinetic measurements when [py] > 0.1 *M*.

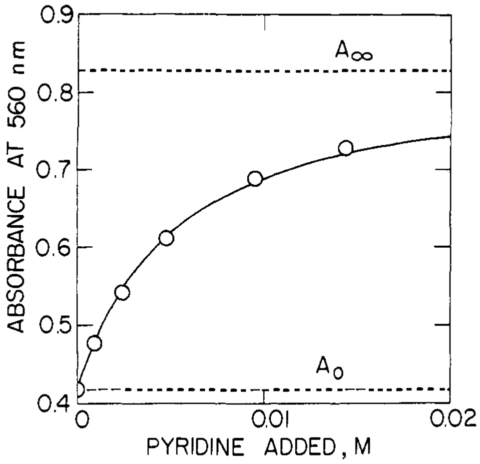

Figure 2. Absorbance change at 560 nm accompanying addition of pyridine to a 4.23×10^{-4} *M* Co(saloph) solution. The curve is calculated by means of eq 9 using $K_f = 2.0 \times 10^2\ M^{-1}$: O, experimental values (from Figure 1).

$$K_f = \frac{[\text{Co(saloph) B}]}{[\text{Co(saloph)}][\text{B}]} = \frac{(A - A_0)}{(A_\infty - A)[\text{B}]} \qquad (9)$$

Values of K_f for the other axial ligands were determined similarly and are summarized in Table I.[15]

Table I. Formation Constants (K_f) of Co(saloph)B in CH_2Cl_2 at 25°

B	K_f, M^{-1}
3-Bromopyridine	$(4.1 \pm 0.7) \times 10$
Benzylamine	$(1.3 \pm 0.2) \times 10^2$
Pyridine (py)	$(2.0 \pm 0.2) \times 10^2$
3,4-Lutidine	$(4.0 \pm 0.5) \times 10^2$
1-Methylimidazole (1-MeIMD)	$(1.2 \pm 0.1) \times 10^3$
Triphenylphosphine[a]	$(1.2 \pm 0.2) \times 10$
Diphenylphosphine	$(4.2 \pm 0.8) \times 10$
Tri(*n*-butyl)phosphine	$(1.2 \pm 0.2) \times 10^3$
Dimethylphenylphosphine	$(1.7 \pm 0.1) \times 10^3$

[a] Determined kinetically from the dependence of k_{obsd} on $[PPh_3]$ (Table II); all other values determined spectrophotometrically.

Stoichiometry and Products. The stoichiometry (corresponding to eq 7) was confirmed for representative reactions by the isolation and characterization of the pure products (*i.e.*, $Co(saloph)B_2^+$ and Co(saloph)BR) as described earlier and by quantitative matching of the spectra of the final reaction solutions with the known spectra of the products. Figures 3 and 4 illustrate this matching for the reactions of Co(saloph)py and Co(saloph)(1-MeIMD), respectively, with $p\text{-CNC}_6H_4CH_2I$. Satisfactory agreement in spectral matching experiments was also observed for the reaction of Co(saloph)(n-Bu_3P) with $p\text{-CNC}_6H_4CH_2I$.

The possibility of performing spectral titrations, *i.e.*, of Co(saloph)B with RX, to demonstrate the stoichiometric ratio of reaction of the two species was precluded by the slowness of the reactions in the concentra-

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(15) The choice of saloph as the Schiff's base in this study, instead of *N,N'*-bis(salicylidene)ethylenediamino (salen), was conditioned in part by the fact that the values of K_f for the Co(saloph)B complexes are considerably larger than for the corresponding Co(salen)B complexes and quantitative formation of the five-coordinate species is, therefore, easier to achieve. The value of K_f for Co(saloph)(1-MeIMD) ($1.2 \times 10^3\ M^{-1}$) is about 45 times the corresponding value (23 M^{-1}) for Co(salen)(1-MeIMD). In general, the reactions of Co(salen)B complexes with organic halides were found to resemble those of the Co(saloph)B complexes and to exhibit similar rate constants.

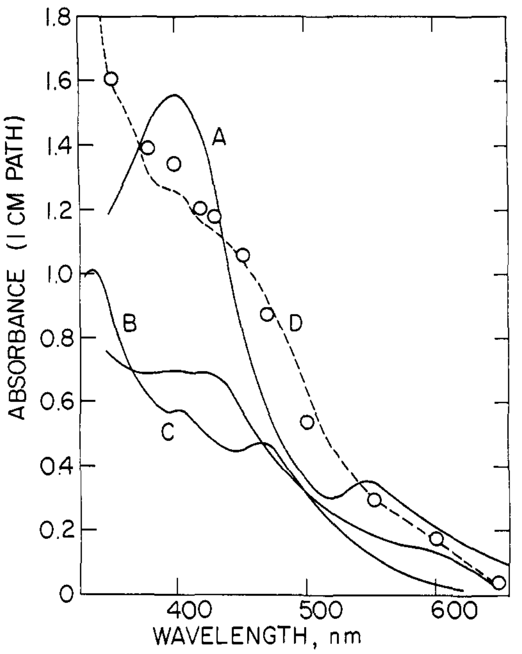

Figure 3. Spectral changes accompanying the reaction of 1.0 × 10^{-4} *M* Co(saloph)(py) with *p*-$CNC_6H_4CH_2I$ in the presence of 1 *M* py: A, initial spectrum [1.0 × 10^{-4} *M* Co(saloph)(py)]; B, spectrum of 0.50 × 10^{-4} *M* [Co(saloph)$(py)_2$]I; C, spectrum of 0.50 × 10^{-4} *M* Co(saloph)(py)($CH_2C_6H_4CN$); D, calculated final spectrum (sum of B and C); ○, experimental absorbance values of final solution after reaction.

tion ranges consistent with the relatively low solubilities of the Co(saloph)B complexes ($<10^{-3}$ *M*). However, such a titration could be performed in CH_2Cl_2 for the much faster reaction of the related but more soluble Schiff's base complex, Co(salen)($P(CH_3)_2Ph$) with *p*-$CNC_6H_4CH_2I$. A sharp end point was obtained at a [Co(salen)($P(CH_3)_2Ph$)]:[*p*-$CNC_6H_4CH_2I$] ratio of 1.96 : 1, in good agreement with the stoichiometry of eq 7.

Kinetics. The results of kinetic measurements in CH_2Cl_2 at 25° were found in every case to conform to the second-order rate law described by eq 10. Since the organic halide was always in large excess, the observed kinetics were pseudo first order in accord with eq 11, where the measured first-order rate constant, $k_{obsd} = 2k[RX]$.

$$-d[Co(saloph)B]/dt = 2k[Co(saloph)B][RX] \qquad (10)$$

$$= k_{obsd}[Co(saloph)B] \qquad (11)$$

Typical first-order rate plots for the reaction of Co(saloph)(1-MeIMD) with *p*-$CNC_6H_4CH_2Br$ are depicted in Figure 5. Kinetic data for several representative reactions, summarized in Table II, demonstrate the validity of the rate law corresponding to eq 10 and the independence of *k* of the concentrations of B and RX over the extensive ranges examined. With one exception, namely Co(saloph)(PPh_3), the values of K_f were sufficiently large so that formation of Co(saloph)B was essentially complete over the applicable concentration range of B and no correction for dissociation of Co(saloph)B was necessary. For Co(saloph)(PPh_3), the value of K_f (12 M^{-1}) was sufficiently low to necessitate such a correction; when this correction was applied the kinetic results conformed to eq 10 (Table II).

Values of *k* for all the reactions examined are listed in Table III.

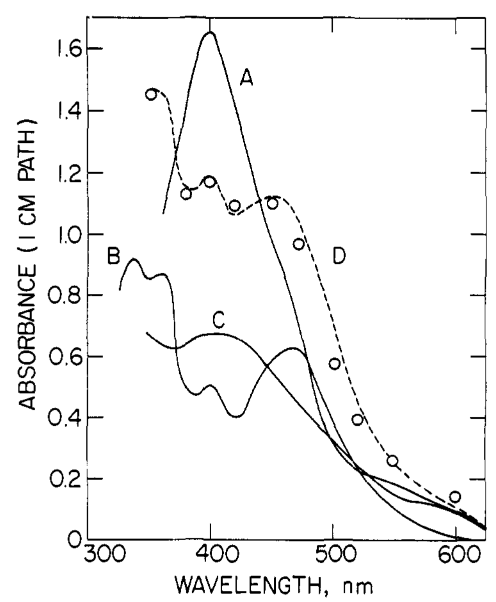

Figure 4. Spectral changes accompanying the reaction of 1.0 × 10^{-4} *M* Co(saloph)(1-MeIMD) with *p*-$CNC_6H_4CH_2I$ in the presence of 1 *M* 1-MeIMD: A, initial spectrum [1.0 × 10^{-4} *M* Co(saloph)(1-MeIMD)]; B, spectrum of 0.50 × 10^{-4} *M* [Co(saloph)(1-MeIMD)$_2$]ClO_4; C, spectrum of 0.50 × 10^{-4} *M* Co(saloph)(1-MeIMD)($CH_2C_6H_4CN$); D, calculated final spectrum (sum of B and C); ○, experimental absorbance values of final solution after reaction.

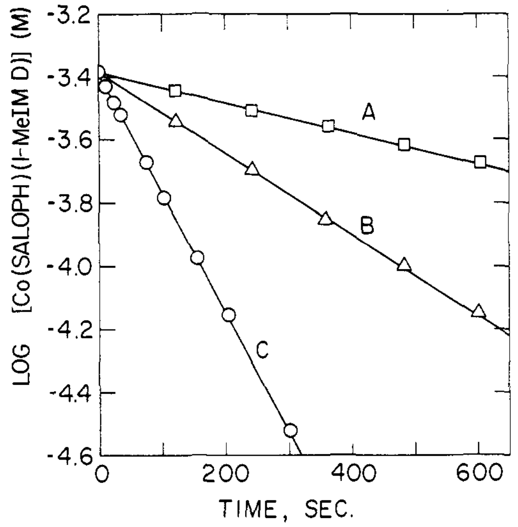

Figure 5. Representative pseudo-first-order rate plots for the reaction of Co(saloph)(1-MeIMD) with *p*-$CNC_6H_4CH_2Br$ in CH_2Cl_2 at 25°. [*p*-$CNC_6H_4CH_2Br$]: A, 0.104 *M*; B, 0.263 *M*; C, 0.71 *M*.

Discussion

The kinetic results are consistent with the proposed mechanism depicted by eq 4–7 in which the rate-determining step (corresponding to the rate constant *k*) involves halogen atom transfer from RX to Co(saloph)B. This mechanism is analogous to the mechanisms (eq 1–3) demonstrated previously for the reactions of other cobalt(II) complexes, notably $Co(CN)_5{}^{3-}$ and $Co(DH)_2B$, with organic halides.[2-4] The principal difference between the present system and the other ones is that, for the reasons already cited, one of the proposed products, namely Co(saloph)BX, is not directly observed but is rapidly transformed instead into Co(saloph)$B_2{}^+$.

Because of the latter circumstance the proposed atom-transfer mechanism is not demonstrated as conclusively for these reactions as for $Co(CN)_5{}^{3-}$ and $Co(DH)_2B$.

Table II. Representative Kinetic Data for Reactions of Co(saloph)B with *p*-Cyanobenzyl Halides (RX) in CH_2Cl_2 at 25° [a]

Axial ligand (B)	X	[B], *M*	[RX], *M*	k_{obsd}, sec^{-1}	*k*, M^{-1} sec^{-1}
Pyridine	Br	0.05	0.109	6.4×10^{-4}	2.9×10^{-3}
Pyridine	Br	0.10	0.227	13.6×10^{-4}	3.0×10^{-3}
Pyridine	Br	0.09	0.273	16.5×10^{-4}	3.0×10^{-3}
Pyridine	Br	0.10	0.458	23.6×10^{-4}	2.6×10^{-3}
Pyridine	Br	0.12	0.615	37.0×10^{-4}	3.0×10^{-3}
1-Methylimidazole	Br	0.06	0.710	8.7×10^{-3}	6.1×10^{-3}
1-Methylimidazole	Br	0.24	0.282	3.3×10^{-3}	5.9×10^{-3}
1-Methylimidazole	Br	0.14	0.263	3.1×10^{-3}	5.9×10^{-3}
1-Methylimidazole	Br	0.06	0.104	1.1×10^{-3}	5.3×10^{-3}
1-Methylimidazole	I	0.06	0.0070	0.7×10^{-2}	0.50
1-Methylimidazole	I	0.06	0.015	1.4×10^{-2}	0.47
1-Methylimidazole	I	0.06	0.025	2.6×10^{-2}	0.52
1-Methylimidazole	I	0.20	0.050	4.5×10^{-2}	0.45
Tri(*n*-butyl)phosphine	Br	0.05	0.014	6.8×10^{-3}	0.24
Tri(*n*-butyl)phosphine	Br	0.05	0.036	16.5×10^{-3}	0.23
Tri(*n*-butyl)phosphine	Br	0.07	0.045	22.4×10^{-3}	0.25
Tri(*n*-butyl)phosphine	Br	0.09	0.067	28.9×10^{-3}	0.22
Triphenylphosphine	I	0.0036	0.100	3.21×10^{-3}	0.38[b]
Triphenylphosphine	I	0.0071	0.048	2.56×10^{-3}	0.34[b]
Triphenylphosphine	I	0.0137	0.086	8.56×10^{-2}	0.36[b]
Triphenylphosphine	I	0.0270	0.025	4.28×10^{-3}	0.35[b]
Triphenylphosphine	I	0.054	0.020	5.78×10^{-3}	0.37[b]
Triphenylphosphine	I	0.081	0.017	5.78×10^{-3}	0.35[b]
Triphenylphosphine	I	0.352	0.011	5.78×10^{-3}	0.33[b]

[a] Initial Co(saloph)B concentration typically $1\text{–}5 \times 10^{-4}$ *M*. [b] Corrected for the dissociation of Co(saloph)B using the expression $k = k_{obsd}(1 + K_f[PPh_3])(K_f[PPh_3][RX])^{-1}$ and the value 12 M^{-1} for K_f. Values of *k* for other reactions are uncorrected.

Table III. Summary of Kinetic Data in CH_2Cl_2 at 25°

		k, M^{-1} sec^{-1}		
Axial ligand (B)	pK_a	*p*-$CNC_6H_4CH_2I$	*p*-$CNC_6H_4CH_2Br$	Other organic halides
3-Chloropyridine	2.8	$(1.4 \pm 0.1) \times 10^{-1}$	$(1.3 \pm 0.2) \times 10^{-3}$	
Pyridine	5.2	$(2.0 \pm 0.3) \times 10^{-1}$	$(2.9 \pm 0.3) \times 10^{-3}$	5.5×10^{-3} (*p*-$NO_2C_6H_4CH_2Br$)
3,4-Lutidine	6.2		$(4.5 \pm 0.2) \times 10^{-3}$	
1-Methylimidazole	7.0	$(4.9 \pm 0.4) \times 10^{-1}$	$(6.0 \pm 1.0) \times 10^{-3}$	
Benzylamine	9.3		$(8.0 \pm 1.0) \times 10^{-3}$	
Triphenylphosphine	2.7	$(3.5 \pm 0.4) \times 10^{-1}$	$(2.9 \pm 0.3) \times 10^{-3}$	
Methyldiphenylphosphine	~4.6	2.7 ± 0.3	$(3.7 \pm 0.1) \times 10^{-2}$	
Dimethylphenylphosphine	6.5		$(4.2 \pm 0.5) \times 10^{-1}$	7.5×10^{-4} (*p*-$CNC_6H_4CH_2Cl$)
Trimethylphosphine	8.7		$(9.0 \pm 0.5) \times 10^{-1}$	
Triethylphosphine	8.7		$(2.6 \pm 0.3) \times 10^{-1}$	
Tri(*n*-butyl)phosphine	8.4		$(2.4 \pm 0.2) \times 10^{-1}$	

Thus, our results would also be consistent with the alternative mechanistic sequence described by eq 12–14 in which the rate-determining step is electron transfer rather than atom transfer.

$$\text{Co(saloph)B} + \text{RX} \longrightarrow [\text{Co(saloph)B}^+ + \text{RX}^-] \longrightarrow$$

$$\text{Co(saloph)B}^+ + \text{R}\cdot + \text{X}^- \quad \text{(rate determining)} \qquad (12)$$

$$\text{Co(saloph)B} + \text{R} \longrightarrow \text{Co(saloph)BR} \qquad (13)$$

$$\text{Co(saloph)B}^+ + \text{B} \longrightarrow \text{Co(saloph)B}_2^+ \qquad (14)$$

However, we consider that the following two features of the results strongly favor the atom-transfer mechanism (eq 4–7) for these reactions. (1) Those reactions between cobalt(II) Schiff's base complexes and nitrobenzyl halides which have been shown to proceed through electron-transfer mechanisms have all involved six-coordinate (*e.g.*, Co(saloph)B_2) rather than five-coordinate complexes and exhibited third-order rate laws of the form k'[Co(saloph)B][RX][B],[8] instead of the second-order rate laws characteristic of atom-transfer reactions. (2) The large dependence of the rate on halogen variation, *i.e.*, $k_{RI}/k_{RBr} \sim k_{RBr}/k_{RCl} \sim 10^2$, is expected for and characteristic of halogen atom-transfer reactions[2–4] and is in marked contrast to the electron-transfer reactions with nitrobenzyl halides which were found to exhibit a much smaller halogen dependence, $k'_{RI}/k'_{RBr} \sim k'_{RBr}/k'_{RCl} < 10$.

The dependence of the rates on the axial ligand B constitutes a feature of the present reactions which was examined to a considerably greater degree than in the earlier related studies on other cobalt(II) complexes. Reference to Table III reveals that this dependence is fairly pronounced, the values of *k* for the reactions of Co(saloph)B with *p*-$CNC_6H_4CH_2Br$ spanning a *ca.* 10^3-fold range from 1.3×10^{-3} M^{-1} sec^{-1} for B = 3-chloropyridine to 0.9 M^{-1} sec^{-1} for B = $P(CH_3)_3$. For the amine ligands, *k* increases systematically with the basicity of B, in line with the expectation that the stabilization of cobalt(III) relative to cobalt(II), and hence the reactivity of the latter, will be enhanced by more basic ligands. However, for the phosphine ligands, among which the variation in *k* is considerably larger, this trend is not quite so clear and there are indications that steric factors[16] as well as ligand basicity may be of importance. We have observed similar trends in the reactivity of Co(DH)$_2$B complexes with organic halides.[3,17]

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