ence between these values and those reported for oxindigo.

[14] Address correspondence to this author.

Daniel L. Ross,[14] **Joseph Blanc, F. J. Matticoli**
RCA Laboratories
Princeton, New Jersey 08540
Received June 5, 1970

Reduction of Organic Halides by Cobalt(II) Schiff's Base Complexes. Evidence for an Electron-Transfer Mechanism

Sir:

Previous work[1-3] 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 = pyridine, triphenylphosphine, etc.) proceed according to the stoichiometry and mechanism depicted by

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

$$L_5Co^{II} + R\cdot \longrightarrow L_5Co^{III}R \quad (2)$$

$$\overline{2L_5Co^{II} + RX \longrightarrow L_5Co^{III}X + L_5Co^{III}R} \quad (3)$$

In this communication, we report the discovery and characterization of another class of reactions between cobalt(II) complexes and organic halides, which proceeds by a different and previously unrecognized mechanism involving "outer-sphere" electron transfer rather than halogen abstraction. Both types of reactions may yield organocobalt products.

The new class of processes that we wish to describe is exemplified by the reaction between *N,N'*-bis(salicylidene)ethylenediamino-1-methylimidazolecobalt(II) [Co(salen)(MeIMD)] and *p*-nitrobenzyl bromide (RX), which was found to proceed quantitatively in CH_2Cl_2 solution in the presence of excess MeIMD, in accord with the stoichiometry described by eq 4. The stoichiometry was established by isolation and full characterization (elemental, spectral, and nmr analysis) of the products [$Co(salen)(MeIMD)_2^+$ isolated as its bromide salt] and by quantitative matching of the spectrum of the final reaction solution with the known spectra of the products.

$$2Co(salen)(MeIMD) + RX + MeIMD \longrightarrow Co(salen)(MeIMD)_2^+ + Co(salen)(MeIMD)R + X^- \quad (4)$$

Kinetic measurements in which the reactions were followed spectrally and in which the initial solution composition was varied over the concentration ranges 1.2×10^{-4}–1.2×10^{-3} *M* Co(salen)(MeIMD), 0.4–3.0 *M* MeIMD,[4] and 1.4×10^{-3}–1.1×10^{-1} *M* RX, yielded the third-order rate law corresponding to eq 5 with $k_{exp} = 2.8 \pm 0.2\ M^{-2}\ sec^{-1}$ at 25° in CH_2Cl_2. We interpret these observations in terms of the mechanism depicted by eq 6–8, in which the rate-determining step is an outer-sphere electron transfer between $Co(salen)(MeIMD)_2$ and RX. According to this interpretation $k_{exp} = 2kK$.

$$-d[Co(salen)(MeIMD)]/dt = k_{exp}[Co(salen)(MeIMD)][RX][MeIMD] \quad (5)$$

$$Co(salen)(MeIMD) + MeIMD \overset{K}{\rightleftharpoons} Co(salen)(MeIMD)_2 \quad \text{(rapid equilibrium)} \quad (6)$$

$$Co(salen)(MeIMD)_2 + RX \xrightarrow{k} [Co(salen)(MeIMD)_2^+ + RX^-] \longrightarrow Co(salen)(MeIMD)_2^+ + R\cdot + X^- \quad \text{(rate determining)} \quad (7)$$

$$Co(salen)(MeIMD) + R\cdot \longrightarrow Co(salen)(MeIMD)R \quad \text{(rapid)} \quad (8)$$

Whether or not a radical anion intermediate (RX^-) of finite lifetime is formed is not established by our observations. However, evidence for such a species (which dissociates into R· and X^-) has previously been advanced in studies on the alkylation of various anions with *p*-nitrobenzyl halides[5] and on the electrochemical reduction of nitrobenzyl halides.[6]

The above reaction pattern appears to be conditioned by the strongly electron-accepting nitro group and has thus far been observed only for nitrobenzyl halides. Other benzyl halides, including, *p*-cyanobenzyl halides, were found to react more slowly with Co(salen)(MeIMD) and related cobalt(II) complexes by the "conventional" halogen-abstraction mechanism (eq 1–3) rather than by electron transfer. Even with *p*-nitrobenzyl halides, the electron-transfer mechanism was found to be favored only for certain ligand bases, notably imidazole (IMD) and MeIMD; with pyridine and substituted pyridines, the alternative abstraction mechanism was observed.[7,8] Kinetic data for several reactions which exhibited electron-transfer mechanisms are summarized in Table I. In a few cases *K* was sufficiently large that formation of the six-coordinate complex ($Co(saloph)(IMD)_2$, etc.) could be detected and the value of *K* determined from the dependence of k_{exp} on the free-ligand (IMD, etc.) concentration. For these reactions the individual values of *k* and *K* are listed; in other cases only limiting values can be given.

The variation in rates among the reactions in Table I is relatively small. A particularly striking feature is the very small reactivity difference between the chloride

---

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

[2] P. W. Schneider, P. F. Phelan, and J. Halpern, *ibid.*, **91**, 77 (1969).

[3] P. B. Chock and J. Halpern, *ibid.*, **91**, 582 (1969).

[4] The dissociation constant of Co(salen)(MeIMD) to Co(salen) + MeIMD was determined spectrophotometrically to be 3.8×10^{-2} *M*. Thus, over the MeIMD concentration range cited, the cobalt(II) was present virtually entirely as Co(salen)(MeIMD). The kinetic behavior described by eq 5 persisted to lower MeIMD concentrations (down to 0.02 *M*), provided that the necessary correction for the dissociation of Co(salen)(MeIMD) was applied.

[5] R. C. Kerber, G. W. Urry, and N. Kornblum, *J. Amer. Chem. Soc.*, **87**, 4520 (1965); N. Kornblum, R. E. Michel, and R. C. Kerber, *ibid.*, **88**, 5660 (1966); G. A. Russell and W. C. Danen, *ibid.*, **90**, 347 (1968).

[6] J. G. Lawless, D. E. Bartak, and M. D. Hawley, *ibid.*, **91**, 7121 (1969).

[7] L. G. Marzilli, P. A. Marzilli, and J. Halpern, submitted for publication.

[8] The magnetic behavior of cobalt(II) Schiff's base compounds is complex and not well understood.[9] The five-coordinate complexes (Co(salen)(MeIMD), etc.) exhibit temperature-dependent magnetic moments, characteristic of high-spin–low-spin equilibria, with values ranging from 2 to 3.5 BM at room temperature and approaching the limiting low-spin value of ~1.9 BM at low temperatures. MeIMD, which favors the high-spin form, is also among the most effective ligands in favoring the electron-transfer mechanism of reaction with *p*-nitrobenzyl halides. This is not unexpected since the equilibrium for formation of the six-coordinate species (eq 5) should be more favorable for high-spin complexes. A detailed account of magnetic studies on these complexes will be published elsewhere.

[9] A. Earnshaw, P. C. Hewlett, E. A. King, and L. F. Larkworthy, *J. Chem. Soc. A*, 241 (1968).

Table I. Kinetic Data in CH_2Cl_2 at 25°

Cobalt(II) complexes[a]	RX	kK (= $\frac{1}{2}k_{exp}$), M^{-2} sec^{-1}	K, M^{-1}	k, M^{-1} sec^{-1}
Co(salen)(MeIMD)	p-$NO_2C_6H_4CH_2Cl$	$(4.7 \pm 0.5) \times 10^{-1}$	<0.1	>4.7
Co(salen)(MeIMD)	p-$NO_2C_6H_4CH_2Br$	1.4 ± 0.1	<0.1	>14
Co(Me_2salen)(MeIMD)	p-$NO_2C_6H_4CH_2Br$	1.0 ± 0.2		
Co(saloph)(MeIMD)	p-$NO_2C_6H_4CH_2Cl$	$(1.8 \pm 0.3) \times 10^{-1}$	<0.5	>0.3
Co(saloph)(IMD)	p-$NO_2C_6H_4CH_2Cl$	2.7 ± 0.3	5.0 ± 0.5	$(5.4 \pm 0.5) \times 10^{-1}$
Co(saloph)(IMD)	p-$NO_2C_6H_4CH_2Br$	4.3 ± 0.5	5.0 ± 0.5	$(8.5 \pm 0.5) \times 10^{-1}$
Co(saloph)($BzNH_2$)	p-$NO_2C_6H_4CH_2Br$	4.0 ± 0.5	<0.5	>8
Co(saloph-Cl)(IMD)	p-$NO_2C_6H_4CH_2Cl$	~ 1	~ 1	1.0 ± 0.2
Co(saloph)(IMD)	o-$NO_2C_6H_4CH_2Cl$	1.5 ± 0.2	5.0 ± 0.5	$(3.1 \pm 0.3) \times 10^{-1}$

[a] In addition to those defined in the text, the following abbreviations are used in this table: Me_2salen = *N,N'*-bis(7-methylsalicylidene)-ethylenediamino, saloph = *N,N'*-bis(salicylidene)-*o*-phenylenediamino, saloph-Cl = *N,N'*-bis(salicylidene)-4-chloro-*o*-phenylenediamino, $BzNH_2$ = benzylamine.

and bromide, $k_{RBr}/k_{RCl} \sim 2$. This is in marked contrast to the reactivity patterns exhibited by those reactions which proceed by the halogen-abstraction mechanism (eq 1–3) for which, typically, $k_{RI}/k_{RBr} \sim k_{RBr}/k_{RCl} \sim 10^3$.[1,3,10] The latter trend reflects the well-known inverse dependence of reactivity on the carbon–halogen bond dissociation energy, and it is not surprising that this dependence should be much smaller for electron transfer than for atom abstraction. Attention is directed to the parallels between the two alternative mechanisms of reduction of organic halides by five-coordinate cobalt(II) complexes, revealed through these studies, and corresponding alternative mechanisms that have been observed in two other systems, namely (i) the reactions of pyridinyl radicals with halocarbons[11] and (ii) the reductions of $Co^{III}(NH_3)_5X$ complexes (X = F, etc.) by $Co(CN)_5{}^{3-}$, which may occur either through inner-sphere electron transfer (corresponding to X atom abstraction by $Co(CN)_5{}^{3-}$) or through outer-sphere electron transfer from $Co(CN)_6{}^{4-}$.[12]

In contrast to the five-coordinate complexes discussed above, six-coordinate cobalt(II) complexes are expected to reduce organic halides only through electron transfer and to exhibit modified stoichiometry, since radical capture by cobalt according to eq 2 or 8 is precluded. These expectations were realized for the high-spin octahedral cobalt(II) complex, bis(*N*-methyl-*N'*-(salicylidene)ethylenediamino)cobalt(II),[13] (Co(sal-Meen)$_2$, μ = 4.6 BM at 22°), which was found to react with a variety of nitrobenzyl halides to form the corresponding bibenzyls (R_2) according to the stoichiometry described by eq 9[14] and according to the second-order rate law $-d[Co(sal\text{-}Meen)_2]/dt = k'[Co(sal\text{-}Meen)_2][RX]$. These results are consistent with the expected mechanism depicted by eq 10 and 11.

$$Co(sal\text{-}Meen)_2 + RX \longrightarrow Co(sal\text{-}Meen)_2{}^+ + \tfrac{1}{2}R_2 + X^- \quad (9)$$

$$Co(sal\text{-}Meen)_2 + RX \xrightarrow{k'} [Co(sal\text{-}Meen)_2{}^+ + RX^-] \longrightarrow Co(sal\text{-}Meen)_2{}^+ + R\cdot + X^- \quad \text{(rate determining)} \quad (10)$$

$$2R\cdot \longrightarrow R_2 \quad (11)$$

Table II. Rate Constants for the Reactions of Co(sal-Meen)$_2$ in CH_2Cl_2 at 25°

Organic halide	k', M^{-1} sec^{-1}
p-$NO_2C_6H_4CH_2I$	$(7.9 \pm 0.4) \times 10^2$
p-$NO_2C_6H_4CH_2Br$	$(6.8 \pm 1.0) \times 10^2$
p-$NO_2C_6H_4CH_2Cl$	$(1.2 \pm 0.1) \times 10^2$
o-$NO_2C_6H_4CH_2I$	$(9.0 \pm 0.6) \times 10^2$
o-$NO_2C_6H_4CH_2Cl$	$(2.2 \pm 0.3) \times 10^2$
m-$NO_2C_6H_4CH_2I$	$(9.2 \pm 0.7) \times 10^{-1}$
m-$NO_2C_6H_4CH_2Br$	$(9.5 \pm 1.0) \times 10^{-2}$ [a]

[a] 2.8 ± 0.3 M^{-1} sec^{-1} in CH_3CN.

The rate constants listed in Table II reveal large decreases in reactivity in going from the *o*- or *p*- to the *m*-nitrobenzyl halides (consistent with the more negative reduction potentials of the latter),[6] but again only a relatively small dependence on halogen variation. The 30-fold increase in the rate of reaction of m-$NO_2C_6H_4CH_2Br$ in going from CH_2Cl_2 to CH_3CN (*i.e.*, with increasing solvent polarity) is consistent with the proposed electron-transfer mechanism.[11]

Acknowledgments. Support of this work through grants from the National Institutes of Health, the National Science Foundation, and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

* Address correspondence to this author.

Luigi G. Marzilli, Patricia A. Marzilli, Jack Halpern*
Department of Chemistry, University of Chicago
Chicago, Illinois 60637

Received July 16, 1970

---

[10] This was found to be the case also for those reactions of cobalt(II) Schiff's base complexes with organic halides which proceed through halogen-abstraction mechanisms.[7]

[11] E. M. Kosower and M. Mohammad, *J. Amer. Chem. Soc.*, **90** 3271 (1968).

[12] J. P. Candlin, J. Halpern, and S. Nakamura, *ibid.*, **85**, 2517 (1963); J. Halpern and S. Nakamura, *Proc. Int. Conf. Coord. Chem., 8th, 1964*, 271 (1965); *J. Amer. Chem. Soc.*, **87**, 3002 (1965).

[13] L. Sacconi, M. Ciampolini, and G. P. Speroni, *Inorg. Chem.*, **4**, 1116 (1965).

[14] The stoichiometry was confirmed by isolation and characterization of the products of reaction with *p*-nitrobenzyl bromide and by matching of the spectra of the final reaction solutions with the known spectra of the products.

Nucleophilic Methylene Transfer Reagents. Anions of *N*-*p*-Toluenesulfonyl Sulfoximines[1]

Sir:

A generalized scheme for nucleophilic methylene transfer reactions to electrophilic double bonds is illustrated in eq 1. The success of reagent **1** is dependent on the ability of group Z to stabilize the adjacent carbanion and to function as a leaving group. In typical cases of such reactions both the reagent **1** and leaving group **3** are neutral molecules; examples are sulfonium ylides[2] and diazoalkanes.[3] In this

---

[1] Part XXVIII in the series "Chemistry of Sulfoxides and Related Compounds." We gratefully acknowledge support by the National Science Foundation (Grant No. GP 8648).

[2] For examples see E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **89**, 1353 (1967); E. J. Corey and M. Jautelat, *ibid.*, **89**, 3912 (1967); C. R. Johnson, E. R. Janiga, and M. Haake, *ibid.*, **90**, 3890 (1968).

[3] C. D. Gutsche, *Org. React.*, **8**, 364 (1954).