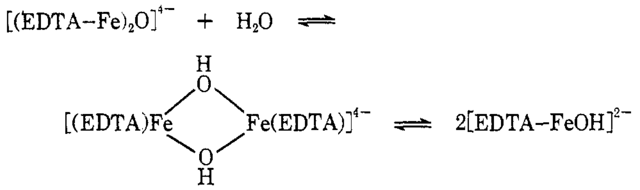
$((H_2O)_4FeOH)_2^{4+}$, a mechanism involving only dissociative activation of the strong Fe–O–Fe bond is not particularly attractive. It is reasonable to expect that oxo-bridged dimer breakup follows a pathway involving some assistance due to binding of an entering H_2O molecule. In our proposed mechanism, a symmetrical dihydroxo-bridged complex presumably acts as an unstable intermediate.



The instability of the dihydroxo-bridged complexes in Fe^{III}-EDTA and Fe^{III}-HEDTA systems can be understood because of the expected strain in the bridge of a seven-coordinate structure.

An alternative process for dimer breakup could involve intramolecular assistance from one of the two acetate groups which are likely to be uncoordinated in each Fe^{III}-EDTA dimer. Such a process does not appear consistent with the qualitative observation that the dimer containing HEDTA dissociates at least as fast as $(EDTA\text{-}Fe)_2O^{4-}$. Independent measurements of k_f for both of these dimers by the stopped-flow technique are now in progress.[19]

Acknowledgments. The initial studies involved chronopotentiometric measurements at Columbia University; we thank Professor William Reinmuth and his group for their help in this work. We also thank Dr. Stephen Feldberg of the Brookhaven National Laboratory for supplying the computer working curves required for the kinetic analysis presented in this paper.

(19) J. Earley, private communication.

Kinetics of the Reactions of Bis(glyoximato)cobalt(II) Complexes with Organic Halides[1]

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Abstract: Various bis(glyoximato)cobalt(II) complexes of the types[2] $Co(DH)_2B$ and $Co(DH)_2B_2$ were found to react quantitatively with benzyl bromide in benzene and acetone solutions to yield $PhCH_2Co(DH)_2B$ and $BrCo(DH)_2B$ according to eq 5 and 6. Evidence is presented that the $Co(DH)_2B_2$ compounds are completely dissociated in solution into $Co(DH)_2B$ and B. All the reactions exhibited second-order kinetics, according to the rate law, $k[Co(DH)_2B][PhCH_2Br]$. At 25°, the value of k for the reaction of pyridinatobis(dimethylgloximato)cobalt(II) in benzene solution is $3.0 \times 10^{-1}\ M^{-1}\ sec^{-1}$. The value of k increases slightly with the basicity of the axial ligand B but is relatively insensitive to variation of the glyoxime ligand. 1-Bromoethylbenzene reacts similarly but at a significantly higher rate. The results are interpreted in terms of a free-radical mechanism, depicted by eq 11 and 12, analogous to that previously proposed for the reactions of pentacyanocobaltate(II) with organic halides. This mechanism involves a rate-determining halogen-atom abstraction by the cobalt(II) complexes.

Considerable interest has been evidenced in recent years in reactions of low-spin complexes of cobalt(I) and cobalt(II) with organic halides to form organocobalt compounds. Such reactions have been described for pentacyanocobaltate(II)[3-5] as well as for cobalt complexes of dimethylglyoxime (cobaloximes),[6-8] and of Schiff bases derived from salicylaldehyde[9] and from acetylacetone.[10] Contributing to the great interest in this subject are the striking parallels, revealed particularly by the work of Schrauzer,[11] between these reactions and the corresponding reactions of the reduced forms of vitamin B_{12}, *i.e.*, vitamin B_{12s} and vitamin B_{12r}.

Two such reactions that have received particular attention and that have been the subjects of kinetic investigations are (i) the reactions of pentacyanocobaltate(II) with a variety of organic halides[3-5] ($RX = CH_3I$, etc.) according to eq 1

$$2Co(CN)_5^{3-} + RX \longrightarrow RCo(CN)_5^{3-} + XCo(CN)_5^{3-} \qquad (1)$$

(ii) the reactions of cobaloximes(I) (*e.g.*, tributylphosphinebis(dimethylglyoximato)cobalt(I), $Co(DMH)_2PBu_3^-$), with organic halides, according to eq 2.

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(2) The following abbreviations are used throughout this paper to designate the various ligands: DH_2 = any glyoxime including one of the following: DMH_2 = dimethylglyoxime, *i.e.*, $HON{=}C(CH_3)C(CH_3){=}NOH$; DPH_2 = diphenylglyoxime; $DMPH_2$ = 4,4′-dimethoxydiphenylglyoxime; $DNPH_2$ = 4,4′-dinitrodiphenylglyoxime. B = any Lewis base serving as an axial ligand including one of the following: PPh_3 = triphenylphosphine; pyr = pyridine; pic = γ-picoline; nic = nicotinamide.

(3) J. Halpern and J. P. Maher, *J. Am. Chem. Soc.*, **86**, 2311 (1964).

(4) J. Halpern and J. P. Maher, *ibid.*, **87**, 5361 (1965).

(5) J. Kwiatek and J. K. Seyler, *J. Organometal. Chem.*, **3**, 421 (1965).

(6) G. N. Schrauzer and J. Kohnle, *Chem. Ber.*, **97**, 3056 (1964).

(7) G. N. Schrauzer and R. J. Windgassen, *J. Am. Chem. Soc.*, **88**, 3738 (1966).

(8) G. N. Schrauzer and R. J. Windgassen, *ibid.*, **89**, 1999 (1967).

(9) G. Costa, G. Mestroni, and G. Pellizer, *J. Organometal. Chem.*, 11, 333 (1968).

(10) G. Costa and G. Mestroni, *ibid.*, **11**, 325 (1968).

(11) See G. N. Schrauzer, *Accounts Chem. Res.*, **1**, 97 (1968), and references therein.

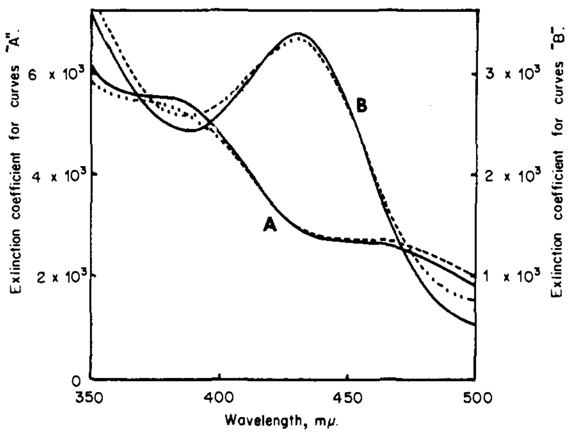

Figure 1. Absorption spectra in benzene solution of (A) $\mathrm{Co(DMH)_2PPh_3}$ (- - -) and $\mathrm{Co(DMH)_2(PPh_3)_2}$ (——); (B) $\mathrm{Co(DMH)_2pyr}$ (- - ·) and $\mathrm{Co(DMH)_2(pyr)_2}$ (——). Addition of up to 0.1 *M* $\mathrm{PPh_3}$ to A and of up to 0.1 *M* pyr to B did not affect the spectra.

$$\mathrm{Co(DMH)_2PBu_3^- + RX \longrightarrow RCo(DMH)_2PBu_3 + X^-} \quad (2)$$

These two reactions have been shown to proceed with quite different mechanisms and to exhibit quite different reactivity patterns (*i.e.*, dependence on variations in RX). For reaction 1, a free-radical mechanism corresponding to eq 3 and 4 has been proposed.[4,5]

$$\mathrm{Co(CN)_5^{3-} + RX \longrightarrow XCo(CN)_5^{3-} + R\cdot}\ \text{(rate determining)} \quad (3)$$

$$\mathrm{Co(CN)_5^{3-} + R\cdot \longrightarrow RCo(CN)_5^{3-}} \quad (4)$$

Reaction 2, on the other hand, and the corresponding reactions of vitamin $\mathrm{B_{12s}}$ have been formulated[12] as direct nucleophilic displacements (SN2 reactions) of the halide by cobalt(I). A striking feature of these reactions is the very high nucleophilicity exhibited by these cobalt(I) complexes.

Because the above two reactions involve complexes of cobalt which differ in respect both of the nature of the ligands and of the oxidation states of the cobalt, it seemed of interest to examine the reactions of organic halides with some cobalt complexes which would permit an assessment of the influence of each of these factors separately. We have therefore examined the kinetics of the reactions, described by eq 5 and 6, of a series of bis(glyoximato)cobalt(II) complexes of the types $\mathrm{Co(DH)_2B}$ and $\mathrm{Co(DH)_2B_2}$[2] with benzyl bromide and with 1-bromoethylbenzene. The results of this investigation, which include an examination of the effects of variation of both the glyoximate ligands, $\mathrm{DH^-}$, and the axial ligands, B, are presented in this paper.

$$\mathrm{2Co(DH)_2B + RX \longrightarrow RCo(DH)_2B + XCo(DH)_2B} \quad (5)$$

$$\mathrm{2Co(DH)_2B_2 + RX \longrightarrow RCo(DH)_2B + XCo(DH)_2B + 2B} \quad (6)$$

Experimental Section

Materials. **α-4,4′-Dimethoxydiphenylglyoxime** ($\mathrm{DMPH_2}$) was prepared from anisoin by oxidation with $\mathrm{KMnO_4}$ to anisil,[13] followed by treatment with $\mathrm{NH_2OH\cdot HCl}$.[14] **α-4,4′-Dinitrodiphenylglyoxime** ($\mathrm{DNPH_2}$) was prepared according to Brydowna[15] from 4,4′-dinitrobenzil which in turn had been prepared by zinc-hydrochloric acid reduction of benzaldehyde to hydrobenzoin[16] followed by nitration and oxidation.[17] **Dimethylglyoxime** ($\mathrm{DMH_2}$) (Baker) was recrystallized from ethanol. **Diphenylglyoxime** ($\mathrm{DPH_2}$) (Eastman, mp 235–237°) was used without purification.

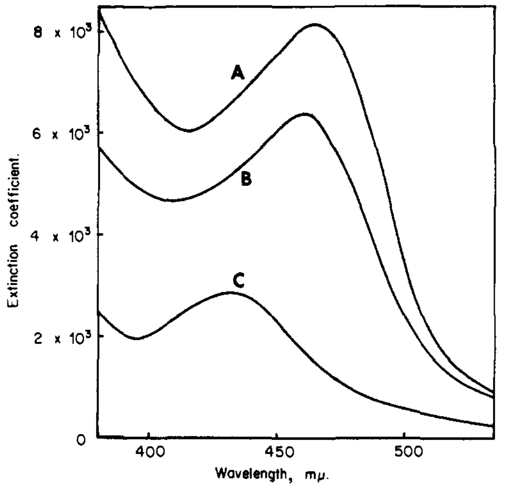

Figure 2. Absorption spectra in benzene solution of (A) $\mathrm{Co(DMPH)_2pyr}$, (B) $\mathrm{Co(DPH)_2(pyr)_2}$, (C) $\mathrm{Co(DMH)_2(pic)_2}$.

Cobaltous acetate, acetone, benzene, methanol, nicotinamide, pyridine, and γ-picoline were AR quality reagents. Triphenylphosphine (Matheson Coleman and Bell) was recrystallized from ethanol. Benzyl bromide (Aldrich) and 1-bromoethylbenzene (Eastman) were redistilled under reduced pressure and the fractions with $n^{20}\mathrm{D}$ 1.5421 and $n^{20}\mathrm{D}$ 1.562, respectively, used for the kinetic measurements.

Preparation of Cobalt(II) Complexes. The bis(glyoximato)cobalt(II) complexes (cobaloximes(II)) were prepared according to Schrauzer and Windgassen,[18] in a system purged continuously with nitrogen (Linde H.P., dry). For complexes of the type $\mathrm{Co(DH)_2B}$, stoichiometric amounts of the ligand B were used; for those of the type $\mathrm{Co(DH)_2B_2}$, B was in at least fourfold excess. In the cases of $\mathrm{Co(DMH)_2(PPh_3)_2}$ and, especially, $\mathrm{Co(DMH)_2(pyr)_2}$, where washing of the product with oxygen-free methanol converted it in part to $\mathrm{Co(DMH)_2B}$, it was necessary to suspend the washed and dried product in oxygen-free benzene, to reflux the solution for 30 min in the presence of an excess of B, and then to filter under nitrogen and wash the product with oxygen-free benzene. With the exception of $\mathrm{Co(DMH)_2pic}$, and possibly also of $\mathrm{Co(DPH)_2pyr}$ and $\mathrm{Co(DMPH)_2(pyr)_2}$, the cobaloximes(II), after drying in a nitrogen atmosphere, were stable in air and showed no sign of decomposition or oxidation over a period of several weeks. Analytical and magnetic data for the cobalt(II) complexes are reported in Table I and their spectra are depicted in Figures 1 and 2.

Synthesis of Reaction Products. Compounds of the type $\mathrm{BrCo(DH)_2B}$ were synthesized according to Tschugaeff.[19] The $\mathrm{PhCH_2Co(DH)_2B}$ compounds were prepared by procedures analogous to those of Schrauzer and Windgassen.[7] *Anal.* Calcd for $\mathrm{PhCH_2Co(DMH)_2pyr}$: C, 52.25; H, 5.71; N, 15.30. Found: C, 52.03; H, 5.96; N, 15.08. Calcd for $\mathrm{BrCo(DMH)_2pyr}$: C, 34.80; H, 4.27; N, 15.65; Br, 17.81. Found: C, 34.90; H, 4.24; N, 15.64; Br, 17.81. Calcd for $\mathrm{PhCH_2Co(DMH)_2PPh_3}$: C, 61.75; H, 5.66; N, 8.71; P, 4.82. Found: C, 62.00; H, 5.61; N, 8.70; P, 4.91. Calcd for $\mathrm{BrCo(DMH)_2PPh_3}$: C, 49.51; H, 4.55; N, 8.88; Br, 12.67. Found: C, 49.71; H, 4.64; N, 8.63; Br, 12.57. The spectra of these compounds are depicted in Figures 3 and 4.

Kinetic Measurements. Because of the sensitivity of the cobaloxime(II) solutions toward oxygen, all manipulations were conducted under a nitrogen atmosphere. The rates of reaction of the cobaloximes(II) with the organic halides, in benzene and acetone solution, were measured spectrophotometrically in a Cary 14 spectrophotometer by following the decrease in the absorbance of the cobaloxime(II) at an appropriate wavelength (see Figures 1 and 2) in the range 400–520 mμ. The solid cobalt(II) complexes, in volumetric flasks, were purged with nitrogen for at least 40 min and then dissolved in deoxygenated benzene or acetone (with slight warming if necessary). Evaporation of the solvent, as well as con-

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[12] G. N. Schrauzer, E. Deutsch, and R. J. Windgassen, *J. Am. Chem. Soc.*, **90**, 2441 (1968).

[13] J. C. Irvine and A. M. Moodie, *J. Chem. Soc.*, **91**, 536 (1907).

[14] R. Stierlin, *Chem. Ber.*, **22**, 377 (1889).

[15] W. Brydowna, *Roczniki Chem.*, **18**, 396 (1938).

[16] S. Danilov, *Chem. Ber.*, **60**, 2390 (1927).

[17] F. D. Chattaway and E. A. Coulson, *J. Chem. Soc.*, 1361 (1928).

[18] G. N. Schrauzer and R. J. Windgassen, *Chem. Ber.*, **99**, 602 (1966).

[19] L. Tschugaeff, *ibid.*, **40**, 3698 (1907).

Table I. Analytical and Magnetic Data for the Cobalt(II) Complexes

	Calcd, %					Found, %					μ_{eff}, BM
Complex	C	H	N	Co	P	C	H	N	Co	P	(±10%)
$Co(DMH)_2PPh_3$	56.60	5.31	10.15	10.68		57.36	5.43	9.89	10.67		2.0
$Co(DMH)_2(PPh_3)_2$	65.00	5.45	16.88	7.25	7.62	65.30	5.66	6.95	7.29	7.75	2.1
$Co(DMH)_2pyr$	42.35	5.20	19.02	16.00		41.99	5.32	18.80	16.08		2.0
$Co(DMH)_2(pyr)_2$	48.32	5.41	18.80	13.25		48.22	5.49	18.90	13.29		1.9
$Co(DMH)_2nic$	40.95	4.91	20.45	14.34		40.89	5.00	20.73	16.35		2.0
$Co(DMH)_2(nic)_2$	45.10	4.92	21.00	11.05		47.77	4.95	21.49	10.94		1.8
$Co(DMH)_2(pic)_2$	50.05	5.94	17.75	12.38		50.10	6.22	17.65	12.83		2.2
$Co(DPH)_2(pyr)_2$	65.50	4.64	12.08	8.45		65.99	4.67	13.96	8.76		2.0
$Co(DMPH)_2pyr$	60.20	4.79	9.50	8.00		59.41	5.19	9.14	8.93		2.2
$Co(DMPH)_2(pyr)_2$	61.75	4.93	10.40	7.22		61.99	5.07	10.23	8.48		1.9
$Co(DNPH)_2pyr$	49.70	2.91	15.80	7.39		48.91	2.93	15.25	8.25		1.9
$Co(DNPH)_2(pyr)_2$	53.00	3.22	15.95	7.73		49.82	2.99	16.04	7.21		1.4

tact of the solvent vapor with the rubber serum caps, was minimized by continuously passing a stream of nitrogen *parallel* to the surface of the solution, at a distance of about 5 cm above the surface, through a cross of glass tubing below the serum cap. Samples were withdrawn with a hypodermic syringe and injected through rubber serum caps into nitrogen-filled quartz spectrophotometer cells. The cells were thermostated at 25 ± 0.2° by immersion in a water bath or storage in the thermostated cell compartment of the Cary 14 spectrophotometer. The reaction was initiated by rapid injection of the organic halide with a hypodermic syringe.

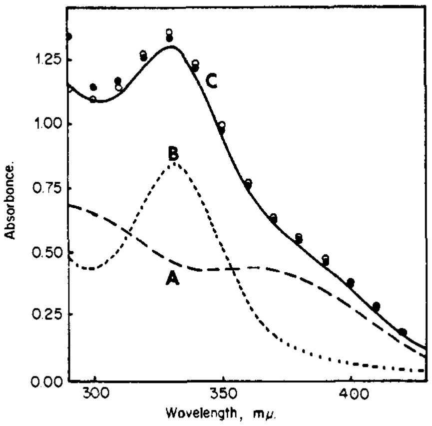

Figure 3. Absorption spectra in benzene solution of (A) 3.0 × 10^{-5} *M* $PhCH_2Co(DMH)_2PPh_3$, (B) 3.0 × 10^{-5} *M* $BrCo(DMH)_2PPh_3$. C is the sum of spectra A and B. The points correspond to the experimental absorbancies of the product solutions from the reaction of excess $PhCH_2Br$ with 6.0 × 10^{-5} *M* $Co(DMH)_2PPh_3$ (○) and with 6.0 × 10^{-5} *M* $Co(DMH)_2(PPh_3)_2$ (●).

Physical Measurements. Ultraviolet and visible spectra were recorded with a Cary 14 spectrophotometer. Magnetic susceptibilities of the solid cobaloximes(II) were measured at room temperature by the Faraday method, using a Cahn RG electrobalance equipped with a Sargent SR recorder and an Alpha 7500 electromagnet operated at 3–8 A. Diamagnetic corrections for the ligands were made using the values given by Figgis and Lewis.[20] The paramagnetism of solutions of the cobaloximes(II) in benzene was demonstrated by the observation of epr signals (Varian E3 epr spectrometer) and by nmr measurements (Varian A-60 nmr spectrometer) according to the method of Evans.[21]

Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. and by Bernhardt Mikroanalytisches Laboratorium, Mülheim, Germany.

Results and Discussion

Constitution of the Cobalt(II) Complexes. Convincing evidence was accummulated during the course of this investigation in support of the conclusions that (i) both the $Co(DH)_2B$ and $Co(DH)_2B_2$ complexes are monomeric in their solid forms, as well as in benzene solution, and (ii) the $Co(DH)_2B_2$ complexes are essentially completely dissociated in solution into $Co(DH)_2B$ and B. These conclusions are supported by the following observations.[22]

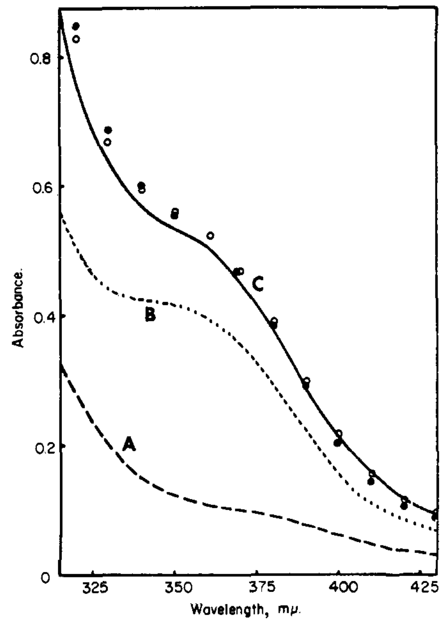

Figure 4. Absorption spectra in benzene solution of (A) 5.0 × 10^{-5} *M* $BrCo(DMH)_2pyr$ and (B) 5.0 × 10^{-5} *M* $PhCH_2Co(DMH)_2pyr$. C is the sum of spectra A and B. The points correspond to the experimental absorbancies of the product solution from the reaction of excess $PhCH_2Br$ with 1.0 × 10^{-4} *M* $Co(DMH)_2pyr$ (○) and with 1.0 × 10^{-4} *M* $Co(DMH)_2(pyr)_2$ (●).

1. All of the solid cobalt(II) complexes examined, both of the $Co(DH)_2B_2$ and $Co(DH)_2B$ types (with the exception of $Co(DNPH)_2(pyr)_2$ which had a slightly lower moment) exhibited paramagnetic moments in the range 1.8–2.2 BM, *i.e.*, close to the values expected for a low-spin d^7 complex having one unpaired electron

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(20) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, p 403.

(21) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(22) These observations and conclusions appear to be at variance with earlier ones of Schrauzer,[23] who described compounds of the composition $Co(DH)_2B$ as being dimeric and, presumably, diamagnetic. The possibility cannot be excluded that, notwithstanding their similar chemical compositions, the compounds prepared by him and by us are different. Similar conflicting evidence has accumulated concerning the monomeric and/or dimeric configurations of another low-spin d^7 complex, $Mn(CO)_4PPh_3$.[24]

(23) G. N. Schrauzer, R. J. Windgassen, and J. Kohnle, *Chem. Ber.*, **98**, 3324 (1965).

(24) H. Wawerisk and F. Basolo, *Chem. Commun.*, 366 (1966).

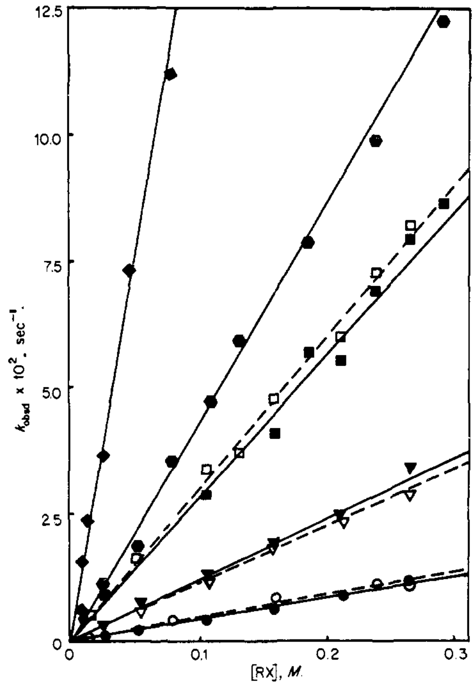

Figure 5. Representative plots depicting the first-order dependence of k_{obsd} on the concentration of RX: (○) $Co(DMH)_2PPh_3$ and (●) $Co(DMH)_2(PPh_3)_2$ (both with $PhCH_2Br$ in benzene); (▽) $Co(DNPH)_2pyr$ and (▼) $Co(DNPH)_2(pyr)_2$ (both with $PhCH_2Br$ in acetone); (□) $Co(DMH)_2pyr$ and (■) $Co(DMH)_2(pyr)_2$ (both with $PhCH_2Br$ in benzene); (⬢) $Co(DMH)_2(pic)_2$ with $PhCH_2Br$ in benzene; (◆) $Co(DMH)_2(pyr)_2$ with $PhCH(CH_3)Br$ in benzene.

(Table I). Powdered samples of $Co(DMH)_2PPh_3$, $Co(DMH)_2(PPh_3)_2$, $Co(DMH)_2pyr$, and $Co(DMH)_2(pyr)_2$ all gave intense epr signals.

2. Magnetic susceptibility and epr measurements confirmed, qualitatively at least, that benzene solutions of complexes of the $Co(DH)_2B$ type as well as of the $Co(DH)_2B_2$ type are paramagnetic. Magnetic susceptibility measurements, made by the Evans method,[21] although of low accuracy, yielded values of the order of 2 BM for the paramagnetic moments of both $Co(DMH)_2PPh_3$ and $Co(DMH)_2(PPh_3)_2$ in benzene solution. Furthermore, the epr spectra of the two solutions were *identical*, as were those of a pair of solutions containing equal concentrations of $Co(DMH)_2pyr$ and $Co(DMH)_2(pyr)_2$. The epr signal in each case was very broad (500–1000 G), and no fine structure due to phosphorus or nitrogen splitting could be resolved even at liquid nitrogen temperatures.[25]

3. The visible–uv spectra of representative $Co(DH)_2B$ complexes and of the corresponding $Co(DH)_2B_2$ complexes, when compared, coincided within experimental errors (see Figure 1) and, furthermore, were unaffected by the addition of up to at least 0.1 *M* excess B.

4. As will be shown subsequently, the rates of reaction with benzyl bromide of the $Co(DH)_2B$ complexes were found to be virtually identical with those of the corresponding $Co(DH)_2B_2$ complexes and were unaffected by the addition of up to about 0.1 *M* excess B.

We thus conclude that in the solutions in which the reactions were studied, all the cobalt(II) complexes were present predominantly in the form of $Co(DH)_2B$ and that the reaction of benzyl bromide, in each case, was with the latter species.

Stoichiometry and Products. While it proved possible in certain cases to isolate, by standard methods, pure samples of the proposed reaction products, $PhCH_2Co(DH)_2B$ and $BrCo(DH)_2B$, from the final reaction solutions and, thus, to provide qualitative support for the proposed stoichiometry, this was insufficient to establish the stoichiometry quantitatively. Quantitative confirmation of the proposed stoichiometry, described by eq 5 and 6, was, however, obtained by comparison of the spectra of the reaction solutions, following completion of reaction, with the spectra of solutions containing the corresponding equimolar concentrations of independently synthesized $PhCH_2Co(DH)_2B$ and $BrCo(DH)_2B$. These comparisons are shown for the reactions of $PhCH_2Br$ with $Co(DMH)_2PPh_3$ and with $Co(DMH)_2(PPh_3)_2$ in Figure 3, and for the reactions of $PhCH_2Br$ with $Co(DH)_2pyr$ and $Co(DH)_2(pyr)_2$ in Figure 4. The observed and predicted spectra, in each case, agree within experimental error. The spectral changes accompanying the other reactions were qualitatively similar to those in Figures 3 and 4 and, although not confirmed quantitatively, it seems safe to assume that the same stoichiometry applies.

Kinetics. Each of the reactions was shown to exhibit second-order kinetics, first order in each of the reactants, according to the rate law

$$-d[Co^{II}]/dt = k[Co^{II}][RX] \qquad (7)$$

where Co^{II} stands for the cobalt(II) complex, the predominant and reactive form of which, as explained earlier, is believed to be $Co(DH)_2B$. Under the conditions of our measurements, *i.e.*, with RX (5×10^{-3} to 3×10^{-1} *M*) in substantial excess over Co^{II} (10^{-4} to 10^{-3} *M*), the observed kinetics were pseudo-first order, *i.e.*

$$-d \ln [Co^{II}]/dt = k_{obsd} = k[RX] \qquad (8)$$

Pseudo-first-order rate constants, determined from the slopes of first-order rate plots, and generally reproducible to ±5%, were plotted against the concentration of RX to yield linear plots such as those in Figure 5, The values of *k*, derived from the slopes of these plots, are summarized in Table II.

The most extensive and detailed kinetic measurements were made in benzene solution.[27] In addition to quantitatively establishing (i) the reaction stoichiometry and (ii) the second-order kinetic behavior in this medium, it was also established (iii) that the rates of reaction were identical within experimental error, for $Co(DMH)_2PPh_3$ and $Co(DMH)_2(PPh_3)_2$ as well as for $Co(DMH)_2pyr$ and $Co(DMH)_2(pyr)_2$ and (iv) that the rate in each case was unaffected by the addition of up to 0.1 *M* B (triphenylphosphine and pyridine, respectively).

Because of solubility limitations, it proved impossible to extend the measurements in benzene to all the cobalt(II) complexes of interest. Some additional kinetic measurements (also summarized in Table II) were

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(25) Similarly broad epr spectra have been observed for cobalt(II) phthalocyanine complexes by Assour.[26]

(26) J. M. Assour, *J. Am. Chem. Soc.*, 87, 4701 (1965).

(27) Initial attempts to examine these reactions in aqueous methanol solution were abandoned because of indications of instability of the cobalt(II) complexes in this medium, particularly at pH >6. This instability is presumably associated with the disproportionation of cobalt(II). Benzene and acetone solutions of the cobalt(II) complexes, on the other hand, proved to be quite stable and well behaved as reaction media.

Table II. Summary of Kinetic Measurements[a]

Complex		k in benzene, M^{-1} sec^{-1}		k in acetone, M^{-1} sec^{-1}	
DH	B	$Co(DH)_2B$	$Co(DH)_2B_2$	$Co(DH)_2B$	$Co(DH)_2B_2$
DMH	PPh_3	$(4.3 \pm 0.3) \times 10^{-2}$ [b]	$(4.2 \pm 0.4) \times 10^{-2}$ [b]	$(4.7 \pm 0.2) \times 10^{-2}$	$(4.8 \pm 0.2) \times 10^{-2}$
DMH	nic	...	...	$(1.9 \pm 0.2) \times 10^{-1}$	$(2.4 \pm 0.2) \times 10^{-1}$
DMH	pyr	$(3.0 \pm 0.2) \times 10^{-1}$ [b]	$(2.8 \pm 0.3) \times 10^{-1}$ [b] (1.4 ± 0.2)[c]	$(3.4 \pm 0.3) \times 10^{-1}$	$(3.8 \pm 0.2) \times 10^{-1}$
DMH	pic	...	$(4.3 \pm 0.2) \times 10^{-1}$	...	$(4.4 \pm 0.3) \times 10^{-1}$
DPH	pyr	...	$(2.6 \pm 0.1) \times 10^{-1}$	...	$(7.3 \pm 0.3) \times 10^{-1}$
DMPH	pyr	$(2.6 \pm 0.2) \times 10^{-1}$	$(2.8 \pm 0.2) \times 10^{-1}$	$(5.3 \pm 0.2) \times 10^{-1}$	...
DNPH	pyr	...	...	$(1.1 \pm 0.1) \times 10^{-1}$	$(1.2 \pm 0.1) \times 10^{-1}$

[a] Values of k are at 25° for the reaction with $PhCH_2Br$ except where otherwise noted. [b] Unaffected by the addition of up to 0.1 M B. [c] This value is for the reaction with $PhCH(CH_3)Br$.

therefore made in acetone solution. These measurements were confined to (i) establishing the second-order kinetic behavior for each of the reactions, (ii) determining the second-order rate constants, k, and (iii) demonstrating that in this solvent also, the variation of k between a given $Co(DH)_2B$ complex and the corresponding $Co(DH)_2B_2$ complex in virtually every case is within the limits of experimental error involved in the comparison.

In addition to the measurements on benzyl bromide, a few kinetic measurements, also summarized in Table II, were made on the reaction of $Co(DMH)_2(pyr)_2$ with the secondary halide, 1-bromoethylbenzene. Some measurements also were attempted with alkyl halides, including methyl iodide, but these reactions proved too slow for study.

The principal trends revealed by the kinetic measurements are as follows.

1. k increases with the basicity of the axial ligand B in accord with the sequence PPh_3 ($pK_a = 2.7$)[28] < nicotinamide ($pK_a = 3.4$)[29] < pyridine ($pK_a = 5.3$)[29] < γ-picoline ($pK_a = 6.1$).[29] The over-all increase in k along this series is about a factor of 10.

2. k is relatively insensitive to the nature of the glyoxime ligand, and no systematic trends can be discerned in the small variations (the largest being about a factor of 5) that do occur when the glyoxime is varied.

3. k increases by a factor of about 5 in going from $PhCH_2Br$ to the corresponding secondary halide $PhCH(CH_3)Br$.

4. For the reactions for which comparison was possible, the effect on k in going from benzene to acetone as solvent is relatively small, the maximum variation being less than a factor of 3.

Mechanism. All the above results are most readily accommodated by a free-radical mechanism, depicted by eq 9 and 10, analogous to that previously proposed[4,5] for the reaction of pentacyanocobaltate(II) with organic halides.

$$Co(DH)_2B + RX \longrightarrow XCo(DH)_2B + R\cdot \qquad (9)$$

$$Co(DH)_2B + R\cdot \longrightarrow RCo(DH)_2B \qquad (10)$$

A possible alternative mechanism which merits consideration is that involving disproportionation of the cobalt(II) complex according to eq 11, followed by an SN2 reaction of the cobalt(I) complex, $Co(DH)_2B^-$, with RX according to eq 2.

$$2Co(DH)_2B \rightleftharpoons Co(DH)_2B^+ + Co(DH)_2B^- \qquad (11)$$

The latter mechanism has been proposed[7] for the reaction of cobaloxime(II) complexes with organic halides in alkaline aqueous methanol solution, but seems unlikely in the systems described in this paper for the following reasons. (i) While not inconsistent with it, this mechanism does not account as readily as the proposed free-radical mechanism for the observed stoichiometry of the reaction, notably the quantitative yield of $BrCo(DH)_2B$. (ii) The absence of an appreciable effect on the rate in going from benzene to the more polar solvent, acetone, is consistent with the proposed free-radical mechanism but not readily reconciled with a mechanism involving the formation of ionic intermediates. (iii) The observed second-order kinetics are not readily reconciled with a mechanism involving reaction 11, either as a preequilibrium or as a rate-determining step; either of these would lead to a higher than first-order dependence on $Co(DH)_2B$. (iv) The increase in reactivity in going from benzyl bromide to 1-bromoethylbenzene (*i.e.*, from a primary to a secondary organic halide) is in the direction expected for the free-radical mechanism, but in the opposite direction to that expected (and observed)[12] for nucleophilic displacement by cobalt(I).

The operation of a halogen-atom abstraction mechanism in these reactions, analogous to that for pentacyanocobaltate(II), and different from the SN2 mechanism observed[12] for the cobaloximes(I), is not unexpected. Such halogen-atom abstraction is clearly a favorable process for a five-coordinate low-spin cobalt(II) complex since it leads directly to formation of the more highly stabilized six-coordinate cobalt(III) derivative. The much lower reactivity of the cobaloxime(II) complexes, compared with pentacyanocobaltate(II), revealed by these studies also is not unexpected in view of the much greater stabilization of cobalt(III), relative to cobalt(II), by cyanide as compared to the glyoxime ligands. In this respect, the cobalamines appear to bear a much closer resemblance to the cobaloximes than to the corresponding cobalt cyanide complexes, the reactivity of vitamin B_{12r} toward organic halides being relatively low, particularly in comparison to vitamin B_{12s}. Some of the important chemical differences among the members of the vitamin B_{12} family and their model compounds are related to this theme.

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[29] H. H. Jaffé and G. O. Doak, *J. Am. Chem. Soc.*, 77, 4441 (1955).