Reactions of Bis(dioximato)cobalt(II) Complexes with Organic Halides. Influence of Electronic and Steric Factors upon Reactivity

Jack Halpern* and Patrick F. Phelan

Contribution from the Department of Chemistry, The University of Chicago, Chicago, Illinois 60637. *Received August 13, 1971*

Abstract: Kinetic measurements are reported for a series of reactions of bis(dioximato)cobalt(II) complexes with organic halides, $2\mathrm{Co(DH)_2B} + \mathrm{RX} \rightarrow \mathrm{RCo(DH)_2B} + \mathrm{XCo(DH)_2B}$, where $\mathrm{DH_2}$ = dimethylglyoxime or 1,2-cyclohexanedione dioxime (nioxime), L is a neutral amine or phosphine ligand, and RX is a benzyl halide. The results are interpreted in terms of the stepwise free-radical mechanism, $\mathrm{Co(DH)_2B} + \mathrm{RX} \rightarrow \mathrm{XCo(DH)_2B} + \mathrm{R}\cdot$ (k) (rate determining), followed by $\mathrm{R}\cdot + \mathrm{Co(DH)_2B} \rightarrow \mathrm{RCo(DH)_2B}$. The rate constant k for reaction with $\mathrm{C_6H_5CH_2Br}$ in benzene at 25° ranged from $2.3 \times 10^{-3}\ M^{-1}\ \mathrm{sec}^{-1}$ for B = $\mathrm{P(c\text{-}C_6H_{11})_3}$ to $7.1\ M^{-1}\ \mathrm{sec}^{-1}$ for B = $\mathrm{P(CH_3)_3}$. The influences of electronic and steric factors upon the reactivities of the cobalt(II) complexes are discussed. The results direct attention to the possible influences of axial ligand replacements in modifying the reactivity of vitamin $\mathrm{B_{12r}}$ for which these cobalt(II) complexes serve as model systems.

We have previously reported[1] that various bis(dioximato)cobalt(II) complexes[2] react with organic halides in solution to form stable organocobalt derivatives in accord with the stoichiometry and mechanism described by

$$\mathrm{Co(DH)_2B} + \mathrm{RX} \xrightarrow{k} \mathrm{XCo(DH)_2B} + \mathrm{R}\cdot \qquad (1)$$

(rate determining)

$$\mathrm{Co(DH)_2B} + \mathrm{R}\cdot \longrightarrow \mathrm{RCo(DH)_2B} \qquad (2)$$

$$2\mathrm{Co(DH)_2B} + \mathrm{RX} \longrightarrow \mathrm{XCo(DH)_2B} + \mathrm{RCo(DH)_2B} \qquad (3)$$

In this paper we report the results of further kinetic studies on such reactions, in the course of which the axial ligands (B) and the organic halides (RX) were varied with a view to elucidating some of the electronic and steric factors that influence the rate of reaction 1.

Experimental Section

The present studies are direct extensions of those described in an earlier publication.[1] Materials and procedures common to both studies have already been described, and only the additional experimental features associated with the present investigation will be detailed here.

Materials. 1,2-Cyclohexanedione dioxime (nioxime) was obtained from Aldrich Chemicals (mp 190°). **Tricyclohexylphosphine** (Strem) was recrystallized, under nitrogen, from deaerated methanol. **Piperidine** (Eastman) was redistilled (bp 100–106°). The following axial ligands were obtained from the sources cited: trimethylphosphine (Orgmet), triethylphosphine (Orgmet), tri-*n*-butylphosphine (Aldrich), diphenylphosphine (Strem), tri-*p*-chlorophenylphosphine (Strem), tri-*p*-methoxyphenylphosphine (Strem), tri-*p*-tolylphosphine (Eastman), trimethyl phosphite (Strem), and 1-methylimidazole (Aldrich).

***p*-Bromobenzyl bromide** (Aldrich) was recrystallized three times from pentane. **α-Bromo-*p*-xylene** (Eastman) was recrystallized twice from methanol, then twice from anhydrous ether at −30°. ***p*-Cyanobenzyl bromide**[3] was prepared by the method of Banse[4] and recrystallized from ethanol; mp 113–115° (lit.[4] mp 115–116°). **α-Bromo-*p*-nitrotoluene** and **benzyl iodide** were Eastman products; the latter compound was recrystallized six times from anhydrous ether at −40°.

Preparation of Cobalt(II) Complexes. The preparation and characterization of several of the cobalt(II) complexes have already been described.[1] Using essentially the same procedures,[1,5] the additional compounds listed in Table I, which were used in the present studies, were synthesized, isolated, and characterized. The following compounds proved insufficiently stable to isolate in pure form and were, accordingly, prepared *in situ* by addition of the appropriate axial ligand to a solution or slurry of $\mathrm{Co(DH)_2}$, $\mathrm{Co(DH)_2P(C_6H_5)_3}$, or $\mathrm{Co(DH)_2(piperidine)}$ [$\mathrm{P(C_6H_5)_3}$ or piperidine being readily and quantitatively displaced by other axial ligands].[6,7] The quantitative formation of the $\mathrm{Co(DH)_2B}$ complexes according to eq 4 or 5 under these conditions is demonstrated by spectral titration plots such as those depicted in Figure 1, which exhibit sharp end points (listed in Table II) at 1:1 ratios of added B to cobalt(II). Addition of excess B had no effect either on the spectra or on the resulting reactivities of the $\mathrm{Co(DH)_2B}$ solutions.

$$\mathrm{Co(DH)_2} + \mathrm{B} \longrightarrow \mathrm{Co(DH)_2B} \qquad (4)$$

$$\mathrm{Co(DH)_2P(C_6H_5)_3} + \mathrm{B} \longrightarrow \mathrm{Co(DH)_2B} + \mathrm{P(C_6H_5)_3} \qquad (5)$$

Synthesis and Characterization of Cobalt(III) Products. The synthesis and characterization of several of the cobalt(III) products, *i.e.*, $\mathrm{RCo(DH_2)B}$ and $\mathrm{XCo(DH)_2B}$, and the demonstration (by matching of the spectra of the product solutions with the known spectra of the corresponding independently synthesized product species) that the stoichiometries of reaction are in quantitative accord with eq 3 have already been described. These particular

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(1) P. W. Schneider, P. F. Phelan, and J. Halpern, *J. Amer. Chem. Soc.*, **91**, 77 (1969).

(2) The following abbreviations are used throughout this paper to designate the various ligands: $\mathrm{DH^-}$ = the anion of any 1,2-dioxime, including that of dimethylglyoxime ($\mathrm{DMH^-}$) and 1,2-cyclohexanedione dioxime ($\mathrm{niox^-}$).

(3) We are grateful to Dr. L. G. Marzilli for the preparation of this compound.

(4) G. Banse, *Chem. Ber.*, **27**, 2161 (1894).

(5) G. N. Schrauzer and R. J. Windgassen, *ibid.*, **99**, 602 (1966).

(6) Only in the case of $\mathrm{PH(C_6H_5)_2}$ was the displacement of $\mathrm{P(C_6H_5)_3}$ from $\mathrm{Co(DMH)_2P(C_6H_5)_3}$ in benzene not quantitative, and an excess of $\mathrm{PH(C_6H_5)_2}$ had to be added to complete the formation of $\mathrm{Co(DMH)_2PH(C_6H_5)_2}$. From the spectral titration curve, the equilibrium constant for the replacement reaction, $\mathrm{Co(DMH)_2P(C_6H_5)_3} + \mathrm{PH(C_6H_5)_2} \rightleftarrows \mathrm{Co(DMH)_2PH(C_6H_5)_2} + \mathrm{P(C_6H_5)_3}$, was estimated to be 9.

(7) In contrast to the corresponding behavior in benzene or acetone, spectral titrations of $\mathrm{Co(niox)_2}$ with typical ligands B such as $\mathrm{P(C_6H_5)_3}$ in methanol did not exhibit sharp end points but, rather, equilibrium behavior. The equilibrium formation constant of $\mathrm{Co(niox)_2P(C_6H_5)_3}$ according to reaction 4 was estimated from the spectral titration curve to have a value of $8.4 \times 10^2\ M^{-1}$. Thus, presumably because of more effective competition from axial coordination by the methanol solvent, formation of $\mathrm{Co(niox)_2PPh_3}$ approached completion only at rather high concentration of excess $\mathrm{PPh_3}$ ($>10^{-2}\ M$). Under these conditions, the quaternization reaction of $\mathrm{PPh_3}$ with most of the organic halides interfered with the study of the desired reaction with $\mathrm{Co(DH)_2B}$. Because of this and of a further complication, namely the tendency (previously observed by Schrauzer and Windgassen[5] and confirmed by us) of our cobalt(II) complexes to undergo disproportionation in methanol to cobalt(I) and cobalt(III), the use of methanol as a solvent was generally avoided in our studies.

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

Complex	Calcd, % C	H	N	Found, % C	H	N
$Co(DMH)_2$	33.22	4.88	19.38	33.19	4.88	19.25
$Co(niox)_2$	42.24	5.32		41.56	5.15	
$Co(DMH)_2$(1-methylimidazole)	42.38	5.78	24.72	42.35	5.69	24.51
$Co(DMH)_2$(piperidine)	41.71	6.73	18.71	40.68	6.80	17.77
$Co(DMH)_2P(c\text{-}C_6H_{11})_3$	54.82	8.32	9.84	55.68	8.38	9.05
$Co(niox)_2(pyridine)_2$	52.90	5.65	16.83	53.16	5.56	16.98
$Co(DMH)_2P(p\text{-}ClC_6H_4)_3$[a]	47.69	4.00	8.56	48.55	3.78	9.42
$Co(DMH)_2P(p\text{-}CH_3OC_6H_4)_3$	54.29	5.50	8.73	54.46	5.39	8.30
$Co(DMH)_2P(p\text{-}CH_3C_6H_4)_3$	58.68	5.94	9.44	59.05	5.86	9.40
$Co(niox)_2P(C_6H_5)_3$	59.70	5.51	9.28	58.96	5.51	9.43

[a] Calcd: Cl, 16.24. Found: Cl, 16.85.

Table II. Spectral Titrations

Initial complex (Co(II))	Added ligand (B)	Solvent	Molar ratio, [B]:[Co(II)] at end point
$Co(DMH)_2$	$(c\text{-}C_6H_{11})_3P$	Acetone	1.05 ± 0.05
$Co(DMH)_2$	Pyridine	Acetone	1.00 ± 0.05
$Co(DMH)_2$	$(n\text{-}C_4H_9)_3P$	Acetone	0.8 ± 0.1
$Co(DMH)_2(PPh_3)_2$	$(C_2H_5)_3P$	Benzene	1.06 ± 0.10
$Co(DMH)_2(PPh_3)_2$	$(CH_3)_3P$	Benzene	1.06 ± 0.10
$Co(DMH)_2$(piperidine)	$(n\text{-}C_4H_9)_3P$	Acetone	0.95 ± 0.05
$Co(DMH)_2(pyridine)_2$	$(n\text{-}C_4H_9)_3P$	Acetone	1.0 ± 0.1
$Co(DMH)_2(PPh_3)$	$(n\text{-}C_4H_9)_3P$	Acetone	0.94 ± 0.05

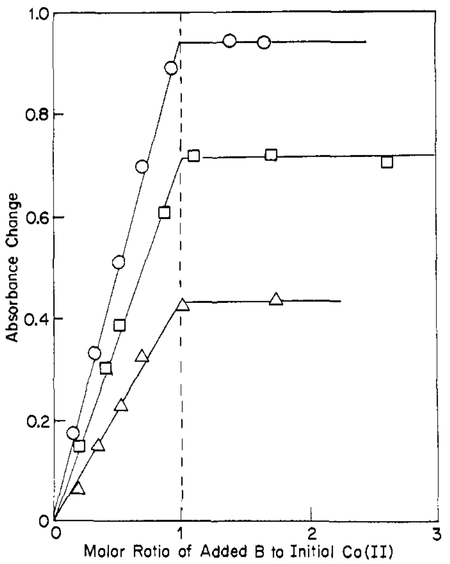

Figure 1. Spectral titrations (1-cm light paths): (○) 6.9 × 10^{-4} M $Co(DMH)_2$(piperidine) with $(n\text{-}C_4H_9)_3P$ in acetone (505 nm), (△) 7.4 × 10^{-4} M $Co(DMH)_2$ with pyridine in acetone (423 nm), (□) 4.7 × 10^{-4} M $Co(DMH)_2(pyridine)_2$ with $(n\text{-}C_4H_9)_3P$ in acetone (505 nm).

experiments were extended in the present study by synthesizing (according to the procedures of Tschugaeff[8] and of Schrauzer and Windgassen,[9] respectively) the additional compounds $BrCo(DMH)_2$(4-picoline) and $C_6H_5CH_2Co(DMH)_2$(4-picoline), and by demonstrating that the spectrum of the product solution from the reaction of $Co(DMH)_2$(4-picoline) with $C_6H_5CH_2Br$ is in quantitative agreement with that of an equimolar mixture of the two cobalt(III) compounds in accord with eq 3 (see Figure 2). *Anal.* Calcd for $C_6H_5CH_2Co(DMH)_2$(4-picoline): C, 53.27; H, 5.96; N, 14.79. Found: C, 51.22; H, 5.83; N, 15.00. Calcd for $BrCo(DMH)_2$(4-picoline): C, 36.38; H, 4.38; N, 15.15; Br, 17.29. Found: C, 36.22; H, 4.57; N, 15.04; Br, 17.23.

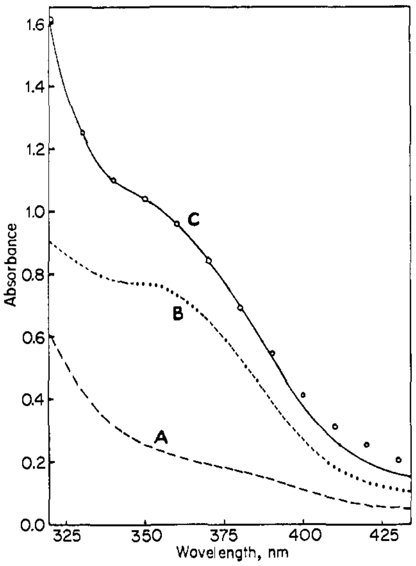

Figure 2. Absorption spectra in benzene of (A) 1.0 × 10^{-4} M $BrCo(DMH)_2$(4-picoline) and (B) 1.0 × 10^{-4} M $C_6H_5CH_2Co(DMH)_2$(4-picoline). (C) is the sum of spectra A and B. The circles correspond to the experimental absorbancies of the product solution from the reaction of excess $C_6H_5CH_2Br$ with 2.0 × 10^{-4} M $Co(DMH)_2(4\text{-}picoline)_2$.

Kinetic Measurements. The kinetic measurements were performed spectrophotometrically by monitoring the spectral changes accompanying the reaction in the 400–500-nm wavelength region, in accord with the procedures described earlier.[1]

Results and Discussion

Kinetics. The kinetic measurements on each reaction typically encompassed the initial concentration ranges 10^{-4}–10^{-3} M $Co(DH)_2B$, 2 × 10^{-3}–5 × 10^{-1} M RX [always in at least tenfold excess over $Co(DH)_2B$], and 0–0.1 M excess B.

As in the earlier studies on these systems[1,10] and on the related reactions of other cobalt(II) complexes, notably pentacyanocobaltate(II)[11,12] and cobalt(II) Schiff's

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[8] L. Tschugaeff, *Chem. Ber.*, **99**, 602 (1966).

[9] G. N. Schrauzer and R. J. Windgassen, *J. Amer. Chem. Soc.*, **88**, 3738 (1966).

[10] It should be noted that the rate constants k reported in our earlier study[1] correspond to $2k$ as defined in the present paper.

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

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

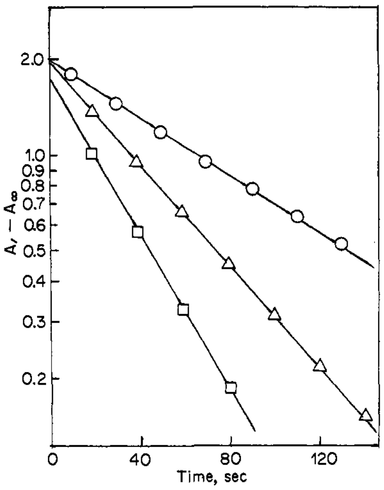

Figure 3. Representative pseudo-first-order rate plots for reactions in benzene at 25°: (○) 1 × 10^{-3} *M* $Co(DMH)_2P(C_6H_5)_3$ with 0.258 *M* $C_6H_5CH_2Br$ (480 nm), (△) 1 × 10^{-3} *M* $Co(DMH)_2P(C_6H_5)_3$ with 0.156 *M* *p*-$BrC_6H_4CH_2Br$ (475 nm), (□) 1 × 10^{-3} *M* $Co(DMH)_2$(piperidine) with 0.131 *M* $C_6H_5CH_2Br$ (440 nm); A_∞ is the final absorbance and A_t is the absorbance at time *t*.

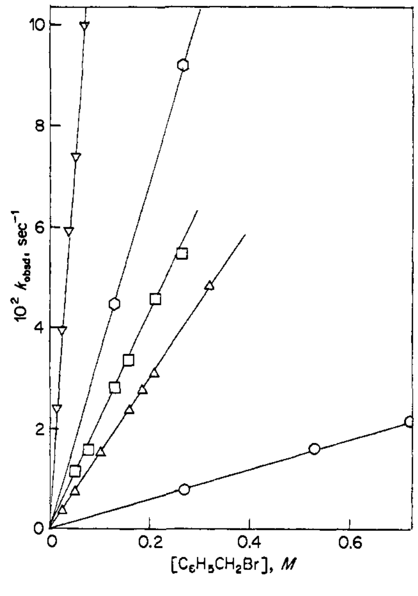

Figure 4. Representative plots of k_{obsd} *vs.* $[C_6H_5CH_2Br]$ for reactions in benzene at 25°: (○) $Co(niox)_2P(OCH_3)_3$, (△) $Co(niox)_2PH(C_6H_5)_2$, (□) $Co(DMH)_2P(C_2H_5)_3$, (⬡) $Co(DMH)_2P(n\text{-}C_4H_9)_3$, (▽) $Co(DMH)_2P(CH_3)_3$.

base complexes,[13] the kinetics conformed to the second-order rate law corresponding to eq 6. Under the conditions of our experiments, with RX always in substantial excess over $Co(DH)_2B$, each experiment exhibited pseudo-first-order kinetics, in accord with eq 7.

$$-d[Co(DH)_2B]/dt = 2k[Co(DH)_2B][RX] \tag{6}$$

$$-d \ln [Co(DH)_2B]/dt = k_{obsd} = 2k[RX] \tag{7}$$

Pseudo-first-order rate plots, such as those depicted in Figure 3, were invariably linear for at least several half-lives. Values of k_{obsd}, derived from the slopes of such plots, were generally reproducible to ±5%. Representative plots of k_{obsd} *vs.* [RX] for several reactions are depicted in Figure 4 and, in accord with eq 7, are seen to be linear and to pass through the origin. In no case was the rate significantly affected by the addition of excess B or by whether $Co(DH)_2B$ or $Co(DH)_2B_2$ was used as the starting cobalt(II) complex (in view of which only one rate constant, *k*, is reported for each reaction). The latter observation is in accord with our earlier conclusion that, under our conditions, the $Co(DH)_2B_2$ compounds are completely dissociated in solution into $Co(DH)_2B$ and B.

Activation Parameters. Rate measurements, over the temperature range 15–35°, for two representative reactions, *i.e.*, those of $Co(DMH)_2P(C_6H_5)_3$ and $Co(DMH)_2$(pyridine) with $C_6H_5CH_2Br$ in benzene, are reported in Table III. These data yielded good Arrhenius plots, from which the following activation parameters were determined: for $Co(DMH)_2P(C_6H_5)_3$, $\Delta H^{\ddagger} = 10.1 \pm 0.5$ kcal/mol, $\Delta S^{\ddagger} = -32 \pm 2$ eu; for $Co(DMH)_2$(pyridine), $\Delta H^{\ddagger} = 9.9 \pm 0.5$ kcal/mol; $\Delta S^{\ddagger} = -29 \pm 2$ eu.

Dependence of Reactivity on Organic Halide. The reactivities of several different organic halides toward a reference cobalt(II) complex, $Co(DMH)_2PPh_3$, are compared in Table IV. The following trends are noteworthy: (i) the marked increase in reactivity along the sequence RCl < RBr < RI ($k_{C_6H_5CH_2I}:k_{C_6H_5CH_2Br} \approx 3 \times 10^2$; $k_{p\text{-}NO_2C_6H_4CH_2Br}:k_{p\text{-}NO_2C_6H_4CH_9Cl} \approx 2 \times 10^3$) and (ii) the enhancement of reactivity of the substituted benzyl bromides by electron-withdrawing substituents. The latter trend is reflected in the Hammett plot in Figure 5 for a series of para-substituted benzyl bromides; the slope corresponds to $\rho = 1.4$.

Table III. Temperature Dependence of the Rate Constants for Reaction with Benzyl Bromide in Benzene

$Co(DH)_2B$	Temp, °C	*k*, M^{-1} sec^{-1}
$Co(DMH)_2P(C_6H_5)_3$	15	$(1.2 \pm 0.1) \times 10^{-2}$
	20	$(1.7 \pm 0.1) \times 10^{-2}$
	25	$(2.1 \pm 0.1) \times 10^{-2}$
	30	$(3.0 \pm 0.1) \times 10^{-2}$
	35	$(3.9 \pm 0.1) \times 10^{-2}$
$Co(DMH)_2$(pyridine)	15	$(8.2 \pm 0.2) \times 10^{-2}$
	20	$(1.1 \pm 0.1) \times 10^{-1}$
	25	$(1.4 \pm 0.2) \times 10^{-1}$
	30	$(1.9 \pm 0.1) \times 10^{-1}$
	35	$(2.5 \pm 0.1) \times 10^{-1}$

Table IV. Reactivities of Various Organic Halides toward $Co(DH)_2P(C_6H_5)_3$ in Benzene at 25°

Organic halide	*k*, M^{-1} sec^{-1}
$C_6H_5CH_2I$	6.3 ± 0.2
$C_6H_5CH_2Br$	$(2.1 \pm 0.1) \times 10^{-2}$
p-$CH_3C_6H_4CH_2Br$	$(2.7 \pm 0.1) \times 10^{-2}$
p-$BrC_6H_4CH_2Br$	$(6.1 \pm 0.2) \times 10^{-2}$
p-$NCC_6H_4CH_2Br$	$(2.2 \pm 0.1) \times 10^{-1}$
p-$NO_2C_6H_4CH_2Br$	$(3.7 \pm 0.1) \times 10^{-1}$
p-$NO_2C_6H_4CH_2Cl$	$(2.0 \pm 0.2) \times 10^{-4}$

Dependence on Ligands and Solvent. Table V lists kinetic data which illustrate the influence on the rate of reaction (*i.e.*, on *k*) of the following three further parameters: (i) the dioxime ligand (notably the comparison of DMH and niox), (ii) the influence of solvent (notably the comparison of acetone and benzene), and (iii)

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(13) L. G. Marzilli, P. A. Marzilli, and J. Halpern, *ibid.*, **93**, 1374 (1971).

Table V. Rate Constants (k, M^{-1} sec^{-1}) for the Reactions of $Co(DH)_2B$ with Benzyl Bromide at 25°

		Benzene solution		Acetone solution	
B	pK_a[a]	$Co(DMH)_2B$	$Co(niox)_2B$	$Co(DMH)_2B$	$Co(niox)_2B$
None[b]				$(3.9 \pm 0.3) \times 10^{-3}$	
Amine ligands					
Nicotinamide	3.3[c]			$(1.0 \pm 0.3) \times 10^{-1}$ [d]	$(1.1 \pm 0.1) \times 10^{-1}$
Pyridine	5.2[c]	$(1.5 \pm 0.1) \times 10^{-1}$ [c]		$(1.7 \pm 0.2) \times 10^{-1}$ [d]	$(1.6 \pm 0.1) \times 10^{-1}$
4-Picoline	6.1[c]	$(2.1 \pm 0.2) \times 10^{-1}$ [c]	$(1.5 \pm 0.1) \times 10^{-1}$	$(2.2 \pm 0.2) \times 10^{-1}$ [d]	$(2.3 \pm 0.1) \times 10^{-1}$
1-Methylimidazole	7.0[c]	$(5.5 \pm 0.2) \times 10^{-1}$	$(5.6 \pm 0.2) \times 10^{-1}$	$(6.7 \pm 0.3) \times 10^{-1}$	
Piperidine	11.1[c]	$(1.0 \pm 0.1) \times 10^{-1}$		$(2.6 \pm 0.1) \times 10^{-1}$	
Phosphine ligands					
$(CH_3O)_3P$		$(1.5 \pm 0.1) \times 10^{-1}$	$(1.5 \pm 0.1) \times 10^{-1}$		
$(C_6H_5)_2PH$	0.03[e]		$(7.5 \pm 0.2) \times 10^{-1}$		
$(p\text{-}ClC_6H_4)_3P$		$(9.7 \pm 0.2) \times 10^{-3}$			
$(C_6H_5)_3P$	2.73[e]	$(2.1 \pm 0.1) \times 10^{-2}$ [c]	$(1.9 \pm 0.1) \times 10^{-2}$	$(2.4 \pm 0.1) \times 10^{-2}$ [d]	$(2.4 \pm 0.1) \times 10^{-2}$
$(p\text{-}CH_3C_6H_4)_3P$		$(3.4 \pm 0.1) \times 10^{-2}$			
$(p\text{-}CH_3OC_6H_4)_3P$	4.46[e]	$(4.8 \pm 0.1) \times 10^{-2}$			
$(n\text{-}C_4H_9)_3P$	8.43[e]	1.6 ± 0.1	1.6 ± 0.1		
$(CH_3)_3P$	8.65[e]	7.1 ± 0.1			
$(C_2H_5)_3P$	8.69[e]	1.1 ± 0.1	1.0 ± 0.1		
$(c\text{-}C_6H_{11})_3P$	9.7[e]		$(2.3 \pm 0.1) \times 10^{-3}$	$(4.4 \pm 0.2) \times 10^{-3}$	

[a] pK_a of BH^+. [b] $Co(DMH)_2$ or $Co(DMH)_2(H_2O)$ in acetone. [c] D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworths, London, 1965. [d] Data from ref 1. [e] C. A. Streuli, *Anal. Chem.*, **32**, 985 (1960).

the axial ligand, B. Some data from our earlier study[1] are also included for comparison.

The values of k for corresponding DMH and niox complexes are seen to be virtually identical, the differences in rate generally being less than 10% except in one case, *i.e.*, $Co(DH)_2$(4-picoline) in benzene. While this is hardly surprising in view of the chemical similarity of the two ligands, earlier comparisons[1] with cobalt(II) complexes of other dioxime ligands (namely diphenylglyoxime, 4,4′-dinitrophenylglyoxime, and 4,4′-dimethoxyphenylglyoxime) also revealed only small differences in reactivity.

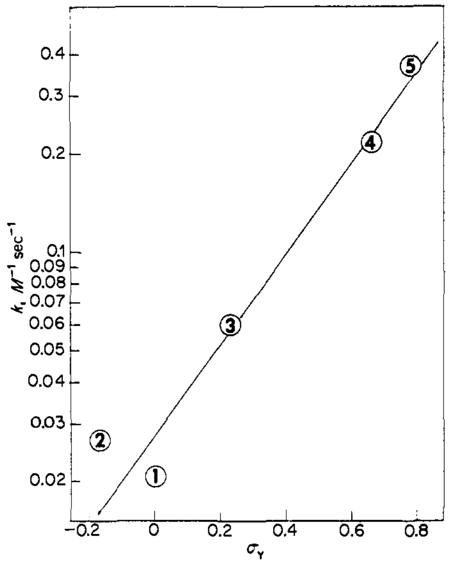

Figure 5. Hammett plot for the reactions of $Co(DMH)_2P(C_6H_5)_3$ with $p\text{-}YC_6H_4CH_2Br$ in benzene at 25°: (1) Y = H, (2) Y = CH_3, (3) Y = Br, (4) Y = CN, (5) Y = NO_2.

Solvent effects on the rates also are seen to be small. The rate constants for a given reaction typically increase slightly in going from benzene to acetone, but the difference is generally considerably less than a factor of two. Earlier measurements[1] on several related reactions revealed similarly small solvent effects.

The influence of the axial ligand (B) on the reactivity, however, is much more dramatic. The reactivity patterns associated with the variations of B (Table V) reflect the influences of both electronic and steric factors, the nature of which is discussed below.

Mechanistic Considerations and Reactivity Patterns. All the results of the present study are accommodated by the mechanism depicted by eq 1–3 that has previously been proposed for the reactions of these and other low-spin cobalt(II) complexes with organic halides.[1,11–14] Previously cited[1] evidence in favor of this mechanism, as it applies to the present systems, includes: (i) the overall stoichiometry of the reactions, (ii) the form of the rate law, (iii) the higher reactivity of secondary, as compared to corresponding primary, organic halides,[1] and (iv) the relatively small dependence on solvent polarity.

Also in accord with this mechanism are the presently reported reactivity sequence, RI > RBr > RCl, and the enhancement of the reactivities of benzyl bromide by electron-withdrawing substituents (Table I and Figure 5). The latter trend presumably reflects some degree of electron transfer from the cobalt(II) to the organic halide in a transition state of the type, $[B(DH)_2Co^{\delta+}\cdots X^{\delta-}\cdots R]^{\ddagger}$.

The most significant new results of the present study relate to the influence of the axial ligands B on the reactivity of the cobalt(II) complexes. The contributions of electronic factors to this influence are most clearly revealed by a comparison of complexes of the para-substituted triarylphosphine ligands, $(p\text{-}YC_6H_4)_3P$, where differences due to steric factors are presumably unimportant. The data for this series of complexes yield a good Hammett plot of log k *vs.* σ_Y, depicted in Figure 6, the slope of which corresponds to $\rho_Y = -1.4$. The enhancement of the rate by electron-donating substituents is consistent with the mechanistic views advanced earlier, namely of a transition state characterized by electron transfer from the cobalt (which is hence stabilized by electron donating ligands) and with the expectation that electron donating ligands should in-

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

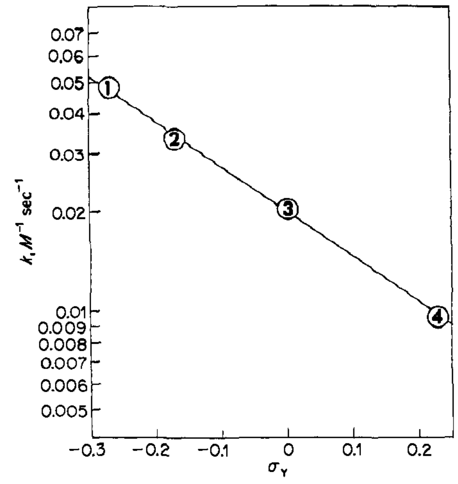

Figure 6. Hammett plot for the reactions of $Co(DMH)_2P(p\text{-}YC_6H_4)_3$ with $C_6H_5CH_2Br$ in benzene at 25°: (1) Y = OCH_3, (2) Y = CH_3, (3) Y = H, (4) Y = Cl.

crease the driving force for a reaction involving the oxidation of cobalt(II) to cobalt(III).

These considerations lead us to expect a general correlation between the reactivities of the $Co(DH)_2B$ complexes and the basicities of the axial ligands B, insofar as basicity is a measure of the electron donor tendency. Examination of the data in Table V reveals some indication of such a trend (using pK_a of BH^+ as a measure of the basicity of B), but the correlation is far from perfect. In particular, complexes of the most bulky ligands, *e.g.*, tricyclohexylphosphine among the phosphines and piperidine among the amines, exhibit rates that are significantly lower than expected on the basis of the ligand basicities suggesting that steric, as well as electronic, factors are important. From studies on ligand exchange equilibria in nickel(0) complexes, Tolman[15] had previously recognized the dominant importance of steric influences in the binding of phosphine ligands to nickel(0) and demonstrated a correlation of the ligand binding ability with the "cone angle" [16] of the phosphine, a parameter introduced by him to define the size or steric influence of the ligand. Figure 7 depicts a plot of log k *vs.* Tolman's cone angle for the phosphine ligands encompassed by this study and does indeed reveal a good correlation with this parameter, suggesting that, in this case also, steric rather than electronic factors dominate the phosphine ligand properties. Possible contributing factors to this trend, which is similar to that noted[13] in the corresponding reactions of cobalt(II) Schiff's base complexes with organic halides, are (i) the lower "effective basicity" of large sterically hindered ligands such as tricyclohexylphosphine due to their inability to approach the cobalt as closely as smaller ligands and (ii) steric resistance to going from the initial five-coordinate cobalt(II) configuration to the possibly more crowded six-coordinate configuration of the cobalt(III) product. The latter effect is likely to be important only if the initial five-coordinate complexes are significantly stabilized by distortion from a square-pyramidal configuration, and in this connection, X-ray structural studies on some of these complexes would be of interest.

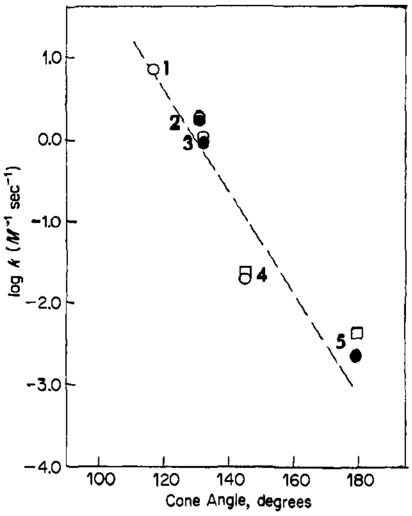

Figure 7. Plot of log k *vs.* cone angle of PR_3 for the reactions of $Co(DMH)_2PR_3$ in benzene (○) and acetone (□) and for $Co(niox)_2PR_3$ in benzene (●) and acetone (■): (1) $P(CH_3)_3$, (2) $P(n\text{-}C_4H_9)_3$, (3) $P(C_2H_5)_3$, (4) $P(C_6H_5)_3$, (5) $P(c\text{-}C_6H_{11})_3$.

The much greater sensitivity of the reactivity of the cobalt(II) complexes to variations of the axial ligands, B, than to variations of the dioxime ligands,[1] is striking. However, this result is not unexpected, since it is likely that the highest occupied orbital of the cobalt(II) complex, containing the electron which is transferred during the oxidation, is the d_{z^2} orbital, which is hence most strongly susceptible to the influence of the axial ligand, B.[17] It should be noted that the influence of the axial ligands on the reactivity is substantial, the values of k for the reaction with $C_6H_5CH_2Br$ extending over an *ca.* 10^3-fold range from 4.4×10^{-3} M^{-1} for $Co(DH)_2P(cyclohexyl)_3$ to 7.1 M^{-1} sec^{-1} for $Co(DH)_2P(CH_3)_3$. Insofar as these cobalt complexes have some relevance as models for the corresponding derivatives of vitamin B_{12},[18,19] this result has important implications for the possible role of axial substitutions in effecting substantial changes in the reactivity of vitamin B_{12r}.

Other Possible Mechanisms. Arguments based on the stoichiometry and kinetics of the reaction and reinforced by the further related results of the present study have already been cited against one possible alternative mechanism.[1] This mechanism, depicted by eq 8 and 9, which we feel can be ruled out in the solvents used in this study,[20] involves the disproportionation of cobalt(II) followed by reaction of the resulting cobalt(I) complex with the organic halide.[21]

$$2Co(DH)_2B \rightleftharpoons Co(DH)_2B^+ + Co(DH)_2B^- \quad (8)$$

$$Co(DH)_2B^- + RX \longrightarrow RCo(DH)_2B + X^- \quad (9)$$

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[15] C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).

[16] The "cone angle" was defined by Tolman[15] as the apex angle of a cone centered on the metal atom, just large enough to enclose the van der Waals radii of the outermost atoms of the ligand. Such "cone angles" were determined from measurements on models.[15]

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

[18] G. N. Schrauzer, *Accounts Chem. Res.*, **1**, 97 (1968).

[19] A. Bigotto, G. Costa, G. Mestroni, G. Pellizer, A. Puxeddu, R. Reisenhofer, L. Stefani, and G. Tauzher, *Inorg. Chim. Acta, Rev.*, **4**, 41 (1970).

[20] It is not unlikely that this mechanism does contribute in methanol solution, where $Co(DH)_2B$ complexes have been shown to undergo such disproportionation, particularly in the presence of base[5] (including excess phosphine).

[21] G. N. Schrauzer and E. A. Deutsch, *J. Amer. Chem. Soc.*, **91**, 3341 (1969).

Our results are also at variance with yet another possible alternative mechanism, depicted by eq 10–12, which merits consideration in view of the recent demonstration of analogous mechanisms for the reactions of certain cobalt(II) Schiff's base complexes with nitrobenzyl halides.[22] This mechanism involves an outer-sphere electron transfer to the organic halide from a *six-coordinate* cobalt(II) complex formed in a prior association step. Three features of our results are at variance with this mechanism, namely (i) the observed second-order rate law (in contrast to the third-order rate law,[22] $k'[\mathrm{Co(DH)_2B}][\mathrm{RX}][\mathrm{B}]$, expected for this mechanism); (ii) the large dependence on halide variation, *i.e.*, $k_{\mathrm{RI}}/k_{\mathrm{RBr}} \sim k_{\mathrm{RBr}}/k_{\mathrm{RCl}} \sim 10^3$, which is characteristic of the halogen atom transfer (eq 1),[11–13] in contrast to the much smaller dependence (*i.e.*, $k_{\mathrm{RI}}/k_{\mathrm{RBr}} \sim k_{\mathrm{RBr}}/k_{\mathrm{Cl}} \sim 1\text{–}10$) characteristic of the electron-transfer mechanism;[22] and (iii) the discrepancy of the overall stoichiometry.

$$\mathrm{Co(DH)_2B + B \rightleftarrows Co(DH_2)B_2} \qquad (10)$$

$$\mathrm{Co(DH)_2B_2 + RX \longrightarrow Co(DH)_2B_2{}^+ + X^- + R\cdot} \qquad (11)$$

$$\mathrm{Co(DH)_2B + R\cdot \longrightarrow RCo(DH)_2B} \qquad (12)$$

The only feature of our results which does not find a ready explanation in terms of the mechanism that we have adopted relates to the large negative $\Delta S^{\ddagger}$ values of the reaction (*ca.* -30 eu). An explanation in terms of solvent electrostriction reflecting a highly polar transition state is not readily reconciled with the rather modest dependence of the rate on solvent polarity. It is, however, noteworthy that comparably large negative activation entropies have been observed for atom- or radical-transfer reactions to cobalt(II) complexes from other neutral substrates (*e.g.*, $\mathrm{Co(CN)_5{}^{3-} + H_2O_2 \rightarrow Co(CN)_5OH^{3-} + OH\cdot}$; $\Delta S^{\ddagger} = -31$ eu).[23] Further investigation of this pattern, for which we cannot presently offer a convincing explanation, is warranted.

Acknowledgments. Support of this research through grants from the National Institutes of Health and the National Science Foundation is gratefully acknowledged. One of us (P. F. P.) also thanks the National Science Foundation for the award of a Predoctoral Fellowship.

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Reaction of Transition Metal Dihydrides. I. Insertion and Substitution at the Metal–Hydride Bonds in Dihydridobis(π-cyclopentadienyl)molybdenum[1]

Akira Nakamura and Sei Otsuka*

Contribution from the Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan. *Received July 29, 1971*

Abstract: Reactivity of $(\pi\text{-C}_5\mathrm{H}_5)_2\mathrm{MoH}_2$ toward various olefins and acetylenes was investigated. An unsaturated bond having electron-attracting groups such as –CN, $-\mathrm{CO_2CH_3}$, or $-\mathrm{CF_3}$ undergoes monoinsertion into one of the Mo–H bonds. Hydrido-σ-alkyl or -σ-alkenyl complexes of formula $(\pi\text{-C}_5\mathrm{H}_5)_2\mathrm{MoH(R)}$ were isolated and characterized for R = $\mathrm{CH(CN)CH_3}$, $\mathrm{CH(CN)CH_2CN}$, $\mathrm{CH(CO_2CH_3)CH_3}$, $\mathrm{CH(CO_2CH_3)CH_2CO_2CH_3}$, *cis*-$\mathrm{C(CO_2CH_3){=}CHCO_2CH_3}$, and *trans*-$\mathrm{C(CF_3){=}CHCF_3}$. Some of these, when treated with excess olefins or acetylenes, produced substitution products of formula $(\pi\text{-C}_5\mathrm{H}_5)_2\mathrm{Mo(Un)}$; Un = $\mathrm{CH_2{=}CHCN}$, $\mathrm{CH_2{=}CHCO_2CH_3}$, *cis*- and *trans*-$\mathrm{CH_3O_2CCH{=}CHCO_2CH_3}$, *trans*-$\mathrm{PhCH{=}CHCO_2CH_3}$, and $\mathrm{PhC{\equiv}CPh}$. One of the hydrido-σ-alkenyl complexes, $(\pi\text{-C}_5\mathrm{H}_5)_2\mathrm{MoH}[\sigma\text{-}trans\text{-}\mathrm{C(CF_3){=}CHCF_3}]$, containing a sterically demanding side chain, emerges in two conformational isomers; possible mechanisms for the observed isomerization were discussed on the basis of the temperature-dependent ^{19}F nmr.

In olefin catalysis such as isomerization and related reactions a metal monohydride species plays an important role. The reversible insertion reactions of olefins into metal–hydrogen bonds have been studied extensively.[2–7] Recently a number of transition metal complexes were found to be able to coordinate molecular hydrogen[8,9] leading to dihydrides. Reactions of the isolated metal–dihydride complexes with olefins have not been studied albeit the importance in catalytic hydrogenations,[10,11] the reason being apparently the elusive nature generally encountered with catalytically active complexes. Exceptions may be Wilkinson's

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[1] A part of this paper was briefly reported before: S. Otsuka, A. Nakamura, and H. Minamida, *Chem. Commun.*, 1148 (1969).

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