Kinetics and Mechanism of Apparent Alkyl Transfer from Alkylcobaloximes to Cobaloxime(I), Cobaloxime(II), and Cobaloxime(III) Reagents

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Abstract: Two main types of reaction take place when alkylcobaloximes react with cobaloxime(II) complexes in methanol or in methylene chloride. First, homolytic displacement of cobaloxime(II) from the alkylcobaloxime takes place by the attack of the cobaloxime(II) reagent on the alkyl group. This reaction is first order in each reagent and occurs with inversion of configuration at the α-carbon of the alkyl group. The second-order rate coefficients for this displacement reaction vary markedly with the nature of the alkyl group, the overall decrease in the sequence Me $\gg$ Et $\gg$ Pr $\sim$ Bu $\sim$ Oct $>$ *i*-Pr $>$ *i*-Bu $>$ *sec*-Bu being approximately 10^6-fold, from $k_2^{Me} \geq 44$ at 0 °C to $k_2^{sec\text{-}Bu} = 2.6 \times 10^{-4}$ dm^3 mol^{-1} s^{-1} in methanol at 28 °C. The activation parameters for the reactions of the *n*-octyl complex have been determined in the two solvents. Secondly, after the onset of alkyl exchange, additional exchange of equatorial ligands between reagent cobaloxime(II) and displaced cobaloxime(II) complexes takes place rapidly. The mechanism of this equatorial ligand exchange has not been elucidated except that incorporation in the alkylcobaloxime of equatorial ligand precursors added to the solution can take place. Displacement of cobaloxime(I) from the alkylcobaloxime complexes by cobaloxime(I) reagents in methanolic solution has similarly been shown to involve a bimolecular reaction of the cobaloxime(I) reagent with inversion of configuration, at the α-carbon of the alkyl group. The rate coefficients for the cobaloxime(I) and cobaloxime(II) promoted processes are remarkably similar. Attempts to study the corresponding electrophilic displacement of cobaloxime(III) from the same alkylcobaloxime complexes by cobaloxime(III) reagents have been thwarted by the very ready incursion of the much more rapid homolytic displacement induced by small traces of cobaloxime(II) impurities. The interrelation between the three types of displacement reaction and the possibilities of electron transfer processes are discussed.

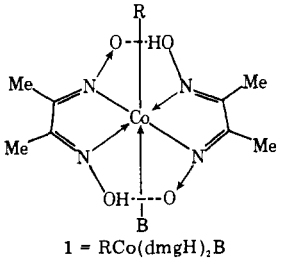
Reactions in which an alkyl group is transferred from one metal to another are of considerable mechanistic interest. The early detailed mechanistic studies of such transfer involved nontransition metals, especially mercury, and were considered mainly in terms of metal-for-metal exchange reactions.[1] More recently attention has turned to transition metals because of their importance in industry and particularly in biochemistry, and the emphasis has been more in terms of transfer of the organic group from one metal to another. For example, there is now widespread interest in the alkyl transfer reactions of cobalt because of their relationship with the dominant role that alkylcobalamins and their derivatives play in a large number of common biological processes.[2] Though many of the important reactions of methylcobalamin involve transfer of the methyl group both to the cobalt atom of a cobalamin from organic substrates such as *N*-methyltetrahydrofolic acid[3] and from methylcobalamin to organic substrates such as homocysteine,[4] there are a number of related biological processes in which the methyl group is transferred from methylcobalamin to another metal. These include transfer to mercury(II) species[5] to form methylmercury(II) complexes, which have been shown to be responsible for brain damage to people in many parts of the world,[6] and transfer to arsenic with the formation of similarly toxic methylarsenic compounds.[7]

Mechanistic studies on methylcobalamin and on synthetic cobalt(III) complexes analogous to methylcobalamin, particularly alkylcobaloximes,[8] alkylpentacyanocobaltates, and related alkylcobalt(III) complexes having a tetradentate nitrogen or nitrogen/oxygen ligand, have concerned alkyl transfer to mercury(II),[9] mercury(I),[10] arsenic,[7] thallium(III),[9c] palladium,[11] platinum(IV) and/or platinum(II),[12] gold(III) and/or gold(I),[12] chromium(II),[13] rhodium(I),[14] and tin(II).[15] However, perhaps the most challenging system involves the transfer of alkyl groups from cobalt to cobalt. Recent semiquantitative studies of synthetic organocobalt(III) complexes have concerned the apparent transfer of alkyl groups from such alkylcobalt(III) complexes to cobalt(III),[16] to cobalt(II),[16,17] and to cobalt(I).[14,16] However, in view of the appreciable ease with which inorganic cobalt(I), cobalt(II), and cobalt(III) complexes may be interconverted, the latter studies are not definitive and it is essential first to ascertain which species is, or are, effective in promoting alkyl transfer in each case. Despite the limitations in the extrapolation of information obtained from such synthetic complexes to those of biological systems, the information gained from such studies would be of value in understanding by what means alkyl groups might be transferred from, for example, unbound to enzyme-bound cobalamins and may assist in our understanding of those processes in which more than one cobalamin site is involved, as in the methylcobalamin catalyzed formation of methionine from homocysteine.[18]

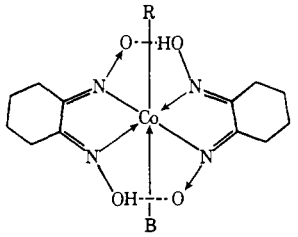
In this paper are described detailed studies of the kinetics and products of reactions of alkylcobaloximes(III) with inorganic cobaloxime(I) and cobaloxime(II) complexes in order to determine the nature of the reactive inorganic species and mechanism or mechanisms of the alkyl transfer reactions.

Results and Discussion

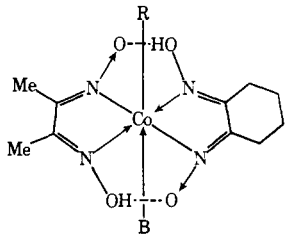
Introduction to the Chosen System. Two types of cobaloxime complexes were chosen for these studies because of the characteristic ^{1}H NMR spectra of their equatorial ligands. These were the alkylbis(dimethylglyoximato)pyridinecobalt(III) complexes (**1a–m**) and the alkylbis(cyclohexanedionedioximato)pyridinecobalt(III) complexes (**2a–m**). The objective being to react the complexes **1** with the bis(cyclohexanedionedioximato)pyridinecobalt(II) (**4**) or the bis(cyclohexanedionedioximato)pyridinecobaltate(I) ion (**6**) and to react the complexes **2** with the bis(dimethylglyoximato)pyridinecobalt(II) complex (**3**) or the bis(dimethylglyoximato) pyridinecobaltate(I) ion (**5**), and to determine the extent of exchange, if any, by isolation and examination by NMR, of the total organocobaloxime(III) after various time intervals. The spectra of the corresponding methylcobaloximes **1a** and **2a** are shown in Figure 1. That of **1a** has a characteristic 12-proton resonance of the dimethylglyoximato ligands at δ 2.09, which is sufficiently separated from the two broad resonances of the cyclohexanedionedioximato ligands of **2a** at δ 1.4–1.9 and 2.5–3.0 that accurate integration may be carried out on



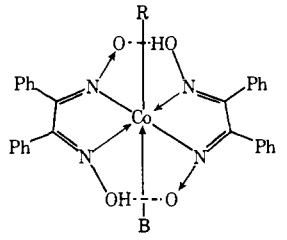
1 = RCo(dmgH)$_2$B



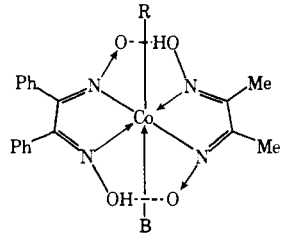
2 = RCo(chgH)$_2$B



9 = RCo(dmgH)(chgH)B



12 = RCo(dpgH)$_2$B



15 = RCo(dpgH)(dmgH)py

	R =	B =
a	Me	py
b	Et	py
c	*n*-Pr	py
d	*n*-Bu	py
e	*n*-Oct	py
f	*i*-Pr	py
g	*i*-Bu	py
h	*sec*-Bu	py
l	*sec*-Oct	py
j	$PhCH_2CH_2$	py
k	*threo*-PhCHDCHD	py
l	*erythro*-PhCHDCHD	py
m	CH_2:$CH(CH_2)_3CH_2$	py
n	$ClCH_2$	py
p	Cl_2CH	py
q	cyclopentylCH_2	py
r	CH_2:CHPh	py
s	Me	MeOH
t	$PhCH_2$	py
u	4-$BrC_6H_4CH_2$	py

$$Co^{II}(xgH)_2B \rightleftharpoons Co^{II}(xgH)_2B_2$$

3, x = dm; B = py — **3b**, x = dm; B = MeOH
3a, x = dm; B = MeOH — **3c**, x = dm; B = py
4, x = ch; B = py — **4b**, x = ch; B = MeOH
4a, x = ch; B = MeOH — **4c**, x = ch; B = py

$$\rightleftharpoons Co^{II}(xgH)_2B(MeOH)$$

3d, x = dm; B = py
4d, x = ch; B = py

$$[Co^{I}(xgH)_2B]^- \rightleftharpoons [Co^{I}(xgH)_2]^- \overset{H^+}{\rightleftharpoons} HCo(xgH)_2B$$

5, x = dm; B = py or MeOH — **5a**, x = dm — **5b**, x = dm
6, x = ch; B = py or MeOH — **6a**, x = ch — **6b**, x = ch

$$RCo(xgH)_2B \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} [RCo(xgH)(xg)B]^- \rightleftharpoons [RCo(xgH)_2OMe]^-$$

1, x = dm — **7**, x = dm; B = py or MeOH — **7a**, x = dm
2, x = ch — **8**, x = ch; B = py or MeOH — **8a**, x = ch

$$HOCo(dmgH)_2OH_2 \overset{H^+}{\rightleftharpoons} Co(dmgH)_2(OH_2)_2^+ \rightleftharpoons Co(dmgH_2)OH_2^+$$

13 — **14** — **16**

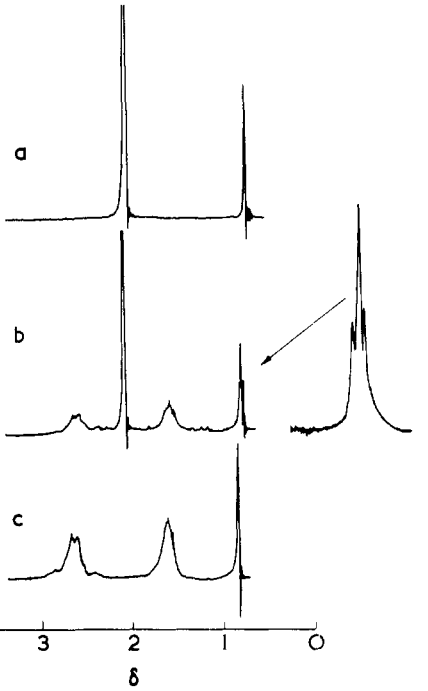


Figure 1. ^{1}H NMR spectra ($CDCl_3$; 33 °C) of: (a) **1a**; (b) final organometallic product (isolated) of reaction of **1a** with **4** or **6** and of **2a** with **3** or **5**; (c) **2a**.

appropriate mixtures of **1** and **2** as a means of determining the proportions of the two species. The alkyl proton resonances of a particular pair of complexes **1** and **2** have very similar though not necessarily identical chemical shifts. Thus, in the simplest case, i.e., a mixture of **1a** and **2a**, the methyl resonances may be distinguished under good resolution, but this is not the case with most higher alkylcobaloximes.

Character of the Reagents. The pyridine complexes of the cobaloximes were chosen because of the ease of preparation, purification, and isolation of the alkylcobalt(III) derivatives **1** and **2** and because of the homogeneity of mixtures of the appropriate reagents at 0 °C under the reaction conditions. This choice does, however, as outlined below, present difficulties in identifying the exact nature of all the species present in solution.

Alkylcobaloxime(III) Complexes. The alkylcobaloxime(III) complexes are essentially six-coordinate in which the pyridine ligand trans to the alkyl group is prone to exchange. Under the conditions of the present work these complexes may be expected, from studies in aqueous solution,[19] to be less than 10% converted into the corresponding methanol complex and to be substantially unchanged in methylene chloride solution. The concentration of the five-coordinate species will be negligible[20] but, in the alkaline solutions used for the cobaloxime(I) reactions, complexes **1** and **2** may be partially converted into their conjugate bases **7** and **8** or **7a** and **8a**.[21]

Cobaloxime(II) Complexes. The pyridinecobaloxime(II) complexes, which are readily oxidized in air,[22] have been reported to exist in methanolic solution as a mixture of three species, observable by ESR spectroscopy, namely, the dimethanol, the dipyridine, and the methanol/pyridine complexes (**3b** and **4b**, **3c** and **4c**, and **3d** and **4d**, respectively).[23] However, since such six-coordinate cobalt(II) complexes would necessarily be 19-electron complexes, it seems as likely that the five-coordinate complexes **3** and **4** or **3a** and **4a** predominate. The acid dissociation constants of these complexes have not been measured, but it is known that, in alkaline solution, disproportionation to the corresponding cobalt(III) and cobalt(I) complexes takes place readily (eq 1),[24] the appearance

of the blue color of the latter coupled with the disappearance of the ESR signal of the cobaloxime(II) complex being readily observed when a molar excess of alkali is added to a neutral solution of the cobaloxime(II).[25] This disproportionation is probably a result of the greater acidity of the cobalt(III) species. It is essential therefore to avoid alkaline solutions when studying the reactions of the cobaloxime(II) complexes. At the commencement of this work it was believed that the above were the essential properties of the cobaloxime(II) complexes but, as demonstrated below, exchange of the equatorial ligands also takes place rapidly compared with the rates of exchange reactions studied in this work.

$$2Co^{II}(xgH)_2py \rightleftharpoons [Co^{I}(xgH)_2py]^- + [Co^{III}(xgH)_2py]^+ \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} Co^{III}(xgH)(xg)py \quad (1)$$

Cobaloxime(I) Complexes. The cobaloxime(I) complexes **5** and **6** are believed to have a very labile fifth ligand, e.g., either pyridine or methanol in methanolic solution, to exist in equilibrium with significant proportions of the four-coordinate species **5a** and **6a,** to be readily oxidized in air, to decompose slowly in protic solvents at room temperature, and to undergo protonation to the hydridocobaloxime(III) complexes **5b** and **6b** in neutral or acidic solution.[26] We have been unable to detect ESR spectra in methanolic solutions of cobaloxime(I) containing an excess of borohydride ion at room temperature, but the blue color of the cobaloxime(I) is slowly discharged within a few hours. As described below, dissociation of the equatorial ligands is now known to take place rapidly in these species.

For simplicity in the following discussions, the above cobaloxime(I) and cobaloxime(II) complexes will be discussed in terms of the five-coordinate formulas **3, 4, 5,** and **6** and the organocobaloxime(III) complexes will be discussed in terms of the six-coordinate species **1** and **2,** except where differences are particularly relevant.

Randomization of Equatorial Ligands in Methylcobaloxime(III) in the Presence of Cobaloxime(I) or Cobaloxime(II). The ^1H NMR spectra ($CDCl_3$) of the equatorial ligands of the methylcobaloxime recovered by extraction after aerobic quenching of an anaerobic mixture of **1a** and the cobaloxime(I) **6** after 5 and 15 min, respectively, at 0 °C in methanol, are identical. They appear to correspond to a mixture containing equal proportions of **1a** and **2a** (eq 2), i.e., two broad multiplets and a sharp singlet in the ratio 8:8:12, respectively. Apparently, equilibrium distribution of the methyl group had been attained even within the shorter period.

$$\underset{\mathbf{2a}}{MeCo^{III}(chgH)_2py} + \underset{\mathbf{5}}{[Co^{I}(dmgH)_2py]^-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\mathbf{1a}}{MeCo(dmgH)_2py} + \underset{\mathbf{6}}{[Co(chgH)_2py]^-} \quad (2)$$

However, under good resolution it is apparent from the alkyl(methyl) resonance (Figure 1) that there are *three* methylcobaloximes present, namely, **1a, 2a,** and **9a** in the ratio 1:1:2, respectively. The mixed ligand complex **9** is thus the main product of reaction (eq 3) but has equatorial ligand resonances coincidental with those of **1** and **2**.

$$\underset{\mathbf{2a}}{MeCo(chgH)_2py} + \mathbf{6} \rightleftharpoons \mathbf{5} + \underset{\mathbf{1a}}{MeCo(dmgH)_2py} \quad (3)$$

$$\underset{\mathbf{9a}}{MeCo(dmgH)(chgH)py}$$

The same mixture of complexes is obtained when methylcobaloxime is prepared by the reaction between methyl iodide and cobaloxime(I) prepared from a mixture of cobalt chloride, dimethylglyoxime, and cyclohexanedione dioxime in the ratio 1:1:1. Clearly, effectively complete randomization of the equatorial ligands has taken place and this could account for the apparent exchange of alkyl groups. Similar randomization also takes place in the reaction between methylcobaloxime and cobaloxime(II) (eq 4).

$$MeCo(dmgH)_2py + \mathbf{4} \rightleftharpoons \mathbf{3} + MeCo(dmgH)_2py \quad (4)$$

$$MeCo(dmgH)(chgH)py$$

Randomization might occur by one or both of two principal routes: exchange of equatorial ligands might occur directly between the alkylcobaloxime(III) complexes **1** and **2** and free ligand or, after an initial alkyl transfer reaction corresponding to eq 2 or 5, the equatorial ligands might exchange rapidly between the original cobaloxime(I) or cobaloxime(II) reagent and the newly displaced cobaloxime(I) or cobaloxime(II) species, respectively, to give the mixed ligand cobaloxime(I) **10** or cobaloxime(II) **11** (eq 6 and 7). Reaction of **10** or **11** with **1** or **2** would thus give rise to the observed product **9** (eq 8 and 9).

$$MeCo^{III}(chgH)_2py + Co^{II}(dmgH)_2py \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} MeCo^{III}(dmgH)_2py + Co^{II}(chgH)_2py \quad (5)$$

$$[Co^{I}(dmgH)_2py]^- + [Co^{I}(chgH)_2py]^- \rightleftharpoons \underset{\mathbf{10}}{2[Co^{I}(dmgH)(chgH)py]^-} \quad (6)$$

$$Co^{II}(dmgH)_2py + Co^{II}(chgH)_2py \rightleftharpoons \underset{\mathbf{11}}{Co^{II}(dmgH)(chgH)py} \quad (7)$$

$$MeCo(chgH)_2py + [Co^{I}(dmgH)(chgH)py]^- \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} MeCo(dmgH)(chgH)py + [Co^{I}(chgH)_2py]^- \quad (8)$$

$$MeCo(chgH)_2py + Co^{II}(dmgH)(chgH)py \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} MeCo(chgH)(dmgH)py + Co^{II}(chgH)_2py \quad (9)$$

The former mechanism is unlikely because, under alkaline or neutral conditions in the absence of **3–6,** but in the presence of a tenfold or larger excess of cyclohexanedionedioxime, neither the mixed complex **9** nor the complex **2a** is formed from **1a** even after several hours at room temperature in methanolic solution. On the other hand, the observations are completely in accord with the second mechanism involving randomization in the cobaloxime(I) and cobaloxime(II) species. The randomization is only apparent in those complexes for which alkyl exchange also takes place, the rate of randomization of the equatorial ligands being a function of the rate of alkyl transfer discussed in detail below. Moreover, *complete* randomization of equatorial ligands in **1** and **2** and in the inorganic species necessitates complete equilibration in the alkyl transfer reaction,[27] though the two processes are *not* concerted.

In view of the absence of an excess or deficiency of the equatorial ligand in these reactions, it seems likely that the randomization involves predissociation of an equatorial ligand, though a bimolecular mechanism involving two molecules of the inorganic cobaloxime cannot be ruled out, particularly in the case of the cobaloxime(II) complexes. The high rate of randomization in the inorganic species under these conditions is, however, surprising and has not hitherto been appreciated.

Randomization of Equatorial Ligands in the Higher Alkylcobaloximes. Similar random exchange of equatorial ligands

Table I. Kinetics of Reaction of Alkylcobaloxime[R'Co] with Cobaloxime(II) [Co^{II}][a]

R'	10^3[R'Co]/M	10^3[Co^{II}]/M	Solvent	10^7R/mol dm^{-3} s^{-1}	10^2k_5/dm^3 mol^{-1} s^{-1}	Temp/°C
Me	1.97	1.97	MeOH	⩾1730	⩾4400	0
Et	4.40	4.40	MeOH	19.6	10	0
n-Pr	6.11	6.11	MeOH	39.4	12	28
n-Pr	3.05	3.05	MeOH	10.7	12	28
n-Bu	4.10	4.10	MeOH	13.5	8	28
n-Oct	4.50	4.50	MeOH	0.337	0.17	−10
n-Oct	5.0	5.0	MeOH	1.60	0.64	0
n-Oct	6.0	6.0	CH_2Cl_2	0.124	0.034	0
n-Oct	6.0	6.0	CH_2Cl_2	0.435	0.12	10
n-Oct	6.0	6.0	CH_2Cl_2	1.38	0.39	20
n-Oct	5.0	5.0	MeOH	17.8	7.1	23
n-Oct[b]	5.0	5.0	MeOH	17.0	6.4	23
n-Oct	6.0	6.0	CH_2Cl_2	3.75	1.0	28
n-Oct	3.0	3.0	CH_2Cl_2	1.08	1.2	28
n-Oct	4.0	4.0	MeOH	30.1	12	28
Hexenyl	5.0	5.0	MeOH	15.4	6.2	28
$PhCH_2CH_2$	4.0	4.0	MeOH	5.83	3.6	28
i-Bu	4.5	4.5	MeOH	0.19	0.094	28
i-Pr	5.0	5.0	MeOH	1.36	0.54	28
sec-Bu	5.0	5.0	MeOH	0.066	0.026	28
PhCHDCHD	2.5	2.5	MeOH	2.5[c]	4.0	28
PhCHDCHD	2.2	2.2	MeOH	3.3[c]	3.7	28

[a] Studied using **2** and **3**; accuracy in k_5 ± 8%. [b] Studied using **1** and **4**; accuracy ±12% [c] From the growth of the β-proton doublet in the spectrum of erythro and threo diasteroisomers; accuracy ±25%.

may also be demonstrated over longer periods in the alkyl exchange reactions of the higher alkylcobaloximes. In most cases such randomization cannot be demonstrated directly from the NMR spectra of the products because of appreciable overlap of the several resonances. However, randomization can be demonstrated, in those cases where alkyl exchange does take place, by treating the alkylcobaloxime **1** (or **2**) with a small amount of **5** (or **6**, respectively) in the presence of a tenfold excess of cyclohexanedione dioxime (or dimethylglyoxime, respectively) under the normal conditions of exchange. The presence of **9** and/or **2** (or **9** and/or **1**) in the reaction product (eq 10) can readily be deduced from the NMR spectrum of the product[28] and by separation of the isomers **1e, 2e,** and **9e** using TLC. However, it is noticeable that, with the excess of equatorial ligand in the solution, the blue color of the cobaloxime(I) fades much more quickly. Reduction of the dioximato ligands is therefore probably one of the prime causes of the instability of cobaloxime(I) solutions.

$$\underset{\mathbf{1}}{RCo(dmgH)_2py} \overset{5 + \text{excess chgH}_2}{\rightleftharpoons} \underset{\mathbf{2}}{RCo(chgH)_2py} + \underset{\mathbf{9}}{RCo(dmgH)(chgH)py} \quad (10)$$

Treatment of the Rate Data for Alkyl Exchange. Were no randomization to accompany the alkyl exchange (i.e., if eq 2 or 5 were solely involved) the rate of growth of the appropriate equatorial ligand resonance, e.g., dimethylglyoximato in the case of the reaction of **2** with **3** or **5**, could clearly be used as a direct measure of the rate of approach to the equilibrium mixture and hence of alkyl exchange. In these cases, where that equilibrium mixture contains equal concentrations of **1** and **2** when derived from equal concentrations of **2** and **3** (or **5**), the rate of exchange is given by the McKay equation (11)[29]

$$-R = \ln (1 - \alpha/0.5)[A_0][B_0]/([A_0] + [B_0])t \quad (11)$$

where R, measured in mol m^{-3} s^{-1}, is the constant rate of exchange of alkyl groups, $[A]_0$ and $[B]_0$ are the initial concentrations of the two reagents, and α is the fraction of new equatorial ligand in the total of organocobaloxime product after time t. Fortunately, as shown in the Appendix, the same equation holds for the rate of exchange even in those cases where all or partial randomization of equatorial ligands occurs, provided that the dimethylglyoximato and cyclohexanedionedioximato ligands have an equal influence on the rates of reaction of the several species (**1–6** and **9**) in which they are contained, i.e., provided the final ratio **1**:**2** is near unity and the maximum proportion of the mixed ligand complex **9** is ca. 50% of the total.[30]

We have verified the applicability of eq 11 by computing the growth of the appropriate ligand resonance in a model reaction between a total of 10^6 mol of **1** and 10^6 mol of **4**, assuming that the reagents react in batches of 10^3. Allowing for either complete or zero randomization of equatorial ligands in the reagent and product cobaloxime(II) species after each batch of reactions, the calculated increases in the size of the appropriate ligand resonance in the organocobalt(III) species are the same, within 1 part in 10^4, despite the approximation involved in selecting batches of molecules for reaction.

In the following discussion therefore the rates of alkyl transfer calculated using eq 11 will be referred to in terms of the simple alkyl transfer corresponding to eq 2 and 5 and the randomization will be neglected except where particularly relevant.

Rates of Alkyl Transfer. (a) Cobaloxime(II) Promoted Reactions. Anaerobic exchange reactions of **1a–m** and/or **2a–m** (more usually the latter) with **4** and **3**, respectively, were carried out in methanol buffered with acetic acid, as shown in Table I. The rates of alkyl exchange R, determined using eq 11, and the second-order rate coefficients, which are the values of R divided by the product of the initial concentrations of the two reagents, are shown in Table I. Though only one or two aliquots could satisfactorily be taken from each reaction mixture, the results from these and from multiplicate reactions with freshly prepared reagents demonstrated that the reaction was reproducible and, as shown in several cases, that the rate of approach to equilibrium (i.e., the rate of growth of one of the equatorial ligand resonances) was clearly first order. Moreover, the values of the second-order rate coefficients k_5 for the *n*-propyl- and *n*-octylcobaloximes were sensibly constant with changes in concentration of the two reagents. It is assumed therefore that k_{-5}, k_8, and k_{-8} are also second-order

Table II. Kinetics of Reaction of Alkylcobaloximes [R'Co] with Cobaloxime(I) [Co[I]] in Methanolic Solution

R'	10^3 [R'Co]/M[a]	10^3 [Co[I]]/M[b]	10^3 [$NaBH_4$]/M	10^3 [NaOH]/M[c]	Recovery[d] method	10^7 R/mol dm^{-3} s^{-1}	10^2 k_2/dm^3 mol^{-1} s^{-1}	T/°C
Me	1.63	1.63	0.82	33	E	≥460	≥1700	0
Et	6.5	6.5	3.2	33	E	45	10.7	0
Et	6.5	6.5	3.2	33	E	40	9.4	0
Et	12.9	12.9	3.2	72	E	117	7.0	0
n-Pr	13	13	6.5	33	P	9.0[g]	0.53	0
n-Pr	13	13	6.5	33	E	6.9	0.41	0
n-Pr[e]	13	13[f]	6.5	33	P	62[g]	3.7	23
n-Pr	13	13	6.5	33	E	7.1	4.2	23
n-Bu	13	13	6.5	33	E	3.9	0.23	0
n-Bu	13	13	6.5	33	E	68	4.0	23
n-Bu	13	13	6.5	33	P	33	1.9	23
n-Octyl	13	13	6.5	33	E	6.7	0.40	0
n-Octyl	12.5	12.5	6.5	72	E	6.2	0.35	0
n-Octyl	13	13	6.5	33	P	11	0.64	0
n-Octyl	13	13	6.5	33	P	9.2	0.55	0
n-Octyl	6.5	6.5	3.3	33	P	3.5	0.82	0
n-Octyl	6.5	6.5	3.3	33	P	2.2	0.50	0
n-Octyl[h]	13	13[f]	13	33	P	7.4	0.44	0
n-Octyl	12.5	12.5	5.4	73	E	10.6	0.68	4.5
n-Octyl	12.5	12.5	5.5	71	E	17.3	1.1	9
n-Octyl	12.5	12.5	5.5	66	E	24.6	1.6	23
n-Octyl	13	13	13	33	P	27.5	1.6	23
n-Octyl	6.5	6.5	6.5	33	P	6.5	1.5	23
n-Octyl	6.5	6.5	0.8	33	P	3.4	0.82	23
n-Octyl	13	13	1.6	33	P	18	1.1	23
n-Octyl	12.5	12.5	5.5	71	E	40.7	2.6	28
i-Butyl	13	13	6.5	33	E	0.45	0.027	28
PhCHDCHD	5	5	5.5	70	E	3.5	1.4	28

[a] Complex **2** unless otherwise stated. [b] Complex **5** unless otherwise stated. [c] Excess over that required to make cobaloxime. [d] E = extraction; P = precipitation. [e] Complex **1c**. [f] Complex **6**. [g] Corrected for loss of **1c** in precipitation method. [h] Complex **1e**.

rate coefficients of the same magnitude. The errors in the calculation of k_5 lie as much with the estimation of the exact concentrations of the reagents as with the measurement of peak areas, the accuracy of the latter being verified with separately prepared mixtures of pure products of known concentration.[31]

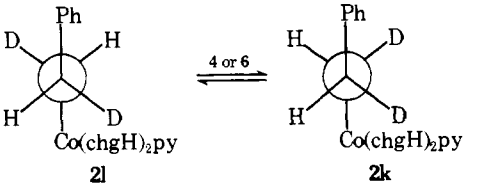
The alkyl exchange reaction of the methylcobaloximes was so fast even at 0 °C using very dilute solutions of the reagents (0.001 65 M), that the half-life for complete equilibration was ca. 30 s and only a lower limit to the exchange rate, and hence to k_5, could be estimated. The reactions of the higher primary alkylcobaloximes were appreciably slower, more easily measured, and reproducible. The *n*-octylcobaloximes were chosen for these more detailed studies because of their ease of recovery in near-quantitative yield.

Similar studies were also carried out in methylene chloride solvent using the *n*-octylcobaloximes and preformed cobaloxime(II). The rates of reaction R in this solvent and the derived second-order rate coefficients are included in Table I. No monochloromethylcobaloximes (**1n**, , **2n**, or **9n**) could be detected in the reaction products from **2e** and **3** in methylene chloride, even after several days, but small amounts of the three dichloromethylcobaloximes **1p**, **2p**, and **9p** (≤2%), identified from the three singlets at ca. δ 5.8 and the singlet dimethylglyoximato resonance at δ 2.18,[34] were formed over these long periods and also from the reaction of cobaloxime(II) with methylene chloride. No chloroform was present in the methylene chloride and cannot therefore account for these products. When the above reaction was carried out in the presence of acetic acid (ca. 2 mol) and phenylacetylene (1 mol), neither the monochloromethylcobaloximes nor α-styrylcobaloximes (**1r**, **2r**, or **9r**) could be detected in the organocobalt product even after reaction times (ca. 2 days) corresponding to appreciable numbers of complete exchanges of the octyl group.

The reaction of the hexenylcobaloxime **1m** was also carried out with the corresponding cobaloxime(II) **3** in methanolic solution for several days at 28 °C corresponding to several complete exchanges of the hexenyl group, but little decomposition could be detected and no cyclopentylmethylcobaloxime (**1q**) could be detected in the product organocobaloxime.

(b) Cobaloxime(I) Promoted Reactions. The reaction of the alkylcobaloximes **1** and **2** with the cobaloxime(I) **6** and **5**, respectively, was similarly studied using (necessarily) alkaline methanolic solutions in the presence of various excess proportions of borohydride ion. The reactions took place at rates similar to those of the cobaloxime(II) promoted reactions as shown by the values of R and the derived second-order rate coefficients k_2 in Table II. However, owing to the instability of the cobaloxime(I) solutions at the higher temperatures, activation parameters were not determined and no rate coefficients could be measured for the less reactive secondary alkyl complexes.

Stereochemistry. The reaction of the β-phenylethylcobaloxime **2j** with the cobaloxime(II) complex **3** was carried out as above to determine the rate of the alkyl exchange reaction at 28 °C in methanol (Table I). The corresponding reaction of the diastereoisomeric dideuterated β-phenylethylcobaloxime **2l** (containing ≤10% of the isomer **2k**) was similarly carried out using the corresponding cobaloxime(II) and cobaloxime(I) species **4** and **6**, respectively, i.e., with a common equatorial ligand (eq 12) throughout. The formation of the diastereo-



2l **2k** (12)

Table III. Influence of Alkyl Group on the Relative Rates of Alkyl Transfer Reactions

Reaction	Solvent (temp, °C)	R							Stereochemistry	Absolute rate R = Et/dm mol^{-1} s^{-1}	Footnotes
		Me	Et	*n*-Pr	*n*-Bu	*i*-Pr	*sec*-Bu	*i*-Bu			
$RCo(dmgH)_2py + Co^{II}(chgH)_2py$	MeOH (0)	≥440	1.0	0.06	0.04	2.7×10^{-3}	1.3×10^{-4}	4.7×10^{-4}	Inversion	10^{-1}	*a*
$RCo(dmgH)_2py + Co^{I}(chgH)_2py^-$	MeOH (0)	≥170	1.0	0.04	0.02			1.4×10^{-4}	Inversion	10^{-1}	*a*
$RCo(dmgH)_2aq + Hg^{2+}·aq$	H_2O (25)	530	1.0	0.07		$<10^{-8}$		0.03	Inversion	1.9×10^{-3}	*b*
$RCr·aq^{2+} + Hg^{2+}·aq$	H_2O (25)	71	1.0	0.25		1.1×10^{-5}				1.4×10^{5}	*c*
$RCr·aq^{2+} + MeHg·aq^{+}$	H_2O (25)	50	1.0	0.61	0.04					1.99×10^{2}	*c*
$RHgX + HgX_2$	EtOH (60–100)	2.4	1.0				0.15		Retention	Various	*d*
$R_2Hg + HCl$	DMSO (50)	0.16	1.0	0.60		0.68			Retention	8.2×10^{-4}	*e*
$RSnMe_3 + Br_2$	AcOH (20)	2.4	1.0	0.19	0.44	2.5×10^{-2}			Inversion	1.21	*f*
'Typical' S_N2	Various	30	1.0	0.4	0.4	2.5×10^{-2}		3×10^{-2}	Inversion	Various	*g*

[a] Some values calculated assuming $\Delta H^{\#}$ same as for R = *n*-octyl. This work. [b] Reference 9d. [c] J. H. Espenson, personal communication. [d] Reference 1. [e] R. E. Dessy, G. F. Reynolds, and J. Y. Kim, *J. Am. Chem. Soc.*, 81, 2683 (1959); Stereochemistry in dioxane solvent. D. L. H. Gale, J. Landgrebe, and F. R. Jensen, *Chem. Ind. (London)*, 118 (1960). [f] S. Boué, M. Gielen, and J. Nasielski, *J. Organomet. Chem.*, 9, 443 (1967). [g] A. Streitweiser, "Solvolytic Displacement Reactions", McGraw-Hill, New York, N.Y., 1962, p 13.

isomeric cobaloxime **2k** was evident from the deuterium decoupled ^1H NMR spectrum (Figure 2) in each case and the rates of approach to equilibrium calculated from the areas of the appropriate doublet resonances,[31] though appreciably less accurate than those calculated from the rate of incorporation of the equatorial ligands in **2j**, were clearly of a similar magnitude to those for the exchange calculated in the latter manner (Tables I and II).

Nature of the Exchange Reaction. (a) Cobaloxime(II). The similar well-ordered behavior of the cobaloxime(II) exchange reactions in methanol and in methylene chloride solution clearly indicate that the neutral cobaloxime(II) complexes **3** or **4** are the reactive inorganic species. A difference of less than 20-fold in the rate coefficients for the reaction of *n*-octylcobaloxime in two such different solvents (ϵ = 33 and 9, respectively)[32] is inconsistent with significant charge separation in either reagents or transition state. The blue cobalt(I) species was not evident in either methanol or methylene chloride and the lack of monochloromethylcobaloxime in the reaction product from methylene chloride solutions also indicates that cobaloxime(I), which reacts with methylene chloride to give that complex,[34] is not present. Moreover, the absence of α-styrylcobaloxime in the product, when the reaction was carried out in the presence of phenylacetylene and acetic acid, similarly indicates that the corresponding hydridocobaloxime(III) species **5b** and **6b**, which are readily trapped by the acetylene,[35] are also absent from the inorganic reagent. The formation of dichloromethylcobaloxime was unexpected and may perhaps be explained if some dichloromethyl radicals, formed by side reactions, are readily captured by the cobaloxime(II) species (eq 13).

The variation of the rate of the alkyl exchange with the character of the alkyl group is completely in accord with a displacement reaction taking place at the α-carbon of that group.[9d,36] The variation in rate is in fact much larger than is normally observed in displacement reactions, as shown from the several collected rate profiles for reactions involving both inversion and retention of configuration at the α-carbon (Table III). However, the only comparable data for a *homolytic* displacement is likely to be that for the displacement of cobaloxime(II) by chromium(II),[13] though this is limited and has not been completely verified.[37]

The rate profile with respect to the alkyl group gives no clear indication of the stereochemistry of the reaction, but the results with the diastereoisomeric β-phenylethylcobaloximes demonstrate that inversion of configuration is, at the least, the predominant process. In view of the low accuracy in the calculation of the rate of exchange from the erythro/threo proportions it cannot be verified that *every* act of substitution involves inversion, though it seems probable that this is so. The large bulk of the incoming and outgoing cobaloximes in the transition state thus results in very large steric compression of the alkyl group, which is greatly increased by any additional substitution at either α- or β-carbon; the presence of both α- and β-substituents, as in the *sec*-butyl group, causes a particularly large rate decrease. Since solvation clearly plays no more than a small part in this reaction, the entropy of activation can be directly attributed to the problem of restriction of the alkyl group in the transition state (for reaction of the *n*-octyl complex

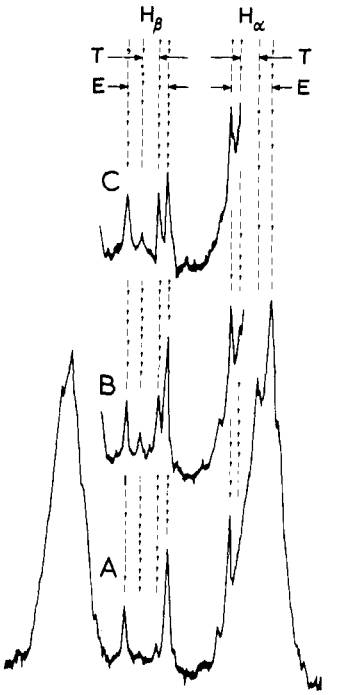


Figure 2. ^2H-Decoupled ^1H NMR spectra of: (A) **21** containing traces of **2k**; (B) organometallic product of reaction of **21** (as in A above) (2.5×10^{-3} M) with **4** (2.5×10^{-3} M) after 5400 s at 28 °C in methanol; (C) the organometallic product of reaction of **21** (5×10^{-3} M) with **6** (5×10^{-3} M) after 6900 s at 28 °C in methanol. E and T indicate the positions of resonances of the erythro and threo complexes **21** and **2k** respectively.

1e $\Delta H^{\ddagger} = 85$ kJ mol^{-1}, $\Delta S^{\ddagger} = 17$ J mol^{-1} K^{-1} (CH_2Cl_2); $\Delta H^{\ddagger} = 76$ kJ mol^{-1}, $\Delta S^{\ddagger} = 25$ J mol^{-1} K^{-1} (MeOH)).

The absence of side reactions involving alternative free radical forming paths, such as that of eq 14, is also evident from the absence of cyclopentylmethylcobaloxime in the product of reaction of the hexenylcobaloxime. Had the attack of cobaloxime(II) been at cobalt rather than at carbon, with displacement of the hexenyl radical, then a significant proportion of the latter would have cyclized[38] to the cyclopentylmethyl radical which would have been largely captured by the high concentration of cobaloxime(II) present in the mixture. Despite the large number of exchanges that must have taken place during this reaction, no part appeared to have generated the cyclized product. In the much slower exchange reactions of some secondary alkylcobaloximes, some other homolytic reactions may well accompany the observed exchange.

$$Cl_2CH\cdot + Co^{II}(xgH)_2py \longrightarrow Cl_2CH\text{-}Co(xgH)_2py \quad (13)$$

$$CH_2{:}CH(CH_2)_4Co(xgH)_2py + Co^{II}(xgH)_2py \not\longrightarrow CH_2{:}CH(CH_2)_3CH_2\cdot + [Co(xgH)_2py]_2 \quad (14)$$

(b) Cobaloxime(I) Exchange Reactions. The main concern with the cobaloxime(I) promoted alkyl exchange reactions is to establish whether cobaloxime(I) or traces of cobaloxime(II) are the reactive species, for in the majority of reactions the latter is slightly the more reactive species. Fortunately, as the rates of reaction of cobaloxime(I) and cobaloxime(II) with ethyl- or *n*-octylcobaloxime in methanol at 0 °C are almost the same, it is most unlikely that the reactions of the bulk, blue, cobaloxime(I) solutions take place through cobaloxime(II) impurities, unless such impurities constitute ca. 90 or 50%, respectively, of the *total* inorganic cobaloxime. Since borohydride reduces cobaloxime(II) to cobaloxime(I), the lack of influence of various excess amounts of borohydride on the rate suggests that cobaloxime(II) is neither present in such large concentration nor the main reactive species. The absence of an ESR signal in these reaction solutions also rules out significant concentrations of cobaloxime(II).[23] The slight decrease in rate as the alkali concentration is increased may be ascribed to partial deprotonation of the complexes **1** and **2** to the corresponding, probably less reactive, conjugate bases **7** and **8**.

In view of the highly nucleophilic character of the cobaloxime(I) species and the fact that a number of "good" polarizable nucleophiles toward saturated carbon (e.g., I^-) are also good leaving groups in nucleophilic substitution, this nucleophilic exchange reaction is not particularly novel, and the observed inversion of configuration is in accord with all other known S_N2 reactions at saturated carbon. We have also observed displacement of cobaloxime(I) from **1** and **2** by rhodoxime(I),[14] and displacement of cobaloxime(I) by conventional nucleophiles has been reported.[39,40]

(c) Cobaloxime(III) Promoted Reactions. The corresponding study of the reaction of alkylcobaloxime(III) complexes with cobaloxime(III) complexes (eq 15) presents numerous problems. We have shown that exchange between methylcobaloxime(III) **2a** and the aquocobaloxime(III) complex **13** is many orders of magnitude slower than the reactions described above. Moreover, even small traces of cobaloxime(II) may catalyze alkyl exchange between cobaloxime(III) complexes. For example, a mixture of the benzylcobaloximes **12t** and **1u** in $CDCl_3$ equilibrates within 24 h giving first the alternative pair of benzylcobaloximes **1t** and **12u** and later the mixed ligand complexes **15t** and **15u**. In the presence of bromotrichloromethane, which rapidly removes traces of cobaloxime(II) from these solutions,[37] the equilibration does not take place; in the presence of small traces of dimethylglyoxime, the rate of equilibration is enhanced, except in the presence of bromotrichloromethane, and the mixed ligand complexes **15t** and **15u** appear near the beginning of the reaction.[41] Clearly, though detailed mechanistic studies of such slow reactions catalyzed by traces of complexes in other oxidation states would prove impracticable in this system, earlier studies on *equilibria* between various alkylcobalt(III) complexes[16] and inorganic cobalt(III) complexes are unaffected by this problem.

However, the leaving group ability of the cobaloxime(III) complex **16** has been amply demonstrated[9] and thus we have the interesting situation in which cobaloxime(I), -(II), and -(III) species are leaving groups in nucleophilic, homolytic, and electrophilic substitutions, respectively, at saturated carbon. We may only speculate that the apparent low reactivity of the inorganic cobaloxime(III) species **13** as a reagent is due to the fact that it is substitution inert having only small or negligible proportions of the reactive five-coordinate species (**16**) present in the reaction solution. The exchange of equatorial ligands between the inorganic cobaloxime(III) complexes is also liable to catalysis by traces of cobaloxime(II) complexes.

$$\underset{\mathbf{13}}{Co^{III}(dmgH)_2(OH)(H_2O)} + RCo^{III}(chgH)_2py \overset{slow}{\rightleftharpoons} RCo^{III}(dmgH)_2py + Co^{III}(chgH)_2(OH)(H_2O) \quad (15)$$

Comparison of the Three Substitution Processes. All three types of alkyl transfer reaction may be viewed as substitution processes; substitution by cobaloxime(I) and by cobaloxime(II) may also be considered as two-electron and one-electron transfer processes, respectively, via a saturated carbon bridge. Any substituion by cobaloxime(III) would involve no net oxidation or reduction. The transition states for all three synchronous substitution processes[42] are likely to be similar; effectively involving three-center linear systems having two paired electrons, one unpaired electron, or zero electrons, respectively, in a nonbonding three-center orbital *located largely on both cobalt atoms*.[43] It seems likely, therefore, that the similarity in the rate coefficients for the cobaloxime(II) and cobaloxime(I) reactions may be a result of the ability of the metal atoms to accommodate these electrons.

However, mechanisms involving electron transfer processes must also be considered. For example the cobaloxime(II) species may act as a nucleophile with the unpaired electron in a low lying orbital which does not directly participate in the bonding changes in the transition state. If this were the case it would be necessary to postulate that the primary products would be the charged alkylcobaloxime(IV) and inorganic cobaloxime(I) species (eq 16) and hence that a subsequent or near-synchronous electron transfer would have to take place rapidly in order to give the observed products (eq 17).

$$RCo(chgH)_2py + Co(dmgH)_2py \rightleftharpoons [RCo^{IV}(dmgH)_2py]^+ + [Co^{I}(chgH)_2py]^- \quad (16)$$

$$[RCo^{IV}(dmgH)_2py]^+ + [Co^{I}(chgH)_2py]^- \rightleftharpoons RCo(dmgH)_2py + Co(chgH)_2py \quad (17)$$

However, if this were so, the principle of microscopic reversibility would dictate that, ignoring the distinction between the two types of equatorial ligand, the alkyl exchange could *equally* involve an *initial* electron transfer, corresponding to the reverse of eq 17, followed by a nucleophilic displacement of cobaloxime(II) from alkylcobaloxime(IV) by cobaloxime(I), corresponding to the reverse of eq 16. This is demonstrated in the three-dimensional potential energy contour diagram of Figure 3, in which the direct homolytic displacement reaction of eq 5 is shown as a diagonal path through a symmetrical transition state and the two two-stage nucleophilic substitution/electron transfer mechanisms are shown as the peripheral clockwise and anticlockwise paths. For convenience, the horizontal axis of Figure 3 represents an electron transfer

reaction coordinate and the vertical axis represents an alkyl transfer reaction coordinate; the square shape of the figure and height of the contours are arbitrarily chosen so that the diagonal mechanism is shown as the more favorable.

There are two reasons for considering the peripheral mechanisms to be unlikely. First, though the kinetic form does not distinguish between these and the diagonal mechanism, the former involves appreciable charge separation in each initial stage, even if this may be in part minimized by allowing the two processes to merge slightly. The small rate variation on changing from methanol to methylene chloride is not consistent with this. Secondly, the redox potentials for electron transfer to cobaloxime(II)[44] and from alkylcobaloxime(III)[45] are both positive and their sum (ca. 2.0–2.5 V) would suggest too high an activation energy for this electron transfer step and hence for either peripheral mechanism.

Similar consideration of the cobaloxime(I) promoted reaction in terms of electron transfer processes cannot readily be expressed in terms of a square potential energy surface. While a corresponding diagram involving electron transfer and alkyl transfer coordinate for the reaction of eq 18 and 19 may be drawn, there is a fundamental problem concerning the nature of the displaced cobaloxime(I) species **17** of eq 19. Application of the principle of microscopic reversibility to reaction 19 clearly shows that a homolytic displacement *of* cobaloxime(II) *by* cobaloxime(I), which must take place at the same rate as the forward reaction of eq 19, can only occur if the reagent cobaloxime(I) species (**17**) is in a high spin excited state. A third reversible reaction (eq 20) not readily accommodated on the potential energy surface must therefore be drawn.

$$RCo^{III}(dmgH)_2py + Co^{I}(chgH)_2py^- \underset{\text{transfer}}{\overset{\text{electron}}{\rightleftharpoons}} RCo^{II}(dmgH)_2py^- + Co^{II}(chgH)_2py \quad (18)$$

$$Co^{II}(chgH)_2py + RCo^{II}(dmgH)_2py^- \underset{\text{transfer}}{\overset{\text{alkyl}}{\rightleftharpoons}} RCo^{III}(chgH)_2py + {}^*Co^{I}(dmgH)_2py^- \quad (19)$$

17

$${}^*Co^{I}(dmgH)_2py^- \rightleftharpoons Co^{I}(dmgH)_2py^- \quad (20)$$

17 **5**

As simple calculations show that the proportion of thermally excited cobaloxime(I) species ($<10^{22}$) is grossly insufficient to account for the observed rate coefficients, this mechanism can be ruled out.

Relevance of Alkyl Transfer Reactions to Biological Systems. Our results are of relevance to biological reactions of organocobalt complexes in two main ways. They illustrate that alkyl groups, particularly methyl groups, may be transferred from one cobalt to another with considerable ease and by a variety of mechanisms. The considerable rate reduction when methyl is replaced by other alkyl groups such as the propyl group may account for the very large inhibitory effect of propylation on the methionine synthetase reaction[18] through inhibiton of transfer of methyl groups from and to the different cobalamin sites.

However, the very ready randomization of the equatorial dioximato ligands indicates that the cobaloximes are clearly not good models for studies of the cobalamins. This lability may also account for the irreversibility of polarographic reduction processes involving alkylcobaloximes[44] in contrast to those of alklycobalt complexes having tetradentate equatorial ligands.

Experimental Sections

Materials. Bis(dimethylglyoximato)pyridinecobalt(II), chloro-, methyl-, ethyl-, *n*-propyl-, isopropyl-, *n*-butyl-, isobutyl-, *sec*-butyl-, *sec*-octyl-, *n*-octyl-, β-phenylethyl-, hexenyl, monochloromethyl-, dichloromethyl-, 4-bromobenzyl-, and benzylbis(dimethylglyoximato)-, and bis(cyclohexanedionedioximato)pyridinecobalt(III) complexes were prepared from commercial laboratory reagents by standard methods,[47] and purified by chromatography and/or recrystallization. Benzyl- and 4-bromobenzylbis(diphenylglyoximato)pyridinecobalt(III) were also prepared by standard methods, samples of the latter being kindly supplied by Mme C. Bied Charreton and Mr. C. J. Cooksey.

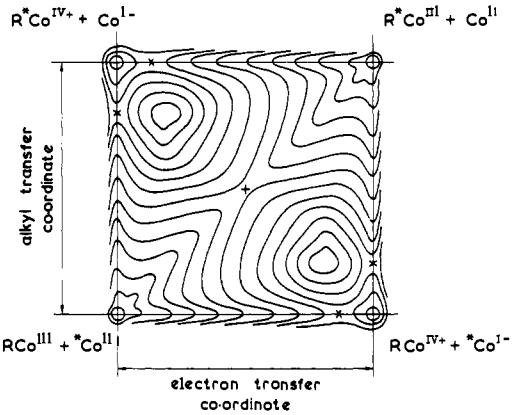


Figure 3. Potential energy surface diagram for a one-step homolytic substitution of labeled cobalt(II) for cobalt(II) in alkylcobalt(III) complexes (diagonal path) and for a two-step electron transfer/nucleophilic substitution mechanism (peripheral paths). All contours are arbitrary.

β-Phenyl-α,β-dideuterioethylbis(cyclohexanedionedioximato)pyridinecobalt(III). A mixture of *cis*- and *trans*-β-acetoxystyrene was prepared by refluxing phenylacetaldehyde in acetic anhydride containing sodium acetate. The trans isomer was recrystallized from pentane (mp 46 °C) and deuterogenated in small batches (~1 g) in ethyl acetate (5 mL) using deuterium gas and a 10% Pd on charcoal catalyst (0.1 g) (Koch-Light), such that not all the styryl acetate was reduced. The mixed product (5.2 g containing ca. 1 g styryl acetate) in dry diethyl ether (ca. 10 mL) was added slowly to lithium aluminum hydride (1.9 g) suspended in dry diethyl ether (20 mL). The excess of the hydride was destroyed by treatment with ethyl acetate, moist ether, water, and aqueous HCl. The alcohol was extracted and the tosylate was prepared by standard methods. β-Phenyl-α,β-dideuterioethylbis(cyclohexanedionedioximato)pyridinecobalt(III) was prepared from the tosylate by standard methods.

Kinetic Studies. Typical runs were carried out as follows.

(a) Cobaloxime(I) in Methanol. Chlorobis(dimethylglyoximato)-pyridinecobalt(III) (0.101 g; 0.25 mmol) was dissolved in methanol (1 mL) under nitrogen. Sodium hydroxide (0.057 g; 1.42 mmol in 0.3 mL of water) was injected and the solution was reduced with sodium borohydride (0.0105 g; 0.27 mmol) in water (0.2 mL) and methanol (1.5 mL) at 0 °C. When reduction was complete, *n*-octylbis(cyclohexanedionedioximato)pyridinecobalt(III) (0.1334 g; 0.25 mmol) in methanol (8.0 mL) at 0 °C was added. After an appropriate time interval, a sample was withdrawn and the reaction was quenched by rapid flushing with oxygen through the solution, which was then poured into water and extracted several times with methylene chloride. The extract was dried ($MgSO_4$) and the residue after evaporation of the solvent was examined by ^1H NMR (60 MHz). In some cases the solution was chromatographed on alumina before measurement of the spectrum and in others, particularly with higher alkylcobaloximes, the quenched reaction solutions were poured directly into water containing a small amount of pyridine and the mixed alkylcobaloxime was filtered off, washed with water, and dried in vacuo. The extent of reaction was determined from measurement of the relative areas of the dimethylglyoximato resonance and the lower field cyclohexanedionedioximato resonance (Figure 1b). The latter was measured from the apparent baseline (usually 15 Hz either side of the midpoint) and increased by 6.4% to allow for the very wide shallow outer parts of this resonance.

(b) Cobaloxime(II) in Methanol. Cobalt acetate tetrahydrate (0.0561 g; 0.225 mmol) and dimethylglyoxime (0.0524 g; 0.45 mmol) were dissolved in methanol (35 mL) under nitrogen and cooled to −10 °C. Pyridine (0.04 mL; 0.5 mmol) was added followed by *n*-octylbis(cyclohexanedionedioximato)pyridinecobalt(III) (0.12 g; 0.225 mmol) in methanol (15 mL) at −10 °C. After an appropriate time interval,

an aliquot was removed, quenched, extracted, and estimated as above.

(c) **Cobaloxime(II) in Methylene Chloride.** Bis(dimethylglyoximato)pyridinecobalt(II) (0.1105 g; 0.30 mmol) was dissolved in dichloromethane (30 mL) under nitrogen. *n*-Octylbis(cyclohexanedionedioximato)pyridinecobalt(III) was added at the appropriate temperature and, after an appropriate time interval, an aliquot was withdrawn, quenched with oxygen as above, chromatographed on alumina, and examined by NMR after evaporation.

Other Reactions. (1) Cobalt acetate tetrahydrate (0.0623 g; 0.225 mmol), dimethylglyoxime (0.0581 g; 0.45 mmol), and pyridine (0.05 mL) were dissolved in degassed methanol (50 mL) under nitrogen, and hexenylbis(dimethylglyoximato)pyridinecobalt(III) (0.114 g; 0.253 mmol) in methanol (10 mL) was added. After 18 days at ambient temperature, the homogeneous solution was quenched and worked up as above. Only unchanged hexenylcobaloxime could be detected in the product.

(2) To bis(dimethylglyoximato)pyridinecobalt(II) (0.1105 g; 0.3 mmol) in methylene chloride (50 mL) were added phenylacetylene (0.12 mL; 1.2 mmol) and acetic acid (0.1 mL; 1.7 mmol). *n*-Octylbis(dimethylglyoximato)pyridinecobalt(III) (0.1601 g; 0.30 mmol) in methylene chloride (10 mL) was then added; after 50 h at ambient temperature, the solution was quenched and worked up as above. Only *n*-octylbis(dimethylglyoximato)pyridinecobalt(III), dichloromethylbis(dimethylglyoximato)pyridinecobalt(III), and phenylacetylene were present in the product. When similar reactions were carried out in the absence of either *n*-octylcobaloxime, acetic acid, or phenylacetylene, dichloromethylcobaloxime was the only metal complex that could be detected in the product.

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Appendix

Kinetics of alkyl transfer measured by changes in equatorial ligand populations under conditions where randomization of equatorial ligands takes place in the inorganic cobaloxime.

	Concentration		
	at t_0	at t'	at t_∞
$RCo(chgH)_2py$	a	x	x_∞
$Co(dmgH)_2py$	b	$b - y - y'$	$b - y_\infty - y'_\infty$
RCo(chgH)-(dmgH)py	0	x'	X'_∞
$RCo(dmgH)_2py$	0	$a - x - x'$	$a - x_\infty - x'_\infty$
Co(chgH)-(dmgH)py	0	y'	y'_∞
$Co(chgH)_2py$	0	y	y_∞

The extent of exchange (X) is represented by the increase in the dmgH component of the total organocobalt.

The rate of total exchange reaction (R) is constant provided the rate coefficients for each individual exchange process are identical.

$$dX/dt = R[2x(b - y - y')/ab + xy'/ab + x'(b - y - y')/ab] - R[2y(a - x - x')/ab + xy'/ab + y'(a - x - x')/ab] = [R[2x/a + x'/a - 2y/b - y'/b]$$

Since the total of chgH is constant,

$$2x + x' + 2y + y' = 2x_\infty + x'_\infty + 2y_\infty + y'_\infty$$

and, at equilibrium, when dX/dt is zero,

$$(2x_\infty + x'_\infty)/a = (2y_\infty + y'_\infty)/b$$

therefore

$$2x_\infty + x'_\infty = a(2y_\infty + y'_\infty)/b$$

therefore

$$2x + x' + 2y + y' = a(2y_\infty + y'_\infty)/b + 2y_\infty + y'_\infty$$

or

$$2x + x' = (a/b + 1)(2y_\infty + y'_\infty) - (2y + y')$$

therefore

$$dX/dt = R[(a/b + 1)(2y_\infty + y'_\infty)/a - (2y + y')/a - (2y + y')/b] = R[(a + b)\{(2y_\infty + y'_\infty) - (2y + y')\}/ab]$$

Since total chgH in the inorganic cobaloxime = total dmgH in the organocobaloxime

$$2y + y' = X_t$$

and

$$2y_\infty + y'_\infty = X_\infty$$

Therefore,

$$dX/dt = R[(a + b)/ab][X - X_t]$$

which is identical with the McKay equation appropriate to the exchange reaction in which no randomization takes place.

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of **1**, **9**, and **2** in the ratio ca. 1:2:1 in the equilibrium mixture from **2a**, implies that this equilibrium condition is fulfilled.
(31) In order to obtain a reasonable value of R the reaction should not have been allowed to proceed too far toward equilibrium. In order to obtain maximum accuracy in the assessment of peak areas, especially in the case of Figure 3 described below, it was necessary to proceed well toward equilibrium. A compromise is therefore necessary.
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The Carbonyl Scrambling Processes in the Isomeric Pentacarbonylguaiazulenediiron and Homologous Ruthenium Molecules; a Novel Mechanism for the Internuclear Processes

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Abstract: The structural and dynamic properties of five compounds of the type $XM_2(CO)_4L$, namely, the geometric isomers **1**, **2** (X = guaiazulene, M = Fe, L = CO), the geometric isomers **3**, **4** (X = guaiazulene, M = Ru, L = CO), and **5** (X = guaiazulene, M = Fe, L = PEt_3), have been studied. In all cases the CO scrambling processes have been studied over a wide temperature range using ^{13}C NMR. For compounds **1**, **2**, and **5** the molecular and crystal structures have been determined by x-ray crystallography. **1** forms triclinic crystals: $P\bar{1}$, a = 13.627 (7) Å, b = 16.993 (8) Å, c = 8.782 (3) Å, α = 98.78 (3)°, β = 99.79 (3)°, γ = 95.34 (4)°, V = 1965.6 (15) Å^3, Z = 4. The structure was refined with Fe atoms only anisotropic to R_1 = 0.12 and R_2 = 0.11. The two molecules in the asymmetric unit are essentially identical and have the $Fe(CO)_3$ group bound to an allylic moiety that does not bear the isopropyl substituent. The mean Fe-Fe distance is 2.791 (10) Å. **2** also forms triclinic crystals: $P\bar{1}$, a = 12.286 (4) Å, b = 14.297 (3) Å, c = 11.029 (3) Å, α = 90.22 (2)°, β = 95.72 (2)°, γ = 97.54 (2)°, V = 1910.9 (8) Å^3, Z = 4. This structure was refined with only the iron atoms anisotropic to R_1 = 0.068 and R_2 = 0.085. The two molecules in the asymmetric unit are chemically identical with the $Fe(CO)_3$ group bound to an allylic moiety having the isopropyl group attached to the center carbon atom. The mean Fe-Fe bond length is 2.808 (4) Å. **5** forms monoclinic crystals: $P2_1/n$, a = 12.487 (5) Å, b = 13.918 (5) Å, c = 15.196 (6) Å, β = 103.90 (3)°, V = 2563.6 (16) Å^3, Z = 4. The structure was refined to R_1 = 0.075 and R_2 = 0.085 with anisotropic temperature factors assigned to the iron atoms, carbonyl C and O atoms, and the P atom only. The structure is derived from that of **1** by replacing the CO group trans to the Fe-Fe bond by PEt_3. The Fe-Fe bond length is 2.800 (4) Å.

For several years we have been studying carbonyl scrambling processes in the class of binuclear molecules that have an $(OC)_nM\text{-}M'(CO)_m$ moiety bonded to a cyclic, or bicyclic, polyene or polyenyl group. This general formulation includes the common symmetrical case where M = M′ and $n = m$, as well as more general cases. Those that we have studied included **6–13**. In this paper we present a detailed report of the structural and dynamic properties of compounds **1–5**. The background for the present work is provided by our previous studies of compounds **6–13**, and we shall therefore begin by summarizing the salient features of compounds **6–13**.

In compound **6**, it was found[2] that the signals for the tricarbonyl moiety coalesce at about 0 °C, whereas up to at least 75 °C, the signal for the equivalent CO groups in the $Fe(CO)_2$ moiety remains distinct and sharp. Thus, no evidence for internuclear scrambling is seen up to 75 °C.

In **7** coalescence that we believe to be (but cannot prove to be) due only to local scrambling within each of the equivalent $Fe(CO)_3$ groups occurs[2] at about −14 °C.

In the related compounds **8**, **9**, and **10**, *only localized* scrambling processes occur,[3,4] with coalescence temperatures ranging from ca. −80 to ca. +60 °C.

In compound **11**[5,6] and the related (guaiazulene)$W_2(CO)_6$[7] and (azulene)$Mo_2(CO)_6$[7] only localized scrambling occurs.

In our most recent paper[8] in this area on **12** and **13**, we have shown that carbonyl scrambling occurs in two well-defined stages. First, localized scrambling in the $M(CO)_3$ group becomes rapid enough to give a single line (T_c = ca. −70 °C for Fe, ca. −15 °C for Ru), after which there is general (i.e., internuclear) scrambling. These systems, (azulene)$M_2(CO)_5$, were the first ones in the general group under consideration here in which internuclear scrambling was observed. In re-