Alkylcobaloximes and Their Relation to Alkylcobalamins

G. N. Schrauzer and R. J. Windgassen

Contribution from Shell Development Company, Emeryville, California.
Received April 9, 1966

Abstract: Methods of preparation of the remarkably stable alkylcobaloximes $RCo(D_2H_2)B$ (with R = alkyl, D = dianions of 1,2-dioximes, B = base) are described. These new and unusual organometallic complexes of cobalt are compared with the alkyl derivatives of vitamin B_{12} with which they bear a remarkable resemblance. Alkylcobaloximes were found to react with boron trifluoride etherate forming cyclic oxime boronic esters of composition $RCo(D_2B_2F_4)B$. Preparation of the first alkylaquocobaloximes, $RCo(D_2H_2)H_2O$, is also reported. These compounds may be dehydrated without cleavage of the Co–C bonds to complexes of composition $RCo(D_2H_2)$ which are isoelectronic with bis(dimethylglyoximato)nickel. For further comparison to analogous vitamin B_{12} derivatives, binuclear cobaloximes containing the unit $Co-(CH_2)_n-Co$ (n = 3, 4) have been synthesized. The complex with n = 3 yields cyclopropane on photolysis or pyrolysis. The reactivity of the Co–C bonds in alkylcobaloximes is discussed and several ligand-exchange reactions are described.

Recently, a number of alkylcobalamins containing direct Co–C bonds have been reported.[1–7] Some of these analogs of coenzyme B_{12}, in particular cobalt methylcorrinoids, were actually isolated from *Clostridium thermoaceticum* which synthesize acetate from glucose and CO_2.[8] They furthermore play a part in the *in vivo* synthesis of methionine from homocysteine[9] and the formation of methane by *Methanosarcina barkeri*.[10] In view of these important biochemical functions of the alkylcobalamins, which, in fact, were considered as "biological Grignard reagents,"[11] it is highly desirable to have simple model compounds available which may be prepared in large quantity and which may serve to test the mechanistic postulates derived from the biochemical experiments. In several recent papers,[12–14] we have shown that bis(dimethylglyoximato) complexes of cobalt ("cobaloximes") chemically closely resemble vitamin B_{12} derivatives. In the present paper we wish to report on the preparation, properties, and reactions of alkylcobaloximes; corresponding compounds with substituted saturated or unsaturated carbon radicals or compounds with bonds between cobalt and elements other than carbon will be described in subsequent papers. The properties of the alkylcobaloximes will be compared to the alkylcobalamins, but the biochemical implications of these findings and the results of model experiments to simulate coenzyme B_{12} catalyzed reactions will be described in a separate publication.

Preparation of Alkylcobaloximes. In initial studies[11] alkylcobaloximes were obtained by the reaction of cobaloxime(III) halides with Grignard reagents or cobaloxime(I) ("cobaloxime$_s$" in analogy to vitamin B_{12s}) with alkyl halides.[15] Other anionic alkylating agents, such as organyls of lithium, sodium, aluminum, boron, and mercury, may be employed instead of the organomagnesium halides.[16] In the reactions with cobaloximes(I) almost all conventional alkylating agents, such as sulfates, phosphates, and phosphites, can be used. Although cobaloximes(I) are easily obtained from cobaloximes(III) by reduction (*e.g.*, with $NaBH_4$), the cobaloximes(II) are actually more convenient starting materials. For instance, a mixture of an alkylating agent with cobaloximes(II) (*e.g.*, $Co(D_2H_2)\cdot 2H_2O$[17]), $Co(D_2H_2)\cdot 2B$,[14,17] or the new dimeric cobaloximes(II)[13]) readily react in the presence of a base and molecular hydrogen at room temperature.

$$Co(D_2H_2)\cdot 2B + RX + 0.5H_2 + OH^- = RCo(D_2H_2)B + X^- + H_2O + B \quad (1)$$

There is no need to preform the cobaloximes(II); thus, treatment of a suspension of cobaltous chloride and dimethylglyoxime in methanol with the appropriate amount of sodium hydroxide and the alkylating agent in the presence of hydrogen constitutes an effective one-step procedure. It must be pointed out, however, that alkylcobaloximes are also formed in the absence of a specific reducing agent since cobaloximes(II) are known to disproportionate into cobaloximes(I) and -(III) in alkaline solution.[13] Addition of NaOH to a mixture of a cobaloxime(II) and an alkylating agent in methanol–water gives yields up to 50% of the total cobalt present. Alkyl halides also react with cobaloximes(II) in polar solvents in the absence of a base.

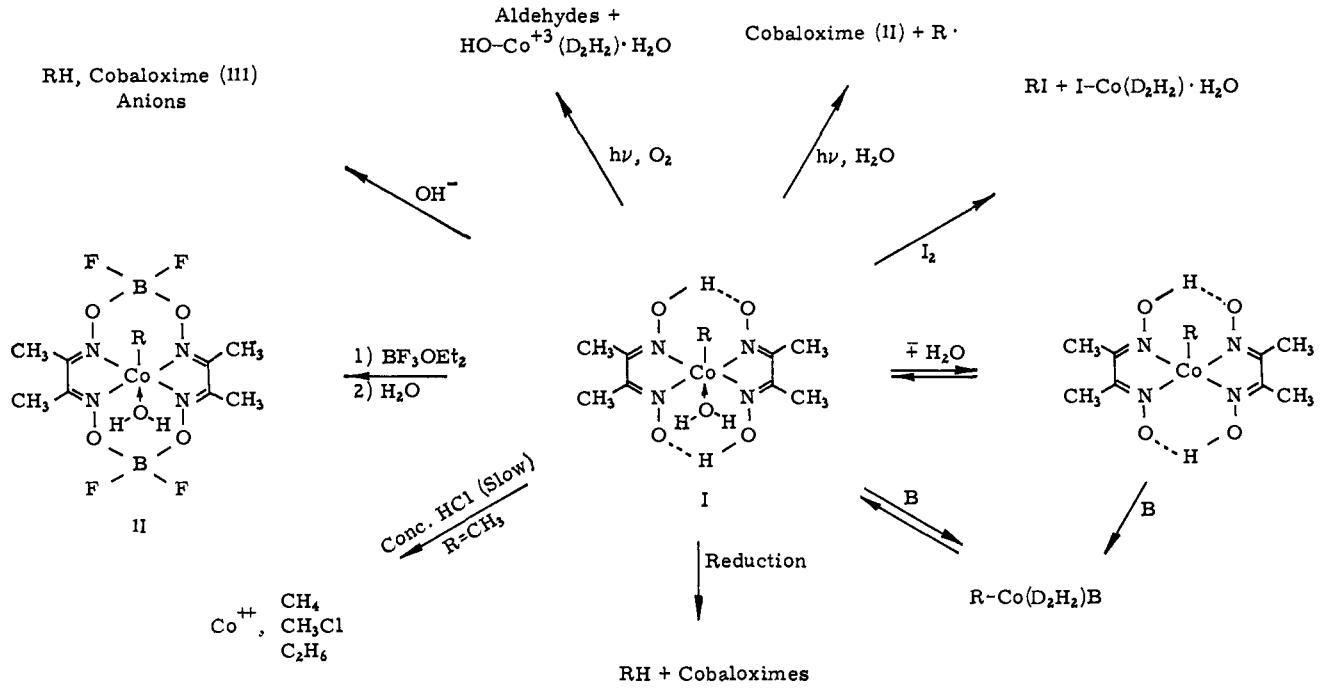
$$\begin{array}{l} B \\ Co(D_2H_2) \\ | \\ Co(D_2H_2) \\ B \end{array} + \begin{array}{l} R \\ | \\ X \end{array} \longrightarrow RCo(D_2H_2)B + XCo(D_2H_2)B \quad (2)$$

$$2Co(D_2H_2)\cdot 2B + RX \longrightarrow RCo(D_2H_2)B + XCo(D_2H_2)B + 2B \quad (3)$$

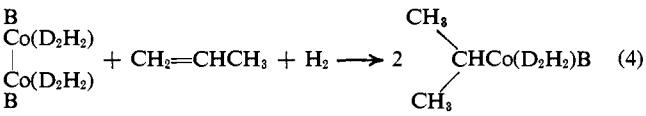
Reaction of substituted olefins with cobaloximes(II) in the presence of hydrogen has likewise been suc-

(1) For general reviews see K. Bernhauer, *et al.*, *Angew. Chem.*, 75, 1145 (1963); R. Bonnett, *Chem. Rev.*, 63, 573 (1963).
(2) A. W. Johnson, L. Mervyn, N. Shaw, and E. L. Smith, *J. Chem. Soc.*, 4146 (1963).
(3) E. L. Smith and L. Mervyn, *Biochem. J.*, 86, 2P (1963).
(4) O. Müller and G. Müller, *Biochem. Z.*, 336, 299 (1962).
(5) E. L. Smith, L. Mervyn, P. W. Muggleton, A. W. Johnson, and N. Shaw, *Ann. N. Y. Acad. Sci.*, 112, 565 (1964).
(6) F. Wagner and K. Bernhauer, *ibid.*, 112, 580 (1964).
(7) D. Dolphin, A. W. Johnson, and R. Rodrigo, *ibid.*, 112, 590 (1964).
(8) L. Ljungdahl, E. Irion, and H. G. Wood, *Biochemistry*, 4, 2771 (1965).
(9) J. R. Guest, S. Friedman, M. J. Dilworth, and D. D. Woods, *Ann. N. Y. Acad. Sci.*, 112, 774 (1964).
(10) B. A. Blaylock, and T. C. Stadtman, *ibid.*, 112, 799 (1964).
(11) L. L. Ingraham, *ibid.*, 112, 713 (1964).
(12) G. N. Schrauzer, and J. Kohnle, *Chem. Ber.*, 97, 3056 (1964).
(13) G. N. Schrauzer, R. J. Windgassen, and J. Kohnle, *ibid.*, 98, 3324 (1965).
(14) G. N. Schrauzer, and R. J. Windgassen, *ibid.*, 99, 602 (1966).
(15) "Cobaloximes(III)" are complexes of Co(III), such as, *e.g.*, $Cl-Co(D_2H_2)py$. Cobaloximes(II) or -(I), respectively, are the corresponding derivatives of Co(II) and Co(I); in analogy to the terminology employed in vitamin B_{12} chemistry, these species are also sometimes referred to as "cobaloxime$_r$" or "cobaloxime$_s$."
(16) Unpublished work, with G. Kratel.
(17) A. G. Sharpe and D. B. Wakefield, *J. Chem. Soc.*, 281 (1957).

Scheme I



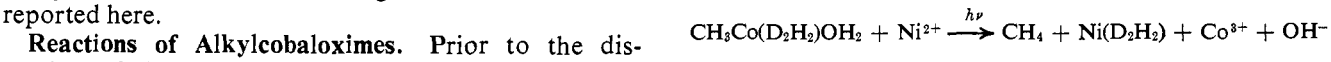
cessful; many derivatives have been prepared and will be reported in a forthcoming paper. Among unsubstituted olefins, propylene is a notable exception as it reacts to form the isopropylcobaloxime in low yield (eq 4). The structure was proved by the alternative synthesis from isopropyl bromide and the nmr spectrum.



$$\begin{matrix}B\\ Co(D_2H_2)\\ |\\ Co(D_2H_2)\\ B\end{matrix} + CH_2{=}CHCH_3 + H_2 \longrightarrow 2\ \begin{matrix}CH_3\\ \diagdown\\ CHCo(D_2H_2)B\\ \diagup\\ CH_3\end{matrix} \quad (4)$$

No product formed with ethylene or cyclohexene, but traces formed with 1-heptene. Butadiene reacts readily, affording the crotyl derivative. All attempts to prepare tertiary alkylcobaloximes have thus far met with failure. As one would expect, cobalt fluoroalkyl derivatives form with ease. At this point we mention CF_3–$Co(D_2H_2)$·pyridine, an orange compound obtained from cobaloxime(I) and CF_3I. Alkylcobaloximes can also be prepared from 1,2-dioximes, such as glyoxime itself, or diphenylglyoxime and 1,2-cyclohexanedione dioxime. When the *o*-monomethyl ether of dimethylglyoxime was employed as the prospective ligand, alkylation of the cobalt atom occurred, but instead of the expected derivative a Co alkyl derivative of bis(iminobiacetyl monoxime) formed in low yield. Formation of Co organyl derivatives was also observed using certain Schiff bases as ligands but will not be reported here.

Reactions of Alkylcobaloximes. Prior to the discussion of the properties of the cobalt–carbon bond, ligand-exchange reactions will be described. A displacement of the axial base component is readily achieved if the entering ligand has stronger donor–acceptor properties than the leaving group. The following order of decreasing affinity toward the cobalt atom was observed at room temperature: $(n\text{-}C_4H_9)_3P \simeq (C_6H_5)_3P$ > py > $(C_2H_5)_2S$ > H_2O > CH_3OH. On the other hand, dimethyl sulfide could be displaced by H_2O on steam distillation of cobaloximes $RCo(D_2H_2)\cdot S(CH_3)_2$, a method which is conveniently employed for the preparation of alkylaquocobaloximes. Although coordinated pyridine could not be displaced by water under comparable conditions, it is displaced in dilute mineral acid. Attempts to exchange the cobalt-bound alkyl groups remained unsuccessful. For instance, a reaction of $CH_3Co(D_2H_2)$py with butyllithium which, in principle, could produce the intermediate $CH_3Co(D_2H_2)$-$C_4H_9^-$ and subsequently eliminate methyl anion did not take place. Exchange reactions of the dioxime ligands, on the other hand, have been successful in at least one case. Heating a mixture of methylaquocobaloxime at 140° with 1,2-cyclohexanedione dioxime in toluene and subsequent addition of pyridine afforded moderate amounts of $CH_3Co(L_2H_2)$py (L = dianion of 1,2-cyclohexanedione dioxime). This interesting ligand-exchange reaction occurs even at room temperature but requires several months for completion. It undoubtedly proceeds by stepwise displacements of the dimethylglyoxime by the new ligand and certainly does not involve ionic intermediates such as CH_3–Co^{2+}. Under identical conditions glyoxime fails to exchange. The complex $CH_3Co(D_2H_2)OH_2$ does not exchange the CH_3–Co^{2+} — ion with Ni^{2+} *in the dark*. In the daylight, however, photolysis of the Co–C bond occurs producing the kinetically labile cobaloxime(II) which subsequently undergoes metal exchange with nickelous ion.

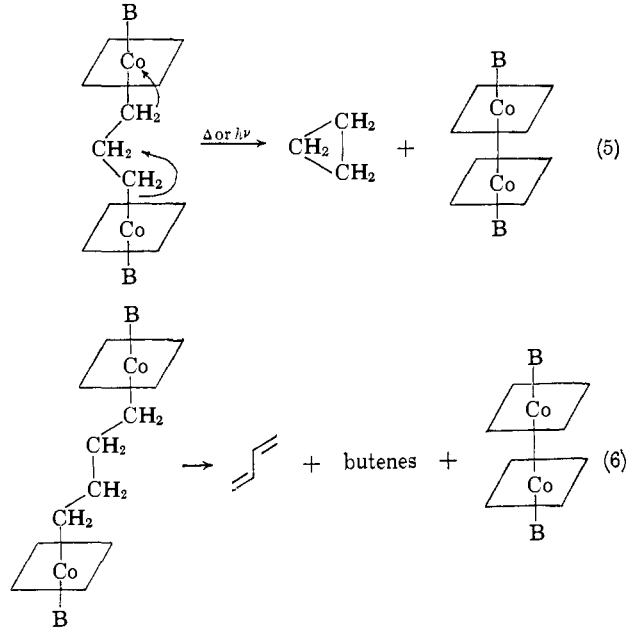


$$CH_3Co(D_2H_2)OH_2 + Ni^{2+} \xrightarrow{h\nu} CH_4 + Ni(D_2H_2) + Co^{3+} + OH^-$$

In the following description of the reactions of alkylcobaloximes, methylaquocobaloxime (complex I, R = CH_3) will be used as a representative example. Some of the reactions are shown in Scheme I and only the less obvious will be discussed in the text. Methylaquocobaloxime, an orange, crystalline material, is moderately soluble in water and in a variety of organic solvents. It is stable for indefinite periods in the dark, but photochemical decomposition of solutions occurs readily on standing in daylight. It resists heating in concentrated

hydrochloric acid to a surprising extent; over several hours partial degradation results in the formation of a 3:1 mixture of methane and methyl chloride, together with dimethylglyoxime degradation products and Co^{2+} ion. It is likewise only slowly attacked by cold concentrated sulfuric acid or KOH. Decomposition with methane evolution is observed in warm concentrated KOH solution. While these reactions strongly suggest the presence of a $Co-CH_3$ bond, a conclusive chemical proof of the structure may be obtained by treating I or other alkylcobaloximes with boron trifluoride etherate. This reagent readily reacts with the two O–H · · O groups in the molecule, affording extremely stable compounds, $RCo(D_2B_2F_4)B$, containing $O-BF_2-O$ bridges.[18] In this complex (II, R = CH_3) the presence of the $Co-CH_3$ bond follows from nmr measurements and the analysis of the degradation products, *e.g.*, methane formed on heating with concentrated KOH solution. Surprisingly, methylaquocobaloxime and certain other aquocobaloximes are dehydrated without cleavage of the Co–C bond to complexes of composition $RCo(D_2H_2)$. Although methylaquocobaloxime dehydrates readily and ethylaquocobaloxime sluggishly in boiling benzene, the complexes $CH_3Co(D_2B_2F_4)OH_2$ and propylaquocobaloxime are uneffected in this solvent. Decomposition occurred when the dehydration was attempted in higher boiling solvents, *e.g.*, xylene. These anhydrides may formally be regarded as isoelectronic with $Ni(D_2H_2)$; they are sparingly soluble, air stable, but mildly hygroscopic. Reaction with bases produces adducts $RCo(D_2H_2)B$ which are identical with those prepared by other routes. It is concluded, therefore, that the base component, at least in these instances, is not essential for the stabilization of the Co–C bonds. It is possible that the anhydrides are associated in the solid state, *e.g.*, *via* interactions between the cobalt atom and the oxime oxygen anions of a neighboring molecule of complex.

Upon heating, all alkylcobaloximes produce hydrocarbon cleavage products of the Co alkyl group which are essentially identical with those obtained on anaerobic photolysis. The products are listed in Table I. The photolysis results can be best explained by assuming the initial step to be the homolysis of the Co–C bond producing a cobaloxime(II) and an alkyl radical. In benzene, for instance, toluene was detected as the principal reaction product. In water, a mixture of methane and ethane in the ratio of 16:1 is formed. Obviously, the alkyl radicals interact with the cobaloxime(II) present in the solution. In the case of the methyl radicals, a reduction takes place and the resulting carbanion subsequently abstracts a proton from the solvent to form methane. Accordingly, the photolysis of trideuteriomethylcobaloxime in water produces CD_3H. Photolysis of ethylcobaloxime, on the other hand, produces ethylene and only small amounts of ethane, indicating that oxidation of the ethyl radial occurred. Formation of olefins was also observed in most other instances. These results parallel in many ways the reactions of alkyl radicals in the presence of transition metal ions.[19] To obtain indications for the lifetime of the radicals in these solutions, a neopentylcobaloxime was prepared and photolyzed. The products, a 10:1 mixture of neopentane with pentenes, suggest that the lifetime of the radicals is shortened by the presence of the low-valent transition metal ions. It is conceivable that a "cage effect" actually prevents complete separation of the radicals from the metal moiety to undergo independent reactions. In the presence of oxygen, aldehydes are the main products of the photolysis of alkylcobaloximes just as in the case of alkylcobalamins.[6,7] In their attempts to obtain a binuclear cobalamin by the reaction of vitamin B_{12s} with aliphatic geminal dihalides, Smith and his co-workers were unable to obtain a product with ethylene dibromide, while trimethylene chlorobromide gave only halogen-containing monomeric products. Tetramethylene dibromide, however, yielded a halogen-free "dimer."[5] Analogous experiments with cobaloximes and ethylene dibromide were likewise unsuccessful; ethylene was formed during the reaction. The three-carbon bridged product was obtained with difficulty. Thermal as well as photolytic decomposition afforded cyclopropane as the exclusive product from the C_3 chain. The analogous butylenedicobaloxime formed with ease. However, according to model considerations the complex would be strain-free only with a transoid conformation of the tetramethylene chain. Consequently, cyclobutane would not be expected to result in decomposition of the complex and was not observed.



The fact that the trimethylene compound was not obtained from B_{12s} may be due to steric effects.[20] For the mechanism of the cyclopropane formation we propose a simple bond shift as indicated, which is equivalent to an intramolecular oxidation–reduction. All alkylcobaloximes are cleaved reductively by H_2 in the presence of a heavy metal catalyst. Other reducing agents, *e.g.*, borohydride ion, or even cobaloxime$_s$ itself are effective. A 1:1 mixture of methylaquocobaloxime and cobaloximes slowly loses its dark color on standing in the dark. Methane and dimeric

(18) G. N. Schrauzer, *Chem. Ber.*, **95**, 1438 (1962). Compounds of this type were also prepared by G. Kratel, in our laboratory at the University of Munich, Germany.

(19) See, *e.g.*, H. E. De La Mare, J. K. Kochi, and F. F. Rust, *J. Am. Chem. Soc.*, **85**, 1437 (1963).

(20) See ref 5, p 570.

Table I. Organic Products from Pyrolysis and Photolysis of Alkylcobalamins

Complex $RCo(D_2H_2)B$ R	B	Photolysis[a] products	Pyrolysis[b] products	Pyrolysis temp,[c] °C
CH_3	H_2O	CH_4, C_2H_6 16:1	CH_4	215–220[d]
CH_3	C_5H_5N	CH_4, C_2H_6 20:1	CH_4	215–220[d]
CH_3	$(C_4H_9)_3P$		CH_4	205–215[d,e]
$CH_3Co(D_2B_2F_4)$	Pyridine	CH_4	CH_4	245[d,g]
CH_3CH_2	C_5H_5N	C_2H_4, C_2H_6 80:1	C_2H_4	185–190
$CH_3CH_2CH_2$	C_5H_5N	$CH_3CH{=}CH_2$	Same	175–180
$(CH_3)_2CH$	C_5H_5N	$CH_3CH{=}CH_2$	Same	145
$CH_3CH_2CH_2CH_2$	C_5H_5N	Butenes		
$(CH_3)_2CHCH_2$	C_5H_5N	Butenes	Same	185
$(CH_3)_3CCH_2$	C_5H_5N	Neopentane / Pentenes 10:1	Neopentane	205–210[d]
$CH_3(CH_2)_4CH_2$	C_5H_5N	Hexene-1[f]		
$-CH_2CH_2CH_2-$	C_5H_5N	Cyclopropane	Same	120
$-CH_2CH_2CH_2CH_2-$	C_5H_5N	Butadiene / Butene 1:1	Same	195–205[d]
D_3C	C_5H_5N	CD_3H	CD_3H	215–220[d]

[a] In methanol *in vacuo;* products analysed by mass spectroscopy. [b] Solid complexes *in vacuo.* [c] Temperature of rapid gas evolution. [d] Complexes underwent gross decomposition giving oxides of nitrogen, ammonia, and acetonitrile. [e] Only complex in liquid state during pyrolysis. [f] Determined by glpc. [g] Explodes.

cobaloxime are formed according to the equation

$$Co(D_2H_2)B^- + CH_3Co(D_2H_2)B \xrightarrow{H_2O} B(D_2H_2)Co\text{–}Co(D_2H_2)B + CH_4$$

It is of interest to note that reductive cleaveage of Co–C bonds in cobalt methylcorrinoids has been suggested as the possible mechanism of methane formation of *Methanosarcina barkeri.*

The reaction of alkylcobaloximes with nucleophilic agents is of interest. Apart from the displacement of the base component B by X^- (eq 7), a nucleophilic cleavage of the Co–C bond also has been observed with X^- = HS^-, CH_3S^-, $C_6H_5S^-$, n-$C_4H_9S^-$, CN^-, and $C_6H_5N(CH_3)^-$ (eq 8). Weaker nucleophilic agents,

$$RCo(D_2H_2)B + X^- \rightleftharpoons RCo(D_2H_2)X^- + B \quad (7)$$

$$RCo(D_2H_2)X + X^- \longrightarrow RX + Co(D_2H_2)X^- \quad (8)$$

e.g., N_3^-, SCN^-, I^-, do not react according to eq 8. The cleavage reaction is relatively slow but proceeds readily in the presence of a large excess of the nucleophile. Similarly, methylcobalamin was found to be stable toward dilute cyanide, in the dark, but is converted to dicyanocobalamin within a few minutes if a large excess is employed. In contrast to organomagnesium halides, alkylcobaloximes were found not to react with alkyl or aryl halides, CO_2, or acyl halides which further demonstrates the great stability of the Co–C bonds in this system. Under these circumstances, it is felt that the cobalt-alkylcorrins should rather not be referred to as "biological Grignard reagents."

Nuclear Magnetic Resonance Spectra. The nmr spectra of the alkylcobaloximes were found to be in complete agreement with the proposed structures. In all cases it was possible to clearly identify the signals of the cobalt-bound alkyl group protons, the methyl groups of the dimethylglyoxime ligands, and the axial base component, as well as the signal of the O–H··O protons. Complex I, for instance, shows the signals of the Co–CH_3– and the dimethylglyoxime protons at τ 9.58 and 8.15 ppm, respectively, and the broad signal of the O–H··O protons at τ −0.6 ppm, all in the correct intensity ratios. In Table II the chemical shifts of the Co–CH_3 and O–H··O resonances are listed for compounds with various bases in the sixth coordination position. With increasing donor action of the axial ligands the methyl resonance moves slightly downfield, whereas the O–H··O signal moves upfield and also becomes less broad. This suggests a weakening of the O–H··O interactions with increasing donor strength of the axial ligands which, in turn, is probably caused by a slight displacement of the dimethylglyoxime ligands. From the chemical shift of the Co–CH_3 signal one may conclude that the protons in these compounds do not have acidic properties. Accordingly, they were found not to undergo acid- or base-catalyzed deuterium exchange reactions.

Table II. Position of the Co–CH_3 and O–H··O Signals in the ^1H Nmr Spectra of Several Methylcobaloximes

Axial component	τ, ppm Co–CH_3	τ, ppm O–H··O
H_2O	9.58	∼−0.6
py	9.16	∼−0.6
$P(OCH_3)_3$	9.15	∼−0.5
$P(n\text{-}C_4H_9)_3$	9.02[a]	+0.05
$P(C_6H_5)_3$	8.81[a]	+0.13

[a] Coupled with ^{31}P, J = 4 cps.

Polarographic Behavior. All alkylcobaloximes show two irreversible polarographic reduction waves in acetonitrile solution which may be attributed to reactions involving the cobalt moiety in the complexes. At higher negative potentials a third wave is observed in several cases which was traced back to the reduction of the pyridine ligand. It is not observed in cobaloximes with base components such as water or tributylphosphine (Table III).

The addition of the first electron to the alkylcobaloximes is accompanied by the cleavage of the Co–C bond. The $E_{1/2}$ potential of the second wave is about the same as that observed for the third reduction wave of typical cobaloxime(III) compounds. The complexes $ClCo(D_2H_2)py$ and $py\text{–}Co^+(D_2H_2)pyClO_4^-$ yield four cathodic waves at −0.67, −1.44, −2.42, and −3.06 v under comparable conditions. The first

Table III. Observed Polarographic Half-Wave Potentials for Several Cobaloximes in Acetonitrile Solution[a]

Complex	Observed cathodic $E_{1/2}$ Potentials[b] I	III	III
$CH_3Co(D_2H_2)H_2O$[d]	−1.7	−2.42	
$CH_3Co(D_2H_2)py$[d]	−1.75	−2.44	−3.01
$CH_3Co(D_2H_2)P(n\text{-}C_4H_9)_3$		−2.12[e]	
$n\text{-}C_4H_9Co(D_2H_2)py$	−1.80	−2.44	−3.05
$CH_3Co(D_2B_2F_4)py$[d]	−1.3	−2.39	−3.08
$NCCo(D_2H_2)py$	−1.1	−1.86	−3.08
Cyanocobalamin[c]	−1.26		−2.27

[a] Measurements performed by D. C. Olson, Emeryville. [b] Relative to the Ag|0.10 *M* $AgNO_3$ electrode at 25°. The first two waves correspond to one-electron transfer reactions if not indicated otherwise. The third (ligand) reduction wave involves more than 1 electron. [c] In 20% water containing acetonitrile. [d] An additional wave around −2.8 v is observed in these cases whose origin has not yet been explained. [e] Two electrons.

corresponds to the reduction of Co(III) to Co(II), the second to Co(II)–Co(I), and the third to the reduction Co(I)–Co(0), whereas the fourth again is due to the reduction of the pyridine. These results clearly indicate that the organocobaloximes are complexes of Co(II). The potential of the first wave somewhat depends on the nature of the axial base component. Of all cobaloximes studied in this series the tributylphosphine complex of $CH_3Co(D_2H_2)$ is least easily reduced. Its first reduction wave actually already overlaps with the second which must be the result of the stronger interactions of the phosphine ligands with the cobalt atom. The two major electrode processes may be summarized by eq 9 and 10:

$$R\text{—}(Co^{2+})B + e \longrightarrow (Co^{+})\cdots B + R\cdot \quad (9)$$

$$(Co^{+})\cdots B + e \longrightarrow (Co^{0}) + B \quad (10)$$

Infrared Spectra. The infrared spectra of the alkylcobaloximes will not be reported in detail. They show the broad band of the O–H··O bridging group around 1740 cm^{-1}, thus, in a range similar to that reported,[21] *e.g.*, $ClCo(D_2H_2)py$. The C=N stretch occurs between 1536 and 1567 cm^{-1} and generally decreases with increasing interaction of the base component with the cobalt atom (observed in complexes of the type $CH_3Co(D_2H_2)B$ with B = H_2O, 1567; $S(C_2H_5)_2$, 1553; py, 1548; $P(OCH_3)_3$, 1548; $P(n\text{-}C_4H_9)_3$, 1538 cm^{-1}). In the spectrum of "CH_3–$Co(D_2H_2)$," the C=N stretch is observed at the low frequency of 1536 cm^{-1} which suggests some association of the molecules in the solid state. The CoN(dimethylglyoxime), and, in complexes with nitrogen-containing axial ligands, the Co–N (axial ligand) stretching vibrations were observed between 520 and 427 cm^{-1}, and the symmetric and asymmetric Co–C stretching modes around 332 and 320 cm^{-1}.

Experimental Section

In view of the large number of organocobaloximes prepared by similar methods, only several examples of representative procedures are described. Decomposition points usually are not given. As with most metal complexes of 1,2-dioximes, the decomposition temperature range varies with the conditions and is no criterion of purity. Most of the reactions described in the text require no special experimental techniques. However, solutions of cobaloximes, and suspensions of cobaloximer must be handled in an inert atmosphere. Characterization of the volatile reaction products was usuallyp erformed by standard glpc and mass spectroscopic techniques. Identification of the solid reaction products was usually done by conventional analytical procedures. The polarographic measurements were made by Dr. D. C. Olson, Emeryville, on an ORNL-controlled potential instrument, Model Q-1988 A, equipped with a Varian F-80 x,y-recorder.

Methylpyridinatocobaloxime. A suspension of 172 g (1.5 moles) of dimethylglyoxime and 178 g (0.75 mole) of $CoCl_2\cdot 6H_2O$ in 2 l. of methanol was stirred until the cobalt chloride had dissolved. There was then added 120 g (1.5 moles) of 50% NaOH and 60.0 g (0.75 mole) of pyridine. The stirred suspension was then cooled to −10° and stirred for 15 min after adding 60 g of 50% NaOH and 4.0 g (0.13 mole) of $NaBH_4$. There was then added 101 g (0.8 mole) of dimethyl sulfate; the solution was then gradually warmed to 20° and stirred for 0.5 hr longer. The solution was evaporated to about 800 ml under a stream of air, then stirred with 2 l. of water and 20 ml of pyridine. The orange crystals were then collected and washed with water, yield 284 g (74%).

Methylpyridinatobisglyoximatocobalt. To a stirred suspension of 23.8 g of $CoCl_2\cdot 6H_2O$ (0.1 mole) and 17.6 g (0.2 mole) of glyoxime in 250 ml of methanol there was added 8.0 g of pyridine and 16.0 g (0.2 mole) of 50% NaOH. At 0°, 10 ml of methyl iodide was added followed by a solution of 0.3 g of $NaBH_4$ and 4.0 g of NaOH. After 10 min the mixture was shaken with 5% NaOH and methylene chloride. From the methylene chloride concentrate, on recrystallization from water, there was obtained 0.8 g (2.5%) of red crystals.

Anal. Calcd for $C_{10}H_{14}N_5O_4Co$: C, 36.70; H, 4.31; N, 21.41. Found: C, 36.53; H, 4.72; N, 21.27.

Methylaquocobaloxime *via* Methyl Dimethylsulfidatocobaloxime. A suspension of 238 g (1.0 mole) of $CoCl_2\cdot 6H_2O$ and 232 g (2.0 moles) of dimethylglyoxime in 1 l. of methanol was stirred for 5 min, and then 1.5 l. of water containing 80.0 g (2.0 moles) of NaOH was added. The solution was then stirred for 15 min and cooled to −20°. Next, 70.0 g of methyl iodide and 80 g of 50% NaOH was added. After 5 min, 20 g of 50% NaOH and 120 g of methyl iodide were added, followed by addition, over 5 min, of a solution of 40.0 g of NaOH and 6.0 g of $NaBH_4$ in 120 ml of water. The solution was stirred 15 min after addition was complete, and then filtered; the filtrate was freed of methyl iodide by a nitrogen stream. The filtrate was mixed with 60 ml of dimethyl sulfide and cooled to −20°, whereupon orange crystals separated. The product was washed with water and dried at 25° (1 mm), yield 215 g (59%).

A suspension of 150 g of methyl dimethylsulfidatocobaloxime in 750 ml of water was stirred and heated to boiling for 0.5 hr. The suspension (500 ml) was cooled to 0° and filtered to yield 113 g (86%) of dark orange crystals of methylaquocobaloxime, which were air dried.

The product, of course, can be prepared directly from cobaloxime(II) but isolation is difficult. It can also be obtained from methylpyridinatocobaloxime by eluting on aqueous methanol solution through a column of strongly acidic resin or by warming a methanolic solution of the pyridinato complex with dimethyl sulfate.

Methylcobaloxime. A solution of methylaquocobaloxime in 200 ml of benzene or methylcyclohexane was slowly distilled until the distillate was no longer moist. The deep red crystals were collected, washed with benzene, and dried at 25° (0.1 mm).

Isopropylpyridinatocobaloxime from Propylene. A suspension of 6.0 g of $[pyCo(D_2H_2)]_2$, 20 ml of ethanol, and 30 ml of propylene was stirred under 500 psi of hydrogen for 12 hr. The mixture was then shaken with 5% NaOH and methylene chloride. The methylene chloride concentrate on recrystallization from methanol–water yielded 0.52 g (7.6%) of yellow crystals, identical with authentic material.

***n*-Butylpyridinatocobaloxime from *n*-Butylboron.** A suspension of 10.0 g of $[pyCo(D_2H_2)]_2$ in 10 ml of tri-*n*-butylboron and 100 ml of benzene was stirred for 24 hr and then shaken with methylene chloride and 5% aqueous NaOH. The methylene chloride layer was concentrated and on crystallization of the residue from methanol–water there was obtained 5.9 g (51%) of *n*-butylpyridinatocobaloxime.

When the same reaction was carried out with $pyCo(D_2H_2)Cl$, the yield of product was only 5%.

Reaction of Isopropyl Iodide and Pyridinatocobaloxime(II). A suspension of 10.0 g of $[pyCo(D_2H_2)]_2$ in 150 ml of methanol and 10 ml of isopropyl iodide was stirred and heated at 70° for 1 hr and

(21) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 6041 (1963).

Table IV. Alkylcobaloximes: Analytical Data

Complex RCo(D_2H_2)B			Calcd, %			Found, %		
R	B	Formula	C	H	N	C	H	N
CH_3	H_2O	$C_9H_{19}N_4O_5Co$	33.55	5.95	17.39	33.51	6.03	17.48
CH_3	C_5H_5N	$C_{14}H_{22}N_5O_4Co$	43.87	5.79	18.28	43.86	5.84	18.67
CH_3	Benzimidazole	$C_{16}H_{23}N_6O_4Co$	45.51	5.59	19.90	45.34	5.52	19.57
CH_3	Aniline	$C_{15}H_{24}N_5O_4Co$	45.34	6.09	17.63	45.56	6.41	17.77
CH_3	$(n\text{-}C_4H_9)_3HP$	$C_{21}H_{44}N_4O_4CoP$	49.79	8.77	11.06	49.71	9.03	11.44
CH_3	$(C_6H_5)_3P$	$C_{27}H_{32}N_4O_4CoP$	57.24	5.70	9.89	57.19	6.15	9.86
CH_3	$(CH_3O)_3P$	$C_{12}H_{26}N_4O_7CoP$	33.67	6.12	13.09	33.28	5.96	13.33
CH_3	$(CH_3)_2S$	$C_{11}H_{23}N_4O_4CoS$	36.06	6.33	15.30	35.91	6.43	15.48
CH_3	$(C_2H_5)_2S$	$C_{13}H_{27}O_4N_4CoS$	39.59	6.91	14.21	39.45	6.97	14.23
CH_3	None	$C_9H_{17}N_4O_4Co$	35.33	5.62	18.42	35.63	5.37	18.66
CD_3	C_5H_5N	$C_{14}H_{19}D_3N_5O_4Co$	43.53	6.51	18.13	43.77	6.18	18.28
C_2H_5	H_2O	$C_{10}H_{21}N_4O_5Co$	35.72	6.30	16.67	35.65	6.33	16.69
C_2H_5	C_5H_5N	$C_{15}H_{24}N_5O_4Co$	45.34	6.09	17.63	45.27	6.41	17.56
C_2H_5	None	$C_{10}H_{19}N_4O_4Co$	37.74	6.02	17.61	37.86	6.07	17.44
$(CH_3)_2CH$	C_5H_5N	$C_{16}H_{26}N_5O_4Co$	46.71	6.37	17.03	46.68	6.34	17.11
$CH_3CH_2CH_2$	C_5H_5N	$C_{16}H_{26}N_5O_4Co$	46.71	6.37	17.03	46.81	6.45	17.24
$CH_3CH_2CH_2$	H_2O	$C_{11}H_{24}N_4O_5Co$	37.60	6.88	15.95	37.84	6.77	16.16
$BrCH_2CH_2CH_2$	C_5H_5N	$C_{16}H_{25}N_5O_4CoBr$	39.19	5.14	14.29	39.26	4.98	14.12
$CH_3CH_2CH_2CH_2$	C_5H_5N	$C_{17}H_{28}N_5O_4Co$	48.01	6.65	16.45	47.69	6.24	16.73
$(CH_3)_2CHCH_2$	C_5H_5N	$C_{17}H_{28}N_5O_4Co$	48.01	6.65	16.45	48.04	6.77	16.55
$(CH_3)_3CCH_2$	C_5H_5N	$C_{18}H_{30}N_5O_4Co$	49.20	6.88	15.94	49.33	7.04	16.38
$CH_3(CH_2)_4CH_2$	C_5H_5N	$C_{19}H_{32}N_5O_4Co$	50.33	7.11	15.45	50.41	7.29	15.59
$-CH_2CH_2CH_2-$	C_5H_5N	$C_{29}H_{44}N_{10}O_5Co_2$	44.73	5.70	17.94	44.47	6.03	18.26
$-CH_2CH_2CH_2CH_2-$	C_5H_5N	$C_{30}H_{46}N_{10}O_8Co_2$	45.46	5.85	17.68	45.81	6.06	17.83

then filtered to yield 6.3 g (93%) of iodopyridinatocobaloxime as brown crystals.

Anal. Calcd for $C_{13}H_{19}N_5O_4CoI$: C, 31.53; H, 3.87; N, 14.15; I, 25.63. Found: C, 31.71; H, 4.11; N, 14.18; I, 25.86.

The filtrate was concentrated and the residue was recrystallized from methanol to yield 3.2 g (57%) of isopropylpyridinatocobaloxime as yellow plates.

n-Propylpyridinatocobaloxime can be prepared by the same procedure from *n*-propyl iodide.

Reaction of Methylaquocobaloxime with Boron Fluoride Etherate. A suspension of 5.0 g of methylaquocobaloxime and 10 ml of boron fluoride etherate in 75 ml of ether was stirred for 24 hr. The ether was evaporated and the residue, on crystallization from methanol–water, afforded 4.2 g (62%) of yellow crystals of $CH_3Co(D_2B_2F_4)$-OH_2.

Anal. Calcd for $C_9H_{17}N_4O_5B_2F_4Co$: C, 25.74; H, 4.08; N, 13.35; Co, 14.04. Found: C, 26.22; H, 4.28; N, 13.72; Co, 14.28

Reaction of Methylpyridinatocobaloxime with Boron Fluoride Etherate. To a stirred suspension of 70.0 g of methylpyridinatocobaloxime and 100 ml of boron fluoride etherate in 600 ml of ether, there was slowly added 60 ml of pyridine. After 48 hr of additional stirring the suspended solids were collected by filtration. On crystallization from acetone there was obtained 62.5 g (71%) of yellow crystals of $CH_3Co(D_2B_2F_4)py$.

Anal. Calcd for $C_{14}H_{22}N_5O_4B_2F_4Co$: C, 35.11; H, 4.63; N, 14.63; Co, 12.31; F, 15.87. Found: C, 35.36; H, 4.69; N, 14.82; Co, 12.5; F, 15.19.

Methylpyridinatobis(cyclohexanedionedioximato)cobalt(II). A suspension of 1.0 g of methylaquocobaloxime and 6.0 g of cyclohexanedione dioxime in 20 ml of toluene was heated for 4 hr at 135° and then concentrated to dryness. The residue was stirred with 20 ml of methanol, 1 ml of pyridine, and 1.0 g of NaOH. Then 20 ml of water was added and the crystals were collected by filtration, yield 0.75 g (59%). The product was recrystallized from ethanol–water.

Anal. Calcd for $C_{18}H_{26}N_5O_4Co$: C, 49.66; H, 6.02; N, 16.09; Co, 13.54. Found: C, 49.61; H, 6.26; N, 16.41; Co, 13.58.

The same product was formed on adding methyl iodide to a material formed on mixing the proper proportions of cyclohexanedione dioxime, pyridine, cobalt chloride, and NaOH in methanol.

Methylpyridinatobis(iminobiacetylmonoximino)cobalt(II). To a homogeneous solution of 26.0 g (0.2 mole) of dimethylglyoxime monomethyl ether and 23.8 g of cobalt $CoCl_2 \cdot 6H_2O$ (0.1 mole) there was added 16.0 g (0.2 mole) of 50% NaOH and 8.0 g of pyridine. This was then cooled to −20°, and then 8.0 g of 50% NaOH and 0.5 g of $NaBH_4$ were added. After 2 min of stirring, 13.0 g of dimethyl sulfate was added and after 15 min of additional stirring the solution was added to 1.5 l. of water and extracted with methylene chloride. The methylene chloride residue was heated *in vacuo* to remove dimethylglyoxime monomethyl ether and then recrystallized from acetone, yield 0.55 g (1.5%).

Anal. Calcd for $C_{14}H_{22}N_5O_2Co$: C, 47.86; H, 6.31; N, 19.94; Co, 16.78. Found: C, 47.81; H, 6.30; N, 19.62; Co, 16.33.

1,3-Propylenebis(pyridinatocobaloxime). A suspension of 95.2 g (0.4 mole) of $CoCl_2 \cdot 6H_2O$ and 92.8 g (0.8 mole) of dimethylglyoxime in 2 l. of methanol was stirred until the cobalt chloride had dissolved, and then 32 g (0.8 mole) of NaOH and 32 g (0.4 mole) of pyridine in 100 ml of water were added. After cooling to 0° there was added a solution of 16 g (0.4 mole) of NaOH and 5.0 g (0.13 mole) of $NaBH_4$ in 100 ml of water. The solution was stirred for 10 min and 20.2 g (0.4 mole) of 1,3-dibromopropane was added. The blue color vanished briefly, reappeared, and gradually faded as the solution was stirred for an additional 2 hr. The solution was filtered and diluted with 2 l. of water. The resulting yellow crystals were washed with water and dried, yield 48.5 g (31%). The compound can be recrystallized from methyl ethyl ketone with some decomposition.

When the above reaction was interrupted shortly after addition of the 1,3-dibromopropane, a 65% yield of 3-bromopropylpyridinatocobaloxime was obtained.

Anal. Calcd for $C_{16}H_{25}O_4CoBr$: C, 39.19; H, 5.14; N, 14.29, Br, 16.31. Found: C, 39.28; H, 4.93; N, 14.15; Br, 15.48.

Crotylpyridinatocobaloxime. To a stirred suspension of 23.8 g (0.1 mole) of $CoCl_2 \cdot 6H_2O$ and 23.2 g (0.2 mole) of dimethylglyoxime in 500 ml of methanol under nitrogen there was added 8.0 g (0.2 mole) of NaOH in 25 ml of water and 10 g of pyridine. After 10 min, 25 ml of butadiene was added and the solution was stirred under hydrogen until gas absorption ceased (1 hr). The solution was filtered and diluted with 1 l. of water; the resulting orange crystals were collected and dried, yield 39.7 g (94%).

Anal. Calcd for $C_{17}H_{26}N_5O_4Co$: C, 48.22; H, 6.19; N, 16.54; Co, 13.92. Found: C, 47.79; H, 6.23; N, 16.68; Co, 13.56.

Trifluoromethylpyridinatocobaloxime. A suspension of [pyCo-(D_2H_2)]$_2$ in methanol was saturated with trifluoromethyl iodide, stirred for 24 hr, and filtered. The filtrate, on concentration to a small volume and dilution with water, afforded crystals of CF_3-$Co(D_2H_2)py$.

Anal. Calcd for $C_{14}H_{19}N_5O_4Co$: C, 38.45; H, 4.38; N, 16.02. Found: C, 38.75; H, 4.51; N, 15.85.

A summary of the analytical data for alkylcobaloximes is given in Table IV.