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Article

Dichloroacetylene Is Not the Precursor to Dichlorinated Vinylcobaloxime and Vinylcobalamin in Cobalt Catalyzed Dechlorination of Perchloro- and Trichloroethylene

Kevin M. McCauley, Scott R. Wilson,[†] and Wilfred A. van der Donk*

Department of Chemistry, University of Illinois at Urbana-Champaign,
600 South Mathews Avenue, Urbana, Illinois 61801

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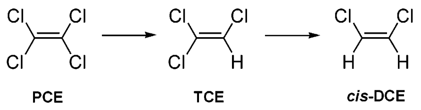
Vitamin B_{12} catalyzes the reductive dechlorination of perchloroethylene (PCE), a process for which vinylcobalamins have been proposed as intermediates. Previous model studies have shown that PCE and trichloroethlylene (TCE) react with cob(I)aloxime to form *cis*-1,2-dichlorovinylcobaloxime (**1**). This compound could be formed by nucleophilic vinylic substitution of cob(I)aloxime on TCE or its *syn*-addition to dichloroacetylene. To evaluate the latter possibility, dichloroacetylene was reacted in this study with cob(I)aloxime. The major product was not complex **1** but a novel cobalt complex, indicating that dichloroacetylene is not involved in the reductive dechorination of PCE catalyzed by cob(I)aloxime. An X-ray structure of the major product was obtained showing an unexpected tricyclic structure in which one of the carbons of dichloroacetylene is a ligand to the metal and the second carbon has formed a C–C bond to one of the oxime carbons. This arrangement connects the axial and equatorial ligands. The cathodic peak potential of this complex is significantly more negative than that of previously characterized chlorinated vinylcobaloximes. Cob(I)alamin also reacts with chloroacetylene to provide *cis*-chlorovinylcobalamin in analogy to cob(I)aloxime, but it does not provide dichlorinated vinylcobalamins in the reaction with dichloroacetylene. Hence, dichlorinated vinylcobalt complexes detected in the reductive dechlorination of PCE catalyzed by cobaloximes or vitamin B_{12} are not derived from a dichloroacetylene intermediate.

Introduction

The priority pollutants perchloroethylene (PCE) and trichloroethylene (TCE) are ubiquitously present in many terrestrial and groundwater environments.[1−3] Vitamin B_{12} in combination with a reductant such as Ti(III)citrate can serve as a catalyst to dechlorinate PCE and TCE in a reductive fashion (eq 1).[4−8] A number of mechanistic studies have been reported suggesting that the initial dechlorination of PCE to TCE takes place via electron transfer from the Co(I) catalyst, whereas the reductive dechlorination of TCE to dichlorinated ethylenes may involve chlorinated vinylcobalamins.[6,9−14] In fact, mass spectrometric analyses of samples taken from



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* To whom correspondence should be addressed. E-mail vddonk@uiuc.edu. Phone: (217) 244 5360. Fax: (217) 244 8024.

[†] To whom inquiries regarding X-ray data should be addressed. E-mail: srwilson@uiuc.edu.

(1) Doherty, R. E. *Environ. Forensics* **2000**, *1*, 69−81.
(2) Squillace, P. J.; Moran, M. J.; Lapham, W. W.; Price, C. V.; Clawges, R. M.; Zogorski, J. S. *Environ. Sci. Technol.* **1999**, *33*, 4176−4187.
(3) Doherty, R. E. *Environ. Forensics* **2000**, *1*, 83−93.
(4) Gantzer, C. J.; Wackett, L. P. *Environ. Sci. Technol.* **1991**, *25*, 715−722.
(5) Lesage, S.; Brown, S.; Millar, K. *Ground Water Monit. Rem.* **1996**, *16*, 76−85.
(6) Glod, G.; Angst, W.; Holliger, C.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1997**, *31*, 253−260.
(7) Burris, D. R.; Delcomyn, C. A.; Smith, M. H.; Robert, A. L. *Environ. Sci. Technol.* **1996**, *30*, 3047−3052.
(8) Burris, D. R.; Delcomyn, C. A.; Deng, B. L.; Buck, L. E.; Hatfield, K. *Environ. Toxicol. Chem.* **1998**, *17*, 1681−1688.
(9) Lesage, S.; Brown, S.; Millar, K. *Environ. Sci. Technol.* **1998**, *32*, 2264−2272.
(10) Glod, G.; Brodmann, U.; Angst, W.; Holliger, C.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1997**, *31*, 3154−3160.
(11) Shey, J. S.; van der Donk, W. A. *J. Am. Chem. Soc.* **2000**, *122*, 12403−12404.
(12) McCauley, K. M.; Wilson, S. R.; van der Donk, W. A. *Inorg. Chem.* **2002**, *41*, 393−404.
(13) Rich, A. E.; DeGreeff, A. D.; McNeill, K. *Chem. Commun.* **2002**, 234−235.
(14) Semadeni, M.; Chiu, P. C.; Reinhard, M. *Environ. Sci. Technol.* **1998**, *32*, 1207−1213.

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dechlorination reactions have detected such mono- and dichlorovinylcobalamins.[9] We recently reported model studies suggesting that monochlorinated vinylcobalamins are generated by reaction of cob(I)alamin with chloroacetylene,[12] a compound observed during reductive dechlorination of PCE.[7,14] We reasoned that the observed dichlorovinylcobalamins might be formed similarly via addition of cob(I)alamin to dichloroacetylene. Cobaloximes are well-known mimics of cobalamins,[15−17] and in this study, we show that cob(I)aloxime reacts readily with dichloroacetylene but produces an unexpected product. Furthermore, we show that cob(I)alamin indeed reacts with chloroacetylene to generate *cis*-chlorovinylcobalamin but that reaction with dichloroacetylene does not lead to dichlorinated vinylcobalamins. These findings are discussed in the context of vitamin B_{12} catalyzed reductive dechlorination of PCE and TCE.

Experimental Section

General Information. All NMR spectra were recorded on Varian U400 or U500 spectrometers. ^{1}H spectra were referenced to $CHCl_3$ at 7.26 ppm, and ^{13}C spectra were referenced to $CDCl_3$ at 77.00 ppm. All B_{12} spectra were taken in methanol-d_4 and referenced to MeOH at 3.31 ppm. Mass spectrometry (MS) experiments were carried out by the Mass Spectrometry Laboratory at the University of Illinois at Urbana-Champaign (UIUC). Infrared (IR) spectra were taken on a Mattson Galaxy Series FTIR 5000. Thin-layer chromatography (TLC) was carried out on Merck silica gel 60 F_{254} plates. Compounds and solvents were obtained from Fisher, Aldrich, Acros, Baker, Fluka, and Mallenkrodt. All manipulations were performed using Schlenk and inert glovebox techniques.

X-ray Structure Analysis. Diffraction data on complex **3**, mounted on thin glass fibers with oil (Paratone-N, Exxon), were collected using a Siemens Platform/CCD diffractometer with graphite-monochromated Mo Kα radiation. Its structure was solved by direct methods and refined by full-matrix least-squares methods against F^2 (SHELX-97-2).[18,19] Crystallographic data for complex **3** are given in Tables 1 and 2. Further details regarding the crystallographic data as well as tables of bond lengths and angles are presented in CIF format in the Supporting Information and have been deposited in the Cambridge Crystallographic Data Center.

Electrochemistry. Cyclic voltammetry measurements were carried out using a CH Instruments Electrochemical Analyzer 617A with a glassy carbon working electrode, Ag^+/AgCl reference electrode (3 M KCl, 0.213 V vs NHE), and a platinum wire counter electrode. All measurements were performed in 0.1 M Bu_4NClO_4 in DMF, at a concentration of 1 mM of complex **3**. An internal reference system (ferrocene/ferrocenium ion) was used, which has been shown to remain constant regardless of media,[20,21] thereby allowing better comparison with other studies by eliminating problems of variable liquid junction potentials.[22−25] Under the conditions used, the reversible Fc/Fc$^+$ potential occurred at 0.53 V ($\{E_p + E_c\}/2$) versus the Ag^+/AgCl electrode (see Figure S1 in the Supporting Information). When using this as an internal reference system and taking the Fc$^+$/Fc couple as 0.40 V versus NHE,[26] the cyclized cobalt complex has a peak potential of −1.63 V.

Table 1. Crystal Data and Details of the Structural Refinement for Complex **3**

	3
formula	$C_{16}H_{22}Cl_4Co_1N_5O_4$
fw	549.12
space group	$P2_1$
T (K)	193 ± 2
λ (Å)	0.71073
a (Å)	10.3145 (19)
b (Å)	15.222 (3)
c (Å)	14.384 (3)
α (deg)	90
β (deg)	90
γ (deg)	90
ρ_{cald} (g cm^{-1})	1.615
Z	4
V (Å^3)	2258.5 (7)
μ (cm^{-1})	12.66
R [$I > 2\sigma(I)$][a]	R1 =0.0430, wR2 = 0.1118
R (all data)[a]	R1 = 0.0525, wR2 = 0.1162

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Complex **3**[a]

	1	3	4[b]
Co1−C14	1.945(4)	1.944(5)	1.946(2) 1.947(3) 1.945(2) 1.949(2)
C14=C15	1.32(3)	1.317(7)	1.314(3) 1.312(3) 1.312(3) 1.311(3)
Co1−N3	1.8933(16)[c] 1.8856(17)	1.957(4)	1.888(2)[c] 1.892(2) 1.886(2) 1.890(2)
Co1−N5	2.030(2)	2.023(4)	2.047(2) 2.046(2) 2.046(2) 2.046(2)
Co1−C14=C15	121(2)	111.0(3)	140.2(3) 139.5(3) 138.6(3) 139.1(3)
C14−Co1−N5	178.5(11)	173.78(17)	176.69(13) 176.75(13) 176.28(12) 177.21(13)

[a] For comparison, the corresponding distances and angles for complex **1** and *cis*-chlorovinylcobaloxime **4** are also presented. [b] Four independent molecules are present in the unit cell of *cis*-chlorovinylcobaloxime.[12] [c] Distances are for the Co1−N1 and Co1−N2 bonds.

Synthesis of Cobalt Complex 3. A 25 mL Schlenk flask was charged with $CoCl_2\cdot 6H_2O$ (0.64 g, 2.7 mmol), 10 mL of degassed MeOH, and a stir bar. After the $CoCl_2\cdot 6H_2O$ dissolved, dimethylglyoxime (0.62 g, 5.4 mmol) was added followed by NaOH (0.32 g, 8.1 mmol). After stirring for 5 min, pyridine (0.21 g, 2.7 mmol)

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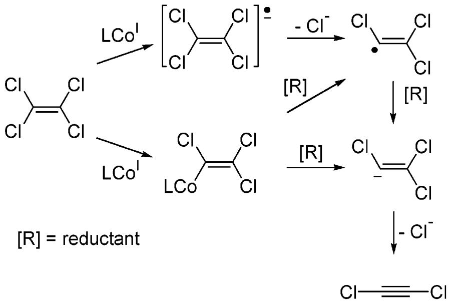
(15) Schrauzer, G. N. *Acc. Chem. Res.* **1968**, *1*, 97−103.
(16) Bresciani-Pahor, N.; Forcolin, M.; Marzilli, L. G.; Randccio, L.; Summers, M. F.; Toscano, P. J. *Coord. Chem. Rev.* **1985**, *63*, 1−125.
(17) Randaccio, L. *Comments Inorg. Chem.* **1999**, *21*, 327−376.
(18) Sheldrick, G. M. *SHELX-97−2. Program for Crystal Structure Solution and Refinement*; Institute für Anorg. Chemie: Göttingen, Germany, 1998.
(19) Bruker AXS Inc., 1998, Madison, WI.
(20) Gutmann, V.; Peychal-Heiling, G.; Michlmayr, M. *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 501−505.
(21) Gutmann, V. *Chimia* **1969**, *23*, 285−292.
(22) Diggle, J. W.; Parker, A. J. *Electrochim. Acta* **1973**, *18*, 975−979.
(23) Gagné, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854−2855.
(24) Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1982**, *54*, 1527−1532.
(25) IUPAC *Pure Appl. Chem.* **1984**, *56*, 461−466.
(26) Koepp, H. M.; Wendt, H.; Strehlow, H. *Z. Elektrochem.* **1960**, *64*, 483−91.

was added to the reaction mixture, and after an additional 20 min, the cobaloxime mixture was reduced with a solution of $NaBH_4$ (0.24 g, 6.3 mmol) and NaOH (0.21 g, 5.3 mmol) in 1.1 mL of H_2O and cooled to 0 °C. Dichloroacetylene (8.40 g, 13.9 mmol) was distilled into the reaction mixture at 0 °C over 2 h as described previously.[27] (**CAUTION**: Dichloroacetylene is explosive in the presence of oxygen. Inert atmosphere conditions must be maintained.) The volume of the mixture was doubled with H_2O, which precipitated an orange solid. The solid was passed through a silica plug eluting with acetone. The orange fractions were collected, the solvent was removed under reduced pressure, and the residue was further purified by silica gel chromatography (hexane/acetone 5:1, $R_f = 0.13$) to remove cobalt complexes **1** and **2**. Acetone wash of the column yielded the desired product as an orange powder (0.22 g, 18%). X-ray quality crystals were obtained from CH_2Cl_2/cyclohexane. FT-IR (KBr) 3136, 1703, 1562, 1225, 1089 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 1.75 (3 H, s, CH_3), 2.11 (3 H, s, CH_3), 2.18 (3 H, s, CH_3), 2.21 (3 H, s, CH_3), 5.41 (1 H, s, NH), 7.45 (2 H, m, Ar H), 7.85 (1 H, m, Ar H), 8.90 (2 H, m, Ar H), 14.144 (1 H, s, OH), 17.677 (1 H, bs, OH); ^{13}C NMR (APT, 125 MHz) δ ppm 11.9 (CH_3), 12.5 (CH_3), 12.5 (CH_3), 30.9 (CH_3), 119.0 (vinyl C_q), 125.9 (Ar CH), 138.6 (Ar CH), 148.3 (C=N, C_q), 151.0 (Ar H); 152.7 (C=N, C_q), 155.7 (C=N, C_q), 207.1 (C–NH, C_q). LRMS-FAB (*m*/*z*): 464 (M + 1).

Reaction of Dichloroacetylene with Cob(I)aloxime under Nonalkaline Conditions. A 100 mL Schlenk flask was charged with $Co(OAc)_2 \cdot H_2O$ (0.50 g; 2 mmol), dimethylglyoxime (0.468 g; 4 mmol), and dry degassed THF (50 mL) or methanol/H_2O (9:1; 10 mL). Pyridine (0.395 g, 6 mmol) and Zn dust (0.664 g; 10.1 mmol) were added to the solution. The solution was heated to reflux for 2 h and cooled to 0 °C in an ice bath followed by distillation of dichloroacetylene into the cobaloxime solution. The pH of the solution when using methanol/H_2O (9:1) was 7.4.

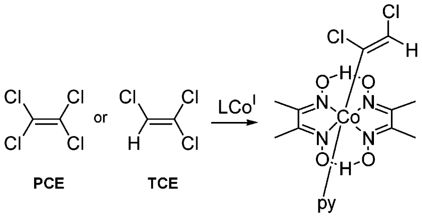
Reaction of Cob(I)alamin with Chloroacetylene and Dichloroacetylene. Under an Ar atmosphere, a 100 mL round-bottom flask was charged with hydroxocobalamin (0.1 g, 0.072 mmol), cobalt nitrate (0.001 g; 0.003 mmol), and 9 mL of degassed, distilled H_2O. $NaBH_4$ (0.020 g, 0.53 mmol) dissolved in 0.5 mL of degassed, distilled H_2O was slowly injected into the cobalamin solution. After reduction was complete, dichloroacetylene or chloroacetylene was distilled into the cob(I)alamin solution as previously described[27,28] at 25 °C for 2 h. (**CAUTION**: Dichloroacetylene is explosive in the presence of oxygen. Although no problems were encountered using chloroacetylene in this study, chloroacetylene may be explosive in the presence of oxygen. Inert atmosphere conditions must be maintained when using both acetylenes.) The cobalamin was extracted with phenol/CH_2Cl_2 (1:1) until the aqueous phase no longer contained any alkylcobalamin. The phenol extracts were combined and were washed a minimum of three times with distilled H_2O ($^1/_3$ volume of the phenol solution). The phenol solution was then diluted with 1-butanol/CH_2Cl_2 (1:1; 10× the volume of the phenol solution), and the alkylcobalamin was extracted into distilled H_2O until the phenolic phase no longer contained any cobalamin. Lyophilization of the aqueous solution resulted in near quantitative yield of the *cis*-chlorovinyl cobalamin product in the reaction of cob(I)alamin with chloroacetylene, whereas no alkylcobalamins could be isolated in the transformation with dichloroacetylene. ESI-MS for *cis*-chlorovinylcobalamin: *m*/*z* 1390 (24, M^+), 695 (100, M^{2+}).

Scheme 1



Results and Discussion

Reaction of Cob(I)aloxime with Dichloroacetylene. In two independent studies, the reaction of cob(I)aloxime with either PCE or TCE has been shown to produce *cis*-dichlorovinylcobaloxime **1** (eq 2).[12,13] This complex could



(2)

be formed by a nucleophilic vinylic substitution[29,30] on TCE by the strongly nucleophilic cob(I)aloxime,[31] or it could be formed by *syn*-addition of cob(I)aloxime to dichloroacetylene. This latter compound could conceivably arise during reductive dechlorination of PCE by a number of pathways, including chloride elimination from a trichlorovinyl anion, or reduction of a trichlorovinylcobaloxime intermediate by the strong reductants present in the dechlorination medium (Scheme 1).[12] In a similar fashion, chloroacetylene has been detected when **1** was reacted with strong reducing agents.[13] To test whether dichloroacetylene was a possible intermediate in the formation of cobaloxime **1**, we generated this reactive compound from a biphasic mixture of TCE and aqueous NaOH[32] and distilled the product into a solution of cob(I)aloxime at alkaline pH. The ^1H NMR spectrum of the reaction product showed a mixture of three complexes. Indeed, complex **1** was present in the product; however, it was not a major component (3%). A second minor product (2%) was characterized as *trans*-dichlorovinylcobaloxime **2** on the basis of its ^1H NMR spectrum (Scheme 2).[12] The ^1H NMR spectrum of the major product exhibited a broad singlet at 5.41 ppm, which decreased in intensity and eventually disappeared when a small amount of D_2O was added to the sample. Drying the NMR sample and dissolving it in a $CDCl_3$/H_2O mixture led to the reappearance of the broad signal indicating that it is associated with a solvent exchangeable proton. Furthermore, the spectrum displayed four different methyl resonances suggesting the complex has low

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(27) Pielichowski, J.; Popielarz, R. *Synthesis* **1984**, *5*, 433–434.
(28) Beit-Yannai, M.; Rappoport, Z.; Shainyan, B. A.; Danilevich, Y. S. *J. Org. Chem.* **1997**, *62*, 8049–8057.
(29) Modena, G. *Acc. Chem. Res.* **1971**, *4*, 73–80.
(30) Rappoport, Z. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 309–349.
(31) Schrauzer, G. N.; Deutsch, E. *J. Am. Chem. Soc.* **1969**, *91*, 3341–3350.
(32) Pielichowski, J.; Popielarz, R. *Synthesis* **1984**, *5*, 433–434.

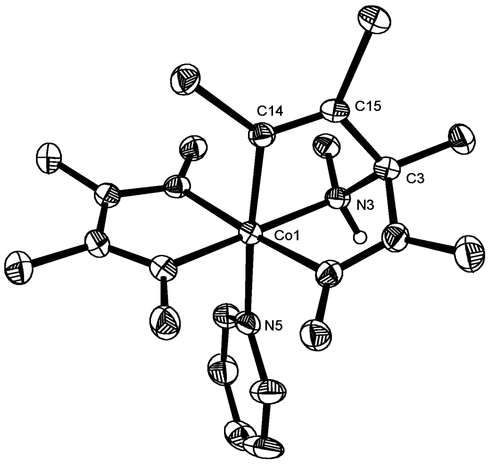
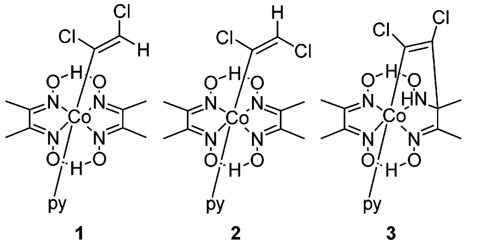


Figure 1. ORTEP diagram of complex **3**. Full details for all structures are provided in the Supporting Information. Hydrogens are omitted for clarity except for the exchangeable hydrogen on N3, and atoms are drawn as 35% thermal ellipsoids.

Scheme 2



symmetry in contrast to products **1** and **2**, which both show only one set of methyl peaks.

The major complex was separated from the other two compounds by silica gel flash chromatography,[33] and X-ray quality crystals were obtained from CH_2Cl_2/cyclohexane. The three-dimensional structure of the complex was solved and is depicted in Figure 1. Remarkably, the crystal structure indicates that, in addition to the anticipated Co—C bond, a C—C bond was also formed during the reaction of cob(I)aloxime with dichloroacetylene. This bond connects one of the former acetylenic carbons with one of the former oxime carbons to generate a [2.2.1]-tricyclic structure (**3**) with cobalt and C3 at the bridgehead positions. In the structure, N3 appears tetrahedral, consistent with the observed electron density of an attached proton and the observation of an exchangeable proton in the ^{1}H NMR spectrum. The five membered ring spanning the axial and equatorial ligands in complex **3** does not severely distort the coordination geometry at cobalt. The C14—Co1—N5 bond angle is 173.78°, displaced by only 5° from the C14—Co1—N5 bond angle of 178.5° in complex **1**.[12] Furthermore, the C14=C15 (1.317 Å) and Co1—C14 bond lengths (1.944 Å) are close to those reported for other chloroethenylcobaloxime complexes (Table 2).[12,13] The additional ring structure is predominantly accommodated by displacement of C3 out of the equatorial plane by 1.034 Å resulting in two puckered five membered metallocycles, and by a decrease in the Co1—C14—C15 bond angle. The cyclic voltammogram of complex **3** is shown in Figure 2. It displays an irreversible cathodic peak potential at −1.63 V versus NHE, significantly more negative than the peak potential of complex **1** ($E_p = -1.26$ V). This negative shift in peak potential could possibly reflect the stronger donating ability of the hydroxylamine nitrogen in complex **3** relative to the oxime nitrogens of **1**, but the longer Co1—N3 bond length in **3** compared to **1** appears to argue against this explanation (Table 2). Alternatively, the disruption of the planarity of the equatorial π-system may result in a decrease in the electron acceptor ability of the complex.

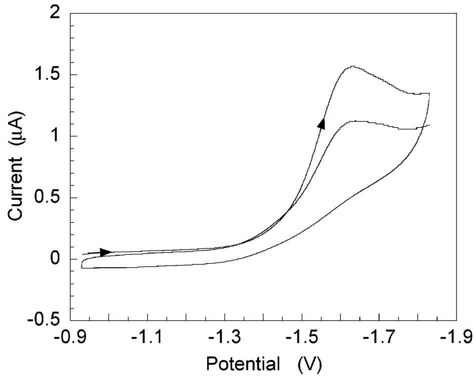


Figure 2. Cyclic voltammogram of cobalt complex **3** (1 mM) in DMF. Potentials are vs NHE, sweep rate 100 mV/s, glassy carbon working electrode, 0.1 M Bu_4NClO_4. The first forward and reverse scans are shown as well as the second forward scan.

Complex **3** was not detected during the reductive dechlorination of PCE or TCE by cob(I)aloxime.[12,13] Thus, despite the fact that a minor amount of **1** is observed in the reaction of cob(I)aloxime with dichloroacetylene, these findings rule out that dichloroacetylene is the source of **1** in the dechlorination of PCE and TCE. The mechanism of the formation of **3** poses an interesting question. At first glance, the reaction resembles a cycloaddition involving two π-electrons of the alkyne, two electrons in the cobalt d_{z^2} orbital, and two π-electrons of the oxime. However, the presence of a proton on N3 suggests that **3** is formed in a stepwise rather than concerted fashion. Moreover, a [2 + 2 + 2] concerted reaction would provide a 20 electron cobalt complex with a Co1=N3 double bond, which is unlikely on the basis of electronic and orbital arguments. The production of small amounts of **1** and **2** is in line with a stepwise mechanism with a vinyl anion intermediate that partitions to the three observed products (Scheme 3). At pH 10.5, at which these experiments were conducted, the addition of cob(I)aloximes to alkynes occurs with *trans*-stereochemistry.[34,35] Protonation of the resulting *trans*-vinyl anion would give product **2**. Isomerization of the *trans*-ethenyl anion to the *cis*-ethenyl anion followed by fast intraligand nucleophilic attack of the axial vinyl anion on the C=N bond of the equatorial oxime ligand would lead to complex **3** (Scheme 3). The small amounts of complex **1** that are observed could derive from competitive protonation of the *cis*-vinyl anion.[36] In this

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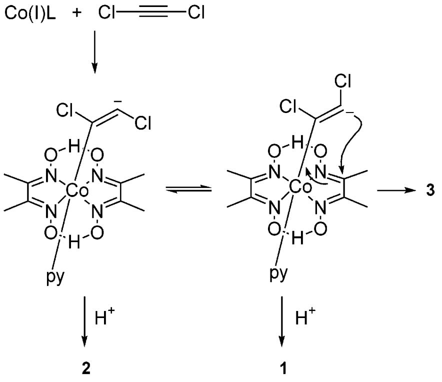
(33) Still, W. C.; Kahn, M.; Mitra, J. *J. Org. Chem.* **1978**, *43*, 2923.

(34) Naumberg, M.; Duong, K. N. V.; Gaudemer, A. *J. Organomet. Chem.* **1970**, *25*, 231−242.

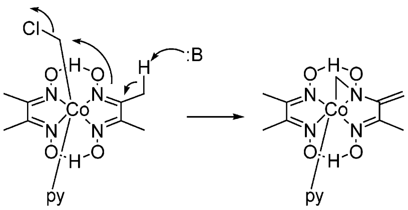
(35) Johnson, M. D.; Meeks, B. S. *J. Chem. Soc. B* **1971**, 185−189.

(36) An alternative mechanism for the generation of **1** in the reaction of dichloroacetylene and cob(I)aloxime involves a *syn*-addition of a cobalt hydride to the alkyne. See refs 34 and 35.

Scheme 3



Scheme 4



scenario, interconversion of the two vinyl anion isomers would need to be faster than protonation, and the intramolecular ring formation would have to be the lowest available reaction pathway for the vinyl anion intermediates. The product distribution would then be under Curtin−Hammett control, and the cyclic structure can be the major product even when the *trans*-vinyl anion is initially formed predominantly.

Scheme 3 predicts that at lower pH the relative yields of complexes **1** and **2** should increase; however, we have been unable to confirm this prediction. Because of the high reactivity of $NaBH_4$ under acidic conditions, cob(I)aloxime was generated by reduction with zinc powder in either MeOH/H_2O (pH 7.4) or THF followed by introduction of dichloroacetylene. Using THF as the reaction solvent, complex **3** was the major product with minor amounts of **2** (6%), while, in MeOH/H_2O, complex **3** was again the major product with only a trace amount of complex **2**. Thus, if a vinyl anion intermediate is indeed formed, it cannot be readily intercepted by protonation. Further insights into the unusual reaction between these two highly reactive species, cob(I)aloxime and dichloracetylene, will require computational approaches.

It is interesting to note that the mode of intramolecular addition in the formation of **3** is in the opposite direction to that observed in organocobalt complexes containing an axial ligand with a halogen on the α-carbon (Scheme 4).[37,38] Under basic conditions, such complexes undergo an intraligand addition of an equatorial imine nitrogen to the axial carbon to form a Co−N−C three membered ring. Similar to these complexes,[38] compound **3** is rather insensitive to light even under aerobic conditions. Presumably, the resistance to photolysis results from the enforced proximity of the resulting Co(II)••R radical pair leading to recombination rather than other follow-up reactions.

Reaction of Cob(I)alamin with Chloroacetylene and Dichloroacetylene. The results presented in this work show that dichlorinated vinylcobaloximes detected in the reductive dechlorination of PCE and TCE catalyzed by cob(I)aloxime are not formed from dichloroacetylene. In contrast, our previous findings have indicated that monochlorinated vinylcobaloximes can be formed from the reaction of cob(I)aloxime and chloroacetylene. To extend these observations to vitamin B_{12} catalyzed dechlorination processes, cob(I)alamin was reacted with both chloroacetylene and dichloroacetylene. From the former transformation, an alkylcobalamin was isolated and purified in 90% yield. The electrospray mass spectrum of the complex showed it contained one chloride, and its ^1H NMR spectrum showed doublet resonances at 5.03 ppm ($^3J = 5.60$ Hz) and 5.73 ppm ($^3J = 5.60$ Hz). These coupling constants are consistent with a *cis*-substituted olefin and are close to those observed for complex **1** (5.69 Hz).[12] The formation of *cis*-chlorovinylcobalamin in this transformation is similar to the observations with cobaloximes. However, the reaction of cob(I)alamin with dichloroacetylene did not lead to the production of any organocobalamins. Collectively, these results suggest that for both catalyst systems dichlorinated vinylcobalt complexes are not generated from dichloroacetylene. Instead, vinylic nucleophilic substitution on TCE or the combination of a dichlorovinyl radical with Co(II) are likely pathways to these products. On the other hand, the involvement of chloroacetylene as an intermediate in the formation of monochlorinated vinylcobalt complexes appears on solid grounds. Chloroacetylene reacts with both cob(I)aloxime[12] and cob(I)alamin, chloroacetylene has been detected during reductive dechlorination of PCE and TCE,[13] and chloroacetylene is generated as a product of reductive dechlorination of dichlorinated vinylcobaloximes.[13]

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Supporting Information Available: Listings of crystallographic data as well as bond lengths and angles for complex **3** in CIF format. Voltammograms with ferrocene as internal standard. This material is available free of charge via the Internet at http://pubs.acs.org.

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(37) Polson, S. M.; Hansen, L.; Marzilli, L. G. *J. Am. Chem. Soc.* **1996**, *118*, 4804−4808.

(38) Dreos, R.; Felluga, G.; Nardin, G.; Randaccio, L.; Siega, P.; Tauzher, G. *Inorg. Chem.* **2001**, *40*, 5541.