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# Synthesis and Characterization of Chlorinated Alkenylcobaloximes To Probe the Mechanism of Vitamin $B_{12}$-Catalyzed Dechlorination of Priority Pollutants

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Vitamin $B_{12}$ catalyzes the reductive dechlorination of several ubiquitous pollutants such as perchloroethylene (PCE) and trichloroethylene (TCE). Several mechanisms have been proposed for these transformations, some of which involve the intermediacy of chlorinated vinylcobalamins. To evaluate the currently unknown chemical and physical properties of such species, various chlorinated vinylcobaloxime complexes [cobaloxime = bis(dimethylglyoximato)-(pyridine)cobalt(III)] were prepared and characterized. X-ray structures are reported for (*cis*-1,2-dichloroethenyl)-cobaloxime (**4**), (*cis*-monochloroethenyl)cobaloxime (**5**), ($\alpha$-chloroethenyl)cobaloxime (**6**), and vinylcobaloxime (**7**), and the reactivities of these isolated complexes were investigated. They were stable in the presence of ethanolic $NaBH_4$ unless external cobaloximes were added. The cob(I)aloxime formed under the latter conditions promoted the conversion of **4** to **5** and **6**, and of **5** and **6** into **7**. Mechanistic studies of these transformations are consistent with a pathway in which the conversion of **4** into **5** and **6** takes place via chloroacetylene as an intermediate, and the conversion of **6** to **7** involves vinyl chloride as an intermediate. Cyclic voltammetry on the chlorinated vinylcobaloximes resulted in irreversible reduction waves, with **4** displaying the least negative and **7** the most negative peak potential. These results are discussed in the context of the $B_{12}$-catalyzed reductive dechlorination of PCE and TCE.

## Introduction

Perchloroethylene (PCE) is an abundant pollutant that ranks high on the priority list of the U.S. Environmental Protection Agency, as its discharge into subsurface environments has extensively contaminated soils and aquifers.[1,2] PCE causes liver and kidney tumors in animal studies[3,4] and has been classified as a probable human carcinogen. Several recent reports have indicated that vitamin $B_{12}$ can function as a catalyst for the reductive dechlorination of PCE (eq 1), suggesting $B_{12}$ may be used for the decontamination of polluted environments.[5−9] Initially, this process produces predominantly (~95%) *cis*-dichloroethylene (DCE),[10] which is further reduced over time to ethene and ethane.[10−12] At present, the mechanistic details of these transformations are unclear. The strong reductants that are required for turnover suggest that the $Co^I$ oxidation state of $B_{12}$ (cob(I)alamin) is essential for catalysis. Assuming that cob(I)alamin indeed initiates the dechlorination process, at least five different mechanisms can be written on the basis of the vast literature

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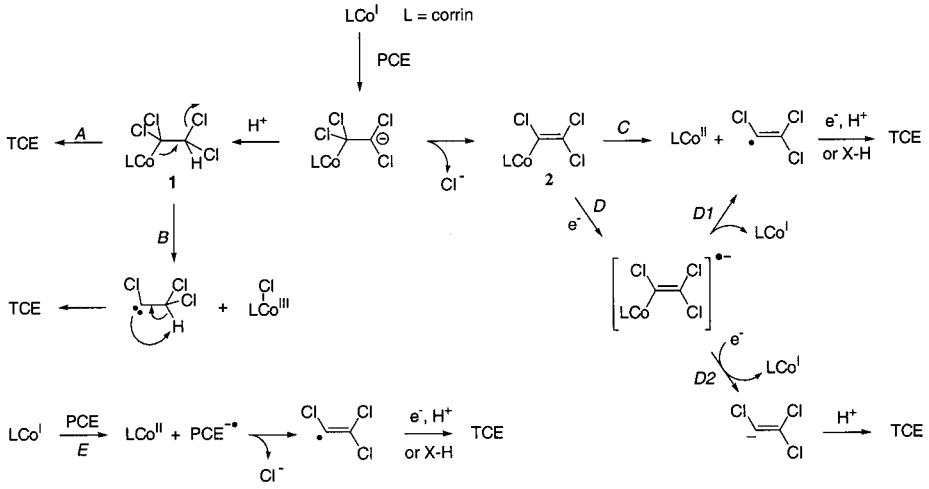
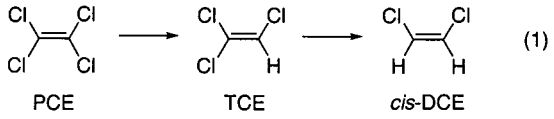
**Scheme 1**




on the chemistry of vitamin $B_{12}$ (Scheme 1).[13] Four of these (pathways A−D) involve the intermediacy of chlorinated alkyl or alkenylcobalamins formed by attack of the strongly nucleophilic[14,15] cob(I)alamin on the electron deficient alkene, possibly after initial $\pi$-complexation.[16] Mechanisms A−D differ in the manner in which chloride is eliminated and the Co−C bond is broken. In pathway A, this occurs via a straightforward $\beta$-elimination from tetrachloroethylcobalamin (**1**). Much precedent exists in the literature for elimination of good nucleofuges from the $\beta$-carbon of alkylcobalamins.[17,18] Alternatively, α-elimination of chloride from the carbenoid **1** could generate a carbene that can undergo C−H[19] or C−Cl[20] bond insertion to provide the product (mechanism B). Carbene species have been proposed previously in rearrangements of putative α,α-dichloroorganocobalt intermediates.[21−23] A third mechanism involves dehydrochlorination of intermediate **1** providing (trichloroethenyl)-cobalamin (**2**). Either homolytic cleavage of the Co−C bond followed by reduction of the resulting vinyl radical (route C) or reductive dechlorination of **2** by electron transfer from one of the strong reductants in the reaction mixture (pathways D) could produce the observed product.




(1)

In contrast to mechanisms A−D, which all involve alkyl- or alkenylcobalamins, mechanism E features a one-electron transfer from cob(I)alamin to PCE. In the gas phase, low-energy electron scattering studies have provided vertical electron attachment energies for PCE.[24] These measurements indicate that the radical anion is unstable and has an energy that lies above the ground state of the neutral alkene. The electron initially attaches to the $\pi^*$ orbital, followed by molecular distortions that lead to occupation of the $\sigma^*$ orbital of the C−Cl bonds resulting in chloride anion elimination.[25−29] The trichlorovinyl radical so produced may be converted to TCE by either hydrogen atom abstraction from a suitable source or reduction to the anion followed by protonation.[30]

We[31] and others[7] have recently provided support for mechanism E in the first step of dechlorination of PCE with cob(I)alamin. Chlorinated ethenylcobalamins, however, are formed in dechlorination reactions as evidenced by their detection by mass spectrometry.[12] Furthermore, Schwarzenbach and co-workers have postulated their intermediacy in the $B_{12}$-catalyzed dechlorination of *cis*- and *trans*-dichloroethylenes (DCEs).[10] What the roles are of these complexes, whether they are catalytic intermediates or dead-end products, is not known. If they are catalytic intermediates, the question arises as to how the Co−C bond is cleaved to release the products and regenerate the catalyst. In an initial study to address some of these issues, we report here the synthesis of several chlorinated alkenylcobaloximes and their spec-

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**Table 1.** Crystal Data and Details of the Structural Refinement for Complexes **4**−**7**

| | **4** | **5** | **6** | **7** |
|---|---|---|---|---|
| formula | $C_{16}H_{22}C1_4Co_1N_5O_4$ | $C_{15}H_{21}C1_1Co_1N_5O_4$ | $C_{15}H_{21}C1Co_1N_5O_4 \cdot 1/3(CH_2Cl_2)$ | $C_{15}H_{22}Co_1N_5O_4$ |
| fw | 549.12 | 429.75 | 458.06 | 395.31 |
| space group | *C*2/*c* | $P\bar{1}$ | $P2_1/c$ | $P2_1/n$ |
| *T* (K) | 223 ± 2 | 193 ± 2 | 193 ± 2 | 183 ± 2 |
| $\lambda$ (Å) | 0.710 73 | 0.710 73 | 0.710 73 | 0.710 73 |
| *a* (Å) | 12.0964(11) | 15.874(2) | 8.8489(8) | 8.8598(6) |
| *b* (Å) | 13.3142(12) | 17.136(3) | 39.436(4) | 14.3906(9) |
| *c* (Å) | 14.9277(14) | 17.314(3) | 16.9814(16) | 14.0123(9) |
| α (deg) | 90 | 60.419(2) | 90 | 90 |
| $\beta$ (deg) | 109.721(2) | 87.617(3) | 101.6100(10) | 95.117(2) |
| $\gamma$ (deg) | 90 | 64.356(2) | 90 | 90 |
| $\rho_{cald}$ (g cm$^{-1}$) | 1.612 | 1.585 | 1.572 | 1.476 |
| Z | 4 | 8 | 12 | 4 |
| *V* (Å$^3$) | 2263.2(4) | 3602.2(9) | 5804.6(9) | 1779.4(4) |
| $\mu$ (cm$^{-1}$) | 12.63 | 11.33 | 11.49 | 9.95 |
| R [$I > 2\sigma(I)$][a] | R1 = 0.0358 | R1 = 0.0468 | R1 = 0.0578 | R1 = 0.0343 |
| | wR2 = 0.0937 | wR2 = 0.0939 | wR2 = 0.0639 | wR2 = 0.0844 |
| R (all data)[a] | R1 = 0.0557 | R1 = 0.1188 | R1 = 0.1786 | R1 = 0.0539 |
| | wR2 = 0.0991 | wR2 = 0.1133 | wR2 = 0.0829 | wR2 = 0.0910 |

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

troscopic, structural, and electrochemical characterization. The implications of these studies for the overall process of $B_{12}$-catalyzed dechlorination of chlorinated alkenes are discussed.

## Experimental Section

**General Information.** All NMR spectra were recorded on Varian U400 and 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 spectra were taken in $CDCl_3$. 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 complexes **4**−**7**, mounted on thin glass fibers with oil (Paratone-N, Exxon), were collected using a Siemens Platform/CCD diffractometer with graphite-monochromated Mo Kα radiation. All structures were solved by direct methods and refined by full-matrix least-squares methods against $F^2$ (SHELX-97-2).[32,33] Crystallographic data for complexes **4**−**7** are given in Tables 1 and 2. Further details regarding the crystallographic data as well as full tables of bond lengths and angles for each complex reported in this paper 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 anhydrous DMF/*t*-BuOH (1:1), at a concentration of 1 mM of each complex. The peak potentials given in the text are referenced to the $Ag^+$/AgCl electrode. In addition, in a separate series of experiments, an internal reference system (ferrocene/ferrocenium ion) was used, which has been shown to remain constant regardless of media,[34,35] thereby allowing better comparison with other studies by eliminating problems of variable liquid junction potentials.[36−39] Under the conditions used, the reversible $Fc/Fc^+$ potential occurred at 0.53 V vs the $Ag^+$/AgCl electrode [$(E_p + E_c)/2$; for an example, see Figure S3 in the Supporting Information]. When using this as an internal reference system and taking the $Fc^+$/Fc couple as 0.40 V vs NHE (Koepp, H. M.; Wendt, H.; Strehlow, H. Z. *Z. Elektrochem.* **1960**, *64*, 483−491), the following peak potentials can be derived vs NHE: −1.26 V for **4**; −1.43 V for **5**; −1.36 V for **6**; −1.58 V for **7**; −1.15 V for **8**; −1.39 V for **13**.

**Table 2.** Selected Bond Distances (Å) and Bond Angles (deg) for Complexes **4**−**7** with Esd's in Parentheses

| | **4** | **5**[a] | **6**[a] | **7** |
|---|---|---|---|---|
| Co(1)−C(14) | 1.945(5) | 1.946(2) | 1.947(4) | 1.953(3) |
| | | 1.947(3) | 1.951(4) | 1.958(8) |
| | | 1.945(2) | 1.952(4) | |
| | | 1.949(2) | | |
| C(14)═C(15) | 1.32(3) | 1.314(3) | 1.341(4) | 1.292(4) |
| | | 1.312(3) | 1.342(4) | 1.291(9) |
| | | 1.312(3) | 1.339(4) | |
| | | 1.311(3) | | |
| Co(1)−N(5) | 2.030(2) | 2.047(2) | 2.035(3) | 2.0518(15) |
| | | 2.046(2) | 2.035(3) | |
| | | 2.046(2) | 2.033(3) | |
| | | 2.046(2) | | |
| Co(1)−C(14)═C(15) | 121(2) | 140.2(3) | 126.7(3) | 127.8(3) |
| | | 139.5(3) | 127.0(4) | 122.4(9) |
| | | 138.6(3) | 126.2(4) | |
| | | 139.1(3) | | |

[a] For compounds **5** and **6** multiple crystallographically independent molecules were present with slight differences in the bond distances and angles listed.

**Synthesis of [Co(dmgH)$_2$(py)(CCl═CHCl)] (4).** 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

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by NaOH (0.22 g, 5.4 mmol). After the reaction mixture was stirred for 5 min, pyridine (0.21 g, 2.7 mmol) was added, and after an additional 20 min, TCE (0.39 g, 5.4 mmol) was added. The atmosphere over the mixture was replaced with $H_2$, and the mixture remained under $H_2$ for 24 h. The volume of the mixture was doubled with $H_2O$, which precipitated an orange solid. The solid was dissolved in acetone, and the solution 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 (5:1 hexane/acetone, $R_f = 0.13$) to yield the desired product as an orange powder. X-ray-quality crystals were obtained by crystallization from $CH_2Cl_2$/cyclohexane (0.23 g, 18%): FT-IR (KBr) 2767, 1563, 1452, 1368, 1237, 1092 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ ppm 2.20 (12 H, s, $CH_3$), 5.80 (1 H, s, C═CHCl), 7.34 (2 H, m, pyr), 7.76 (1 H, m, pyr), 8.57 (2 H, m, pyr), 18.00 (2 H, bs, OH); $^{13}C$ NMR (APT, 125 MHz) $\delta$ ppm 12.5 ($CH_3$), 107.3 (CH), 125.5 (Ar CH), 138.3 (Ar CH), 150.1 (Ar CH), 151.2 (C═N, $C_q$); LRMS-FAB (*m*/*z*) 464 (M + 1).

**Synthesis of *cis*-[Co(dmgH)$_2$(py)(CH═CHCl)] (5).** 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 the reaction mixture was stirred for 5 min, pyridine (0.21 g, 2.7 mmol) was added, 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 $H_2O$. Chloroacetylene (8.40 g, 13.9 mmol) was distilled into the reaction mixture over 2 h as described previously.[40] (*Caution! Although no problems have been encountered in this study, chloroacetylene is potentially explosive.*) 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 (5:1 hexane/acetone, $R_f = 0.13$) to yield the desired product as an orange powder. X-ray-quality crystals were obtained from $CH_2Cl_2$/cyclohexane (0.023 g, 2%). A higher yield (11%) can be obtained when less NaOH is added initially (0.22 g, 5.4 mmol) producing a mixture of **5** and **6**. The ratio of **5** to **6** was dependent on the pH of the reaction mixture: **5**:**6** was 95:5 at pH 11, 7:3 at pH 10, and 1:3 at pH 9. FT-IR (KBr): 2949, 1558, 1448, 1240, 1090 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ ppm 2.16 (12 H, s, $CH_3$), 5.85 (1 H, d, $J = 5.69$ Hz, ═CHCl), 6.01 (1 H, d, $J = 5.69$ Hz, CoCH═) 7.36 (2 H, m, pyr), 7.77 (1 H, m, pyr), 8.62 (2 H, m, pyr) 18.24 (2 H, bs, OH). $^{13}C$ NMR (APT, 125 MHz): $\delta$ ppm 12.1 ($CH_3$), 125.4 (Ar CH), 126.6 (CH), 137.9 (Ar CH), 149.8 (Ar CH), 150.6 (C═N, $C_q$). LRMS-FAB (*m*/*z*) 430 (M + 1).

**Synthesis of [Co(dmgH)$_2$(py)(CCl═CH$_2$)] (6).** Complex **6** was obtained from 1,1-dichloroethylene using similar experimental conditions as described for complex **4** except the reaction mixture was kept under an $H_2$ atmosphere for 12 h. The volume of the mixture was doubled with $H_2O$, which precipitated a yellow solid. The solid was dissolved in acetone, and the solution 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 (5:1 hexane/acetone, $R_f = 0.13$) to yield the desired product as a yellow powder. X-ray-quality crystals were obtained from $CH_2Cl_2$/cyclohexane (0.27 g, 23%): FT-IR (KBr) 3118, 3051, 2925, 1565, 1450, 1238, 1091 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ ppm 2.18 (12 H, s, $CH_3$), 5.05 (1H, d, $J = 2.07$ Hz, ═$CH_2$), 5.24 (1 H, d, $J = 2.07$ Hz, ═$CH_2$), 7.32 (2 H, m, Ar H), 7.73 (1 H, m, Ar H), 8.58 (2 H, m, Ar H) 18.03 (2 H, bs, OH); $^{13}C$ NMR (APT, 125 MHz) $\delta$ ppm 12.4 ($CH_3$), 119.3 (═$CH_2$), 125.4 (Ar CH), 138.0 (Ar CH), 150.1 (Ar CH), 150.6 (C═N, $C_q$); LRMS-FAB (*m*/*z*) 430 (M + 1).

**Synthesis of [Co(dmgH)$_2$(py)(CH═CH$_2$)] (7).** Two different methods were used to synthesize complex **7**. Under an argon atmosphere, a 100 mL round-bottom flask was charged with Co(dmgH)$_2$(py)(CCl═CHCl) (**4**) (0.10 g, 0.22 mmol), cobaloxime dimer **8** (0.081 g, 0.11 mmol), and 50 mL of MeOH. A solution of $NaBH_4$ (0.24 g, 6.3 mmol) and NaOH (0.21 g, 5.3 mmol) in 1.1 mL of $H_2O$ was added, and the reaction was stirred for 2 h. MeOH and $H_2O$ were removed under reduced pressure, and the crude product was passed through a silica plug eluting with acetone followed by purification using silica gel chromatography (5:1 hexane/acetone, $R_f = 0.13$) to yield an orange-yellow powder. X-ray-quality crystals were obtained by crystallization from $CH_2Cl_2$/cyclohexane (2 mg, 2%). Although complete dechlorination of complex **4** resulted in the formation of complex **7**, a more practical synthesis was used to prepare complex **7** in higher yields. Using similar reaction conditions as described for complex **5**, vinyl bromide in THF (1 M) was substituted for chloroacetylene (yield of **7**, 0.54 g, 51%): FT-IR (KBr) 2960, 2925, 1571, 1450, 1236, 1089, $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ ppm 2.12 (12 H, s, $CH_3$), 4.67 (1H, dd, $J = 6.86$, 1.64 Hz, ═$CH_2$), 4.81 (1 H, dd, $J = 15.14$, 1.64 Hz, ═$CH_2$), 6.41 (1 H, dd, $J = 15.14$, 6.81 Hz, CoCH═), 7.33 (2 H, m, Ar H), 7.74 (1 H, m, Ar H), 8.63 (2 H, m, Ar H), 18.32 (2H, bs, OH); $^{13}C$ NMR (APT, 125 MHz) $\delta$ 12.1 ($CH_3$), 120.5 (═$CH_2$), 125.3 (Ar CH), 137.7 (Ar CH), 149.4 (C═N, $C_q$), 150.1 (Ar CH); LRMS-FAB (*m*/*z*) 396 (M + 1).

**Synthesis of *trans*-[Co(dmgH)$_2$(py)(CH═CHCl)] (13).** A 25 mL Schlenk flask was charged with $CoCl_2 \cdot 6H_2O$ (0.35 g, 1.5 mmol), 10 mL of degassed MeOH, and a stir bar. After the $CoCl_2 \cdot 6H_2O$ dissolved, dimethylglyoxime (0.63 g, 5.4 mmol) was added followed by NaOH (0.22 g, 5.4 mmol). After the reaction mixture was stirred for 5 min, pyridine (0.23 g, 3.0 mmol) was added, and after an additional 25 min, *trans*-1,2-DCE (0.52 g, 5.4 mmol) was added. The atmosphere over the mixture was replaced with $H_2$, and the mixture remained under $H_2$ for 2.5 h. An orange solid precipitated from the solution, and it was filtered off using a medium frit. The volume of the filtrate was doubled with $H_2O$ and cooled to −20 °C, which precipitated an orange solid. The solid was dissolved in acetone, and the solution 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 (5:1 hexane/acetone, $R_f = 0.13$) to yield the desired product as a yellow powder (0.007 g, 1%): FT-IR (KBr) 3040, 2849, 1560, 1452, 1222, 1092 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ ppm 2.14 (12 H, s, $CH_3$), 5.29 (1H, d, $J = 12.57$ Hz, ═CHCl), 6.22 (1H, d, $J = 12.57$ Hz, CoCH═), 7.33 (2 H, m, pyr), 7.74 (1 H, m, pyr), 8.57 (2 H, m, pyr), 18.15 (2 H, bs, OH); $^{13}C$ NMR (APT, 125 MHz) $\delta$ ppm 12.2 ($CH_3$), 109.6 (CH), 125.4 (Ar CH), 138.0 (Ar CH), 150.0 (Ar CH), 150.2 (C═N, $C_q$); HRMS-FAB (*m*/*z*) calcd for $C_{15}H_{22}N_5O_4ClCo$ (M + 1) 430.0692, found 430.0690.

## Results and Discussion

Alkylbis(dimethylglyoximato)(pyridine)cobalt(III) complexes (RCo(dmgH)$_2$py), designated henceforth in this report as alkylcobaloximes, have been extensively used as structural

(40) Beit-Yannai, M.; Rappoport, Z.; Shainyan, B. A.; Danilevich, Y. S. *J. Org. Chem.* **1997**, *62*, 8049−8057.

and functional mimics for vitamin $B_{12}$.[41−43] Although these compounds do not accurately reproduce all chemical properties of $B_{12}$,[44] the wealth of available information on their reactivities in comparison with $B_{12}$ derivatives renders cobaloximes good starting points for understanding the properties of chlorinated ethenylcobalamins. Of particular interest with respect to the proposed mechanisms of $B_{12}$-catalyzed dechlorination are the thermal stability, redox properties, and mechanisms of formation and reduction of these complexes.

**Synthesis and Structural Characterization of Chloroethenyl Cobaloximes**. Purified homogeneous compounds were required for the investigation of the chemical and physical properties of various chlorinated ethenylcobaloximes. We evaluated several synthetic routes to these products by reaction of cob(I)aloximes ($Co^{I}(dmgH)_2$) with PCE or TCE. In these experiments, cob(I)aloxime was formed either by reduction of in situ generated $Co^{II}(dmgH)_2py$ (**3**) with $NaBH_4$ or by stirring **3** under an atmosphere of $H_2$. With PCE both methods resulted in the isolation of chlorinated vinylcobaloximes in low yields[45] (10−25%) producing heterogeneous mixtures, the composition of which was difficult to control (eq 2). The reaction product obtained from the reaction under $H_2$ with 2 equiv of TCE on the other hand consisted only of the cis-dichlorinated complex **4** in 18% yield, which was further purified by silica gel flash chromatography.[46] The identity of the compound was confirmed by FAB mass spectrometry and $^1$H NMR spectroscopy, which showed a singlet at 5.80 ppm assigned to the vinylic proton. The stereochemistry of the double bond was unambiguously established by X-ray crystallography as depicted in Figure 1A. The vinyl ligand in this structure is situated over the protons that bridge between two oxygens of each dimethylglyoximato ligand.[47] The Co−C bond length of 1.945(5) Å is close to those reported for other alkenylcobaloximes (e.g. 1.966(6) Å in vinylCo[dmgH]$_2$py,[48] 1.971(13) Å in [{*p*-ClPh}$_2$C═CCl]Co[dmgH]$_2$py,[49] and 1.958(3) Å in [ClHC═CCl]Co[dmgH]$_2$py[47]) and shorter than found for alkylcobaloximes[42] as expected for an sp$^2$-hybridized ligand.

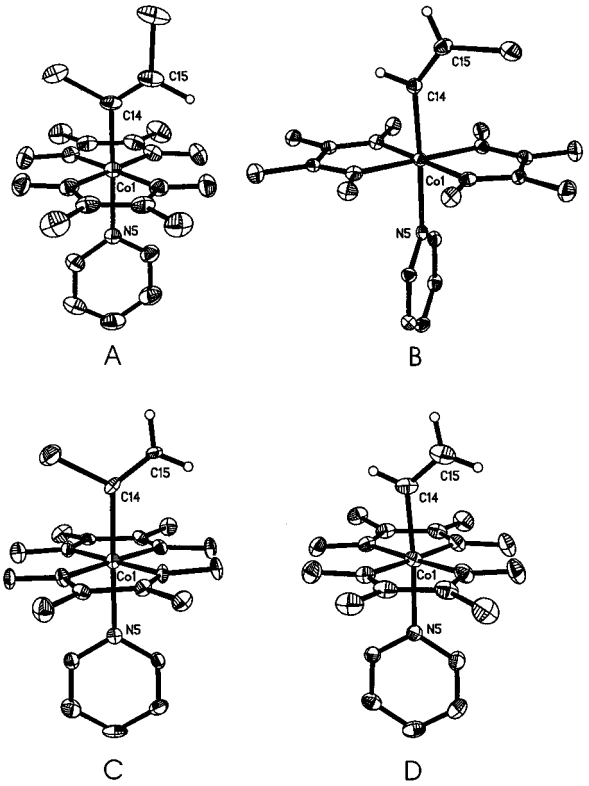
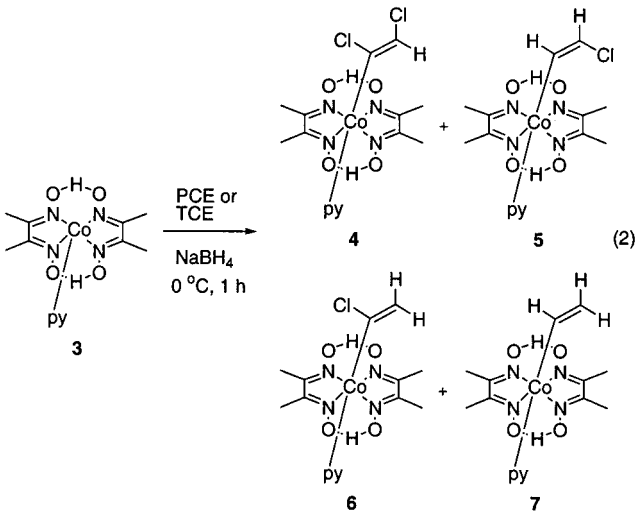



**Figure 1.** ORTEP diagrams of complexes **4** (panel A), **5** (B), **6** (C), and **7** (D). For compounds containing more than one molecule in the unit cell with slightly varying geometries, only one molecule is depicted here. Full details for all structures are provided in the Supporting Information. Hydrogens are omitted for clarity except for the vinyl hydrogens, and atoms are drawn as 35% thermal ellipsoids. Complexes **4**, **6**, and **7** have the vinyl ligand situated above the oxime moieties of the equatorial ligand, whereas the vinyl ligand in the cis-complex **5** is located above the backbone of the equatorial ligand.

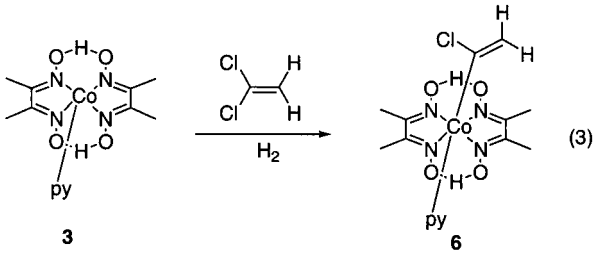



As indicated in eq 2, two isomeric monochlorinated ethenylcobaloximes **5** and **6** were also observed in the

(41) Schrauzer, G. N. *Acc. Chem. Res.* **1968**, *1*, 97−103.
(42) Bresciani-Pahor, N.; Forcolin, M.; Marzilli, L. G.; Randaccio, L.; Summers, M. F.; Toscano, P. J. *Coord. Chem. Rev.* **1985**, *63*, 1−125.
(43) Randaccio, L. *Comments Inorg. Chem.* **1999**, *21*, 327−376.
(44) For instance, the Co(I)/(II) and Co(II)/(III) redox potentials for cobalamins and cobaloximes differ with the latter being about 0.4 V more negative. See: (a) Elliott, C. M.; Hershenhart, E.; Finke, R. G.; Smith, B. L. *J. Am. Chem. Soc.* **1981**, *103*, 5558−66. (b) Finke, R. G.; Smith, B. L.; Droege, M. W.; Elliott, C. M.; Hershenhart, E. *J. Organomet. Chem.* **1980**, *202*, C25−C30. Furthermore, Co−C bond dissociation energies have been reported to be generally lower for cobalamins than for cobaloximes (Halpern, J.; Ng, F. T. T.; Rempel, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 7124−7126). E.g. for benzylcobalamin and -cobaloxime, compare (i) and (ii) with (iii): (i) Brown, K. L.; Brooks, H. B. *Inorg. Chem.* **1991**, *30*, 3420−3430. (ii) Schrauzer, G. N.; Grate, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 5541−5546. (iii) Toscano, P. J.; Seligson, A. L.; Curran, M. T.; Skrobutt, A. T.; Sonnenberger, D. C. *Inorg. Chem.* **1989**, *28*, 166−168.
(45) These low yields of formation of chlorinated ethenylcobaloximes are comparable to previously reported reactions of chlorinated styrenes with cob(I)aloximes that provided ethenylcobaloximes in low yield (10%). See for instance ref 64.
(46) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923−2925.
(47) The structure is generally in agreement with that reported by Jones and co-workers (Jones, P. G.; Yang, L.; Steinborn, D. *Acta Crystallogr., Sect. C* **1996**, *C52*, 2399−2402) although the current structure was solved in the *C*2/*c* space group instead of the *P*1 space group.
(48) Bresciani-Pahor, N.; Calligaris, M.; Randaccio, L. *J. Organomet. Chem.* **1980**, *184*, C53−C56.
(49) Stotter, D. A.; Sheldrick, G. M.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1975**, 2124−2128.

reaction of cob(I)aloxime with PCE. Unfortunately, despite much effort, chromatographic purification of significant amounts of complex **5** did not prove possible from this reaction due to coelution with **4** and **6**. However, as described below, the complex could be obtained in larger quantities by reaction of $Co^{I}(dmgH)_2$ with chloroacetylene. Its $^1H$ NMR spectrum showed doublet resonances at 5.85 ppm ($^3J = 5.69$ Hz) and 6.01 ppm ($^3J = 5.69$ Hz), consistent with a cis-substituted olefin. This assignment was subsequently corroborated by X-ray diffraction (Figure 1B) indicating an unusually large Co−C═C angle, 139.4°, in comparison to the angles in known vinylcobalt complexes.[50−55] A similarly large Co−C═C angle has been previously reported for another cis-substituted ethenyl cobaloxime, ([*p*-ClPh]$_2$C═CCl)Co[dmgH]$_2$py (133.0°).[49]

The geminal complex **6** was obtained in pure form by reaction of $Co^{II}(dmgH)_2$py with 1,1-dichloroethene (1,1-DCE, 2 equiv) under an atmosphere of $H_2$ (eq 3). The $^1H$ NMR spectrum of the yellow solid showed doublet resonances for the vinyl protons at 5.05 and 5.24 ppm ($^3J = 2.07$ Hz), and the compound was unambiguously identified as the α-chlorovinyl complex **6** by X-ray diffraction (Figure 1C). Vinylcobaloxime **7** was obtained by treating a mixture of complexes **4**−**6** with $[Co^{II}(dmgH)_2py]_2$ (**8**) and $NaBH_4$. FAB mass spectrometry and $^1H$ NMR spectroscopy of **7** confirmed its identity. An X-ray structure was obtained (Figure 1D) that is in agreement with a previously reported structure.[48] However, the C−C bond length of the vinyl ligand in the current structure is 1.292 Å compared to the previously reported bond length of 1.149 Å.[56]




**3** **6** (3)

The four structures in Figure 1 provide the opportunity to extract trends for this series of vinylcobaloximes. The Co−$N_{py}$ bond length increases slightly in the order **4** < **6** < **5** < **7**, which reflects the decreased electron-withdrawing strength of the vinyl group in this series (Table 2). A similar effect has been observed previously in substituted methylcobaloximes.[42] The Co−C bond lengths show a similar albeit smaller trend (close to experimental error, **4** < **6** < **7**), in line with reported shortening of the Co−C bond in a series of progressively higher fluorinated alkylcobaloximes.[43] The Co−C bond in the cis-substituted complex **5** does not clearly fit this order, probably because both steric and electronic effects are involved as indicated by the large Co−C═C bond angle.

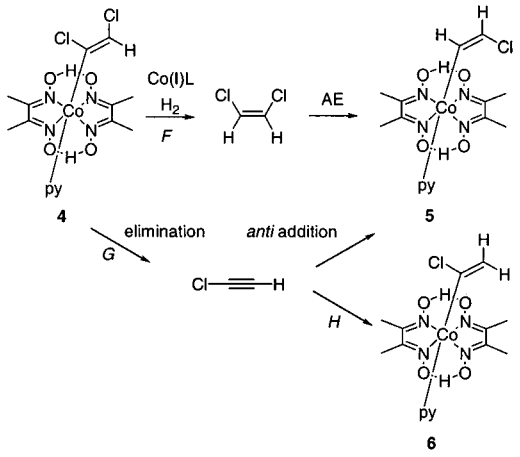
The α-carbon of the axial ligands in complexes **4**−**7** is $sp^2$-hybridized predicting a significantly stronger Co−C bond than in alkyl cobaloximes. Qualitatively all four organocobaloximes indeed proved quite stable at room temperature in air. Furthermore, although all preparations were conducted in the dark, isolated complexes **4**, **6**, and **7** could be handled in visible light without special precautions. These observations suggest that once formed, these complexes are unlikely to reenter a catalytic process by thermal homolytic scission of the Co−C bond to generate vinyl radicals and Co(II). Cobaloxime **5** was more reactive toward photodecomposition and required handling in the dark. This may perhaps be due in part to strain imposed by the large Co−C═C bond angle compared to the considerably smaller angles for the other complexes in Figure 1.

**Reductive Dechlorination of (Chloroethenyl)cobaloximes.** With purified cobaloxime **4** in hand, we tested the possibility of converting dichlorinated into monochlorinated ethenyl complexes as proposed in the literature for vitamin $B_{12}$ derivatives.[12] Complex **4** proved inert when treated with $NaBH_4$ or $H_2$ alone, but addition of catalytic amounts of $[Co^{II}(dmgH)_2py]_2$ (**8**) resulted in the disappearance of **4** and the generation of **5** and **6**. The transformation was considerably accelerated when a stoichiometric amount of **8** was added. With time the only ethenylcobaloxime remaining in the reaction mixture was complex **7**. These conversions were generally low yielding with $NaBH_4$ (5−10%); using $H_2$ as the reductant usually resulted in a slower reaction from which higher yields of dechlorinated cobaloximes (25%) could be recovered. Presumably, these low yields are due to the formation of volatile products derived from the axial alkyl ligand or possibly because of base-catalyzed degradation as has been reported for other cobaloximes.[57−59]

**Conversion of (Dichloroethenyl)cobaloxime 4 to (Monochloroethenyl)cobaloximes 5 and 6 and Vinylcobaloxime 7.** At least three different mechanisms can be proposed for the reductive conversion of **4** to **5**. Homolytic or heterolytic scission of the Co−C bond followed by hydrogen atom or proton transfer, respectively, would produce *cis*-dichloroethylene (pathway F, Scheme 2). Subsequent reaction of *cis*-DCE with cob(I)aloxime via addition−elimination (AE) with retention of configuration would provide complex **5**. The mechanisms of such vinylic nucleophilic substitutions have

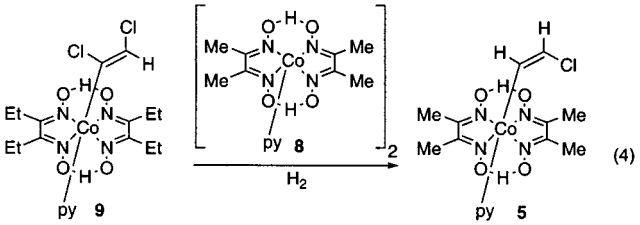
(50) Brueckner, S.; Calligaris, M.; Nardin, G.; Randaccio, L. *Inorg. Chim. Acta* **1968**, *2*, 416−20.
(51) Smalley, T. L., Jr.; Wright, M. W.; Garmon, S. A.; Welker, M. E.; Rheingold, A. L. *Organometallics* **1993**, *12*, 998−1000.
(52) Wright, M. W.; Smalley, T. L., Jr.; Welker, M. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 6777−91.
(53) Adams, T. A.; Welker, M. E.; Liable-Sands, L. M.; Rheingold, A. L. *Organometallics* **1997**, *16*, 1300−1307.
(54) Adams, T. A.; Welker, M. E.; Day, C. S. *J. Org. Chem.* **1998**, *63*, 3683−3686.
(55) Dreos, R.; Geremia, S.; Nardin, G.; Randaccio, L.; Tauzher, G.; Vuano, S. *Inorg. Chim. Acta* **1998**, *272*, 74−79.
(56) In both structures, the vinyl ligand occupies two positions above the dimethylglyoximato ligands. The previous report treated the position of the α-carbon in both vinyl groups as identical during the analysis of the diffraction data, which may have led to the short bond length between the vinyl carbons. On the other hand, current technology allowed the structure reported here to be refined by treating each vinyl ligand as an individual moiety leading to a C−C distance that is more in line with other reported organocobalt compounds containing a vinyl ligand. See refs 50−55.
(57) Brown, K. L. *Inorg. Chim. Acta* **1978**, *31*, L401−L403.
(58) Brown, K. L. *J. Am. Chem. Soc.* **1979**, *101*, 6600−6.
(59) Brown, K. L.; Hessley, R. K. *Inorg. Chem.* **1980**, *19*, 2410−14.

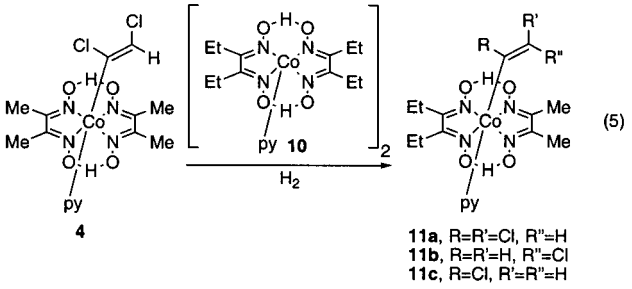
**Scheme 2**




been studied extensively for numerous reactions[60,61] including substitutions involving cob(I)aloximes and halogenated styrenes[62−64] or alkenes.[65] In these investigations, substitution occurred with retention of configuration consistent with pathway F. However, despite the fact that halogenated styrenes as well as vinyl chloride[66] readily react with cob(I)aloximes to give vinylcobaloximes, we did not succeed to produce any detectable monochlorinated ethenylcobaloximes by treating *cis*-1,2-DCE with cob(I)aloxime under a variety of reaction conditions. Thus, pathway F is not feasible for the observed production of **5** from **4**.

The inability to provide support for pathway F led us to explore whether the dechlorination might occur without breaking the cobalt−carbon bond. Such a pathway has been proposed for the $B_{12}$-catalyzed dechlorination with Ti(III) citrate as the reductant,[12] although no details regarding the possible mechanisms of the transformation were suggested. We employed a crossover strategy using the (1,2-dichloroethenyl)bis(diethylglyoximato)(pyridine)cobalt(III) complex **9** (eq 4). Reaction of **9** with 1 equiv of the bis(dimethylglyoximato) dimer **8** under an atmosphere of hydrogen produced (*cis*-chloroethenyl)dimethylcobaloxime **5**.[67] No corresponding monochlorinated diethylcobaloximes were detected, and no ligand exchange was detected in recovered complex **9**. The observed complete crossover is consistent with cleavage of the Co−C bond during the transformation. We also attempted the reverse experiment starting with **4** and the bis(diethylglyoximato)(pyridine)cobalt(II) dimer **10** (eq 5). Unfortunately, the Co(I) form of **10** is much less reactive than the analogous methyl-substituted cob(I)aloxime, and in the time frame of the reaction of **10** with complex **4**, ligand exchange was observed leading to an uninformative mixture of complexes containing a mixed ethyl/methylglyoximato equatorial ligand set (e.g. **11a**−**c**, eq 5). Regardless, the results in eq 4 strongly suggest that the axial vinyl ligand is removed from the cobalt during its dechlorination.

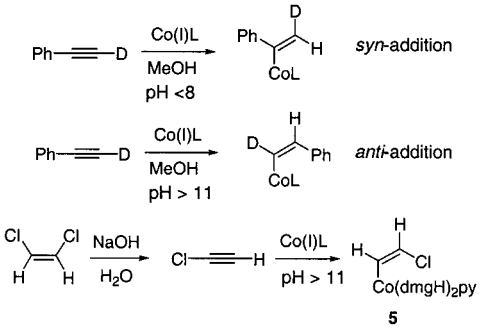


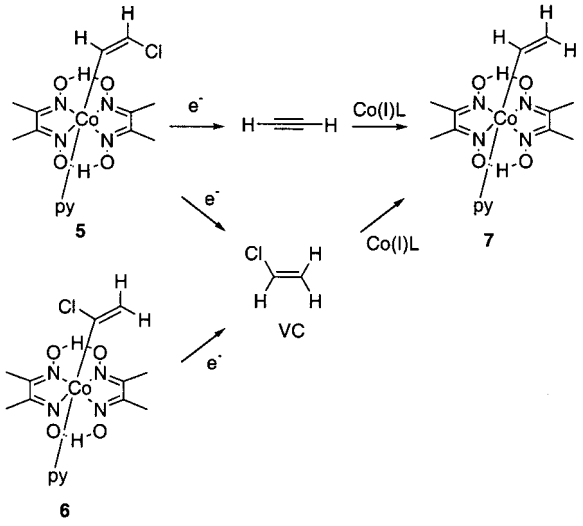

A third mechanism for the conversion of **4** to **5** involves an elimination−addition with chloroacetylene as an intermediate (pathway G, Scheme 2). For this pathway to be viable for generation of the cis-complex **5**, the addition must occur with regio- and antistereoselectivity. Gaudemer and Johnson have shown in an elegant set of studies that cob(I)aloximes can add either stereospecifically syn or anti to alkynes, depending on the reaction conditions.[63,72] Below the p$K_a$ of the protonated form of cob(I)aloxime (i.e. the p$K_a$ of the cobalt-bound proton in "hydridocobaloxime" estimated to be ∼10.5),[68] the metal hydride adds selectively syn to phenylacetylene, probably via a stepwise process of hydrogen atom addition followed by trapping of the resulting vinyl radical with cob(II)aloxime.[69−71] Above the p$K_a$, addition of "free" cob(I)aloxime followed by protonation by solvent occurs in anti fashion (Scheme 3).[72] Furthermore, the regioselectivity was reversed giving (α-phenylethenyl)cobaloxime below pH ∼ 8 and (*cis*-*β*-phenylethenyl)cobaloxime at alkaline pH. We evaluated the feasibility of pathway G by reaction of cob(I)aloxime with chloroacetylene, generated in small scale by gently heating a biphasic mixture of 1,2-dichloroethylene in diethyl ether and aqueous sodium hydroxide in the presence of a phase transfer catalyst.[40] The gaseous chloroacetylene produced was led directly into a reaction vessel containing cob(I)aloxime, which rapidly changed color from the characteristic purple

(60) Modena, G. *Acc. Chem. Res.* **1971**, *4*, 73−80.
(61) Rappoport, Z. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 309−349.
(62) Duong, K. N. V.; Gaudemer, A. *J. Organomet. Chem.* **1970**, *22*, 473−478.
(63) Johnson, M. D.; Meeks, B. S. *J. Chem. Soc. B* **1971**, 185−189.
(64) Dodd, D.; Johnson, M. D.; Meeks, B. S.; Titchmarsh, D. M.; Duong, K. N. V.; Gaudemer, A. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1261−1267.
(65) Tada, M.; Kubota, M.; Shinozaki, H. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1097−1100.
(66) Schrauzer, G. N.; Windgassen, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 1999−2007.
(67) Control experiments showed that chlorinated ethenylcob(III)aloximes do not exchange the equatorial ligands under these conditions.
(68) Schrauzer, G. N.; Holland, R. J. *J. Am. Chem. Soc.* **1971**, *93*, 1505−1506.
(69) Baldwin, D. A.; Betterton, E. A.; Chemaly, S. M.; Pratt, J. M. *J. Chem. Soc., Dalton Trans.* **1985**, 1613−1618.
(70) Garr, C. D.; Finke, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 10440−10445.
(71) Ng, F. T. T.; Rempel, G. L.; Mancuso, C.; Halpern, J. *Organometallics* **1990**, *9*, 2762−2772.
(72) Naumberg, M.; Duong, K. N. V.; Gaudemer, A. *J. Organomet. Chem.* **1970**, *25*, 231−242.

**Scheme 3**




**Scheme 4**




of Co(I) to the yellow-orange of organocobaloximes. The *cis*-chloroethenyl complex **5** was the major product formed at pH 11 (**5**:**6** = ∼95:5). The α-chlorinated ethenylcobaloxime **6** was formed along with **5** when the reaction was performed at pH 10 (**5**:**6** = 7:3), and **6** was formed as the major product at pH 9 (**5**:**6** = 1:3), although the reaction was less clean under these latter conditions. The formation of ethynylcobaloxime was not observed in these experiments, similarly to the absence of ethynylcobalamin formation in $B_{12}$-catalyzed dechlorinations of PCE and TCE.[12] This contrasts with a previous study that reported the formation of ethynylcobalamin as the major product and bromoethenylcobalamin as a minor product in the reaction between cob(I)alamin and bromoacetylene.[73] This difference may be attributed to the better leaving group ability of bromide compared with chloride, resulting in products that are presumably formed by addition−elimination for the former and via addition and protonation for the latter. In summary, pathway G, Scheme 2, is the most likely route to convert **4** to **5**, and chloroacetylene can also account for the formation of **6** (pathway H, Scheme 2).

With regards to the formation of **7**, submitting either **5** or **6** to the reductive conditions induced slow consumption of the starting complexes and formation of a substoichiometric quantity (10−20%) of vinylcobaloxime **7**. These findings can be accounted for by the formation of volatile products in the reductive dechlorination of **5** and **6** that are trapped to some extent to provide **7**. These volatile products could be acetylene (sublimation point −81 °C) or vinyl chloride (VC, bp −13 °C). Both compounds are known to form vinylcobaloxime when reacted with cob(I)aloxime (Scheme 4).[66,74]

**Electrochemical Properties of (Chloroethenyl)cobaloximes**. An important unanswered question that arises from the studies presented above is how the Co−C bonds are cleaved in the chlorinated vinylcobaloximes. As mentioned, these complexes appear to be thermally quite stable and do not appreciably eliminate chloride on the time scale of the dechlorination process when cob(I)aloxime is not present. The conversion of **4** into **5**−**7** only after addition of cob(I)aloxime suggests that the latter is responsible for promoting these transformations. One conceivable mechanism involves one-electron transfer followed by cleavage of the Co−C bond. Alkylcobaloximes with a pyridine axial base generally exhibit one electron redox potentials that are significantly more negative than the Co(I)/Co(II) redox potential of cob(I)aloxime, questioning whether the latter is a sufficiently strong reductant to transfer an electron to complexes such as **4**−**7**. Several studies have shown, however, that the one-electron reduction potentials for alkylcobaloximes show a trend to less negative values when more electron withdrawing axial alkyl ligands are present.[75−79] Scheffold and co-workers reported that alkylcobalamins (RCbl) containing alkyl ligands with a p$K_a$ less than ∼30 for R−H have reduction potentials less negative than that of the Co(I)/Co(II) couple of $B_{12}$.[79] For instance, in protic solvents, cob(I)alamin was found to be a sufficiently strong electron donor to reduce (methoxycarbonyl)methylcobalamin ($MeO_2CCH_2Cbl$).[78] The p$K_a$ of vinyl chloride has been reported as 31,[80] and that of *cis*-DCE has been estimated to be ∼34 (in MeOH),[81] whereas a value of 30−31 has been determined for methyl acetate (in DMSO).[82] These p$K_a$'s suggest reductive cleavage of the Co−C bond in the cobalamin analogues of **4**−**6** may in fact be feasible. To gain insights into the redox properties of this type of complexes cyclic voltammetry was applied to **4**−**7**.

The cyclic voltammogram of purified (*cis*-chloroethenyl)cobaloxime **5** is shown in Figure 2 along with the voltammogram of dimer **8**. Whereas the latter displayed an electrochemically reversible wave with a cathodic peak potential of −1.02 V vs $Ag^+$/AgCl ($i_{pc} = i_{pa}$, $\Delta E_p$ = 75 mV),[83] the wave for **5** was completely irreversible at scan

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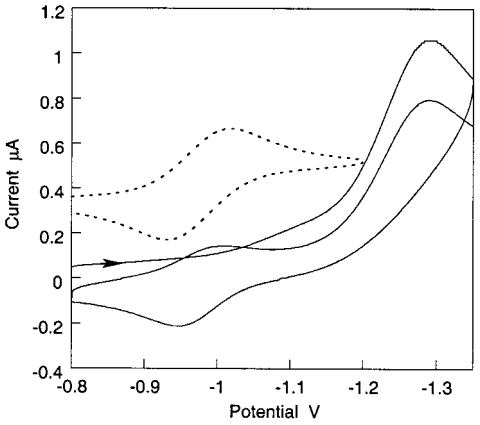


**Figure 2.** Cyclic voltammogram of complex **5** (1 mM) in DMF/*tert*-butyl alcohol (1:1). Dashed line: CV of dimer **8**. Potentials are vs $Ag^+/AgCl$,[83] with sweep rate 100 mV $s^{-1}$, glassy carbon working electrode, and 0.1 M $Bu_4NClO_4$.

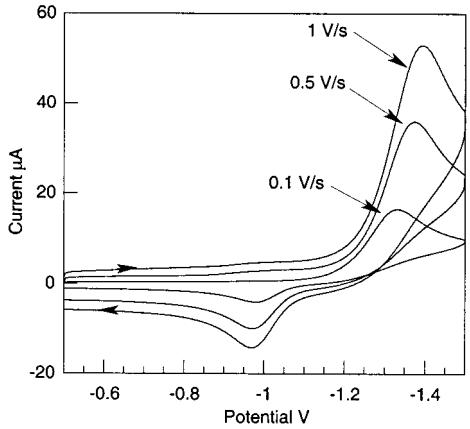


**Figure 3.** Dependence of the peak positions in the cyclic voltammogram of complex **5** on the scan rate. Potentials are vs $Ag^+/AgCl$,[83] with sweep rate 100 mV $s^{-1}$, glassy carbon working electrode, 0.1 M $Bu_4NClO_4$, and solvent DMF.

rates up to 1 V/s with a peak potential of −1.30 V at 100 mV/s. An anodic return wave was observed at −0.96 V, suggestive of the oxidation of cob(I)aloxime to cob(II)aloxime. Indeed when multiple scans were performed, a cathodic peak corresponding to the reduction of cob(II)aloxime to cob(I)-aloxime was visible in the second scan (Figure 2). Thus, during the reduction of complex **5**, cob(I)aloxime is formed, although not in stoichiometric quantitities as the anodic peak current ($i_{pa}$) for the Co(I) → Co(II) conversion is only about one-third that of the cathodic peak current ($i_{pc}$) for the reduction of **5**. On the basis of these observations, it is likely that the initial reversible electrochemical reduction is followed by one or more fast irreversible chemical step(s) as has been observed previously for other alkylcobaloximes.[84,85] In the initial chemical step, the Co−C bond is cleaved and either Co(I) and an alkyl radical or Co(II) and an alkyl anion are formed. These species can undergo various follow-up reactions including migration of the alkyl radical to the ligand[86] and/or formation of bisalkylated cobaloximes.[85,87−91] As expected for such EC type mechanisms,[92] the peak potential shifted to more negative potentials with faster scan rates (Figure 3). Since reversibility was never observed,[93] the peak potential for **5** in Figure 2 is probably less negative than the true reduction potential.

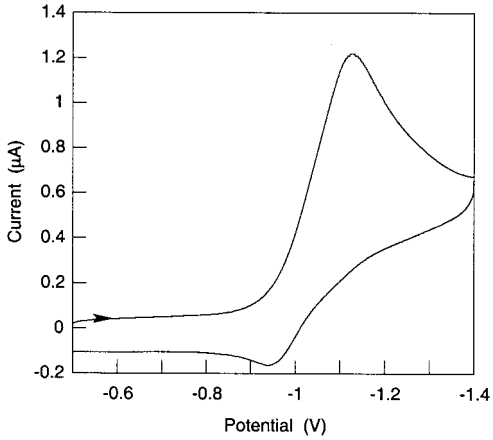


**Figure 4.** Cyclic voltammogram of complex **4** (1 mM). Experimental conditions as in Figure 2.

The cathodic scan of dichlorinated complex **4** produced a broad wave with a peak potential of −1.13 ± 0.03 V vs $Ag^+/AgCl$ (Figure 4). As observed for complex **5**, the cathodic peak potential shifted to more negative values upon increasing the scan rate (data not shown). The 1,1-disubstituted complex **6** gave a voltammetric profile exhibiting two cathodic peaks (Figure 5). The anodic return scan also exhibits two anodic waves, suggesting at first glance that the two redox processes may be partially reversible. The anodic peak at −1.18 V, however, is not due to the reoxidation of a species formed in the first reduction wave (at −1.23 V), because when the switching potential was set at −1.35 V, no anodic peak was observed at −1.18 V (see Figure S1 in the Supporting Information). Interestingly, the second cathodic peak as well as both anodic peaks are also present in the CV of vinylcobaloxime **7** (dashed line). This observation suggests that in the electrochemical reduction of **6** dechlorination occurs to give **7**, followed by reduction of **7** itself. From the voltammogram of the latter species (dashed line, Figure 5), it appears that its reduction is partially reversible. Indeed at higher scan rates (>1 V/s), the reduction of **7** appears chemically reversible ($\Delta E_p$ = 72 mV, $i_{pc} = i_{pa}$).[95]

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(92) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706−23.
(93) In contrast to Costa-type complexes,[85] addition of excess axial ligands such as *N*-methylimidazole or pyridine did not lead to reversible electrochemical behavior.

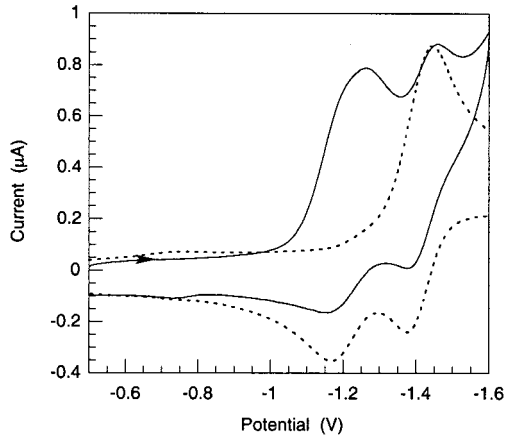


**Figure 5.** Cyclic voltammogram of a 1 mM solution of complex **6** (solid line). Dashed line: cyclic voltammogram of vinylcobaloxime **7**. Instrument settings and experimental conditions as in Figure 2.

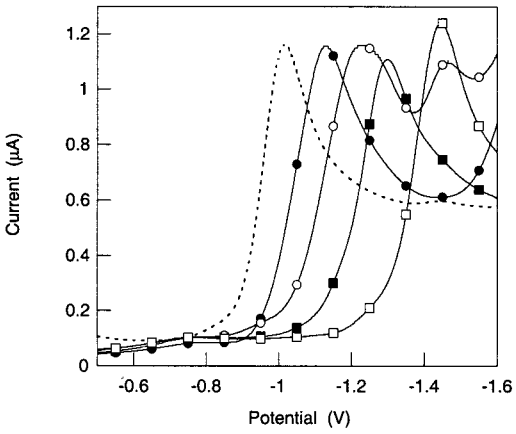


**Figure 6.** Comparison of the cathodic peaks of dimer **8** (- − -) and complexes **4** (closed circles), **5** (closed squares), **6** (open circles), and **7** (open squares). Potentials are vs $Ag^+/AgCl$,[83] with sweep rate 100 mV $s^{-1}$ and glassy carbon working electrode.

Comparison of the voltammograms of all species shows that complex **4** containing two chlorides displays a less negative peak potential ($-1.13 \pm 0.03$ V) than the monochlorinated complexes **5** ($-1.30 \pm 0.01$ V) and **6** ($-1.23 \pm 0.01$ V), whereas vinylcobaloxime **7** has the most negative peak potential ($-1.45 \pm 0.01$ V) in this series (Figure 6).[96] This trend is consistent with the expected acidity of the vinyl ligands in these complexes and parallels the trends in Co−$N_{pyr}$ and Co−C bond lengths. Although reductive cleavage of the Co−C bond in **4**−**6** accounts qualitatively for the observed dechlorination in eq 2, the peak potentials of dimer **8** and the chlorinated complexes are still at least ∼130 mV apart. Assuming that the difference in peak potentials provides a rough estimate of driving force, the equilibrium constant for electron transfer from cob(I)aloxime to **4** would be $\sim 1.4 \times 10^{-2}$ or smaller.[97] This unfavorable equilibrium for an outer sphere electron-transfer process may be driven toward the reduced vinylcobaloximes by coupling the electron-transfer event to a fast, irreversible chemical follow-up reaction. Martin and Finke have shown that one electron reduction of methylcobalamin reduces the Co−C bond strength by 21 ± 4 kcal/mol resulting in a $\geq 10^{15}$ enhancement of the rate of bond breakage.[98,99] A similar large rate acceleration induced by electron transfer to the complexes discussed herein may compensate to some extent for the unfavorable preequilibrium. An alternative or additional increase in the rate of reductive Co−C bond cleavage could potentially be achieved if the reduction took place via an inner-sphere electron-transfer process. Further experiments that are beyond the scope of the current investigation are in progress to address these issues for the complexes reported here.

**The Elusive (Trichloroethenyl)cobaloxime and −cobalamin**. It is noteworthy that (trichloroethenyl)cobaloximes were never detected in the studies described above, similar to the absence of (trichloroethenyl)cobalamins in mass spectrometric analysis of reaction mixtures containing $B_{12}$, Ti(III) citrate, and PCE.[12] In previous work, we[31] and others[7] have provided support for the first dechlorination (PCE to TCE) to take place via an electron-transfer mechanism producing Co(II) and, presumably, a trichlorovinyl radical. This is consistent with the lack of detectable (trichloroethenyl)cobalt(III) complexes. However, it is not clear why cob(II)alamin, observed during stopped-flow analysis of the dechlorination of PCE,[31] would not rapidly combine with the trichlorovinyl radical to form (trichloroethenyl)cobalamin. The rates of combination of alkyl radicals and cob(II)alamin is at the diffusion controlled limit,[100−103] and combination of Co(II) with the trichlorovinyl radical could be even more favorable if electron transfer were to take place in a solvent

(94) This transformation occurred in low yield (∼1−2%), but sufficient quantities could be obtained for full characterization by $^1$H and $^{13}$C NMR spectroscopy as well as high-resolution mass spectrometry. The $^1$H NMR spectrum of **13** displayed doublets at 6.22 and 5.29 ppm with a coupling constant of 12.6 Hz, which forms the basis for the assignment of trans-geometry of the metal and chlorine substituents. Thus, as reported for halogenated styrenes,[62−64] cob(I)aloxime reacts with *trans*-DCE with retention of configuration.

(95) At high scan rates, when the reduction of **7** appears reversible, the anodic peak at −1.18 V is still present. Furthermore, this peak is quasi-reversible as an associated cathodic peak appears in multiple scan experiments (see Figure S2 in the Supporting Information). Two possible explanations can been envisioned. One mechanism involves the formation of a new species upon reduction of **7**: $\mathbf{7} + e^- \rightarrow \mathbf{X}$. This new species is then oxidized on the return wave at −1.37 V to give compound **Y**, which is further oxidized at −1.18 V. A different mechanism produces two species upon reduction of **7**: $\mathbf{7} + e^- \rightarrow \mathbf{X} + \mathbf{Y}$, which are oxidized in the return wave giving rise to the two observed anodic peaks. To differentiate between these possibilities and to determine the identity of the reduction products of **7**, controlled-potential bulk electrolysis and OTTLE experiments are ongoing.

(96) Because the peak potentials in Figure 6 are associated with irreversible processes, the rate constants for the follow-up reactions affect the observed position of the peak. Thus, the order of the true one-electron reduction potentials could change if these rate constants are widely different for the individual complexes.

(97) Using the same assumptions, the equilibrium constants for electron transfer to the other complexes can be estimated as $\sim 2 \times 10^{-5}$ for **5** and $\sim 3 \times 10^{-4}$ for **6**.

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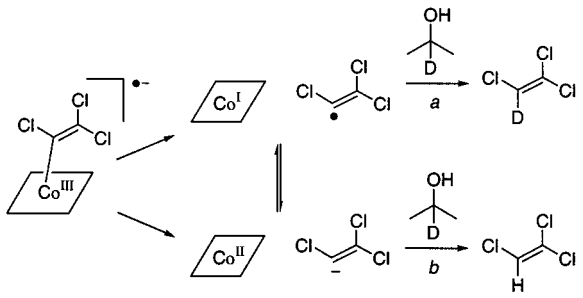
**Scheme 5**



cage.[103−105] Rapid reduction of (trichloroethenyl)cobalt complexes under the reaction conditions might present a possible explanation for their absence. As discussed in the previous section, the reduction potentials of alkylcobalamins are shifted to less negative values for axial alkyl ligands (−R) that have a low p$K_a$ (R−H). A value of 18 has been reported for the p$K_a$ of TCE from polarographic measurements.[80] Based on this value, reductive Co−C bond cleavage of a putative (trichlorovinyl)cobalt complexes could be quite facile. Such reduction could lead to a partitioning resulting in formation of trichlorovinyl radical as well as the corresponding anion that is subsequently protonated (Scheme 5). This scenario is consistent with the results of a labeling study in which $B_{12}$-catalyzed dechlorination of PCE was carried out in a $H_2O$/2-$d_1$-$^i$PrOH solvent mixture. The observed distribution of deuterium in the TCE product suggested the simultaneous involvement of both homolytic and heterolytic mechanisms of product formation (Scheme 5).[7]

The reduction potentials of (trichloroethenyl)cobaloxime and -cobalamin are not available, but the data in Figure 2 can be used to estimate the former. Comparing vinylcobaloxime to the *cis*-chlorovinyl complex **5**, the peak potential is shifted by approximately 150 mV to less negative potentials for the latter. Substituting the other two hydrogens with chlorines resulted in a shift of 320 mV in going from **7** to **4**. If the changes in peak potential induced by these substitutions are additive, then a tentative shift in peak potential of 470 ± 40 mV (320 + 150) might be expected when replacing all three hydrogens of **7** with chlorines, predicting a peak potential of ∼ −1.0 V for a putative (trichloroethenyl)cobaloxime. This value is in fact close to that for the Co(I)/Co(II) couple of dimer **8** ($E_{pc}$ = −1.02 V) and suggests that reduction of such a species by cob(I)aloxime could indeed be thermodynamically favorable. To evaluate the additivity hypothesis, (*trans*-chloroethenyl)cobaloxime **13** was prepared by reaction of *trans*-DCE with cob(I)aloxime.[94] With compound **13** in hand, additivity of peak potential shifts upon replacement of hydrogens in **7** with chlorines was experimentally tested. The $E_p$ of **13** was determined to be −1.26 V vs $Ag^+$/AgCl, 190 mV less negative than **7**. Therefore, using the potentials for **6**, **7**, and **13**, one arrives at a cumulative shift of 410 mV for substituting two protons for chlorines and a predicted peak potential of −1.04 V for **4**, somewhat less negative than the experimentally observed value of −1.13 V. Thus, the change in redox potential upon replacement of a hydrogen with a chlorine is not strictly additive in a quantitative sense, and the putative (trichloroethenyl)cobaloxime would likely have a peak potential between that of (dichloroethenyl)cobaloxime **4** (−1.13 V) and that calculated for a purely additive process (−1.0 V). Therefore, although we cannot accurately predict its reduction potential, the reduction potential of a putative trichlorinated vinylcobaloxime is likely to be in the vicinity of the cob(I)/(II)aloxime potential supporting its rapid reduction under the conditions of eq 2.

**Table 3.** Calculated LUMO Energies and Vertical Attachment Energies (VAE) for Various Chlorinated Alkenes

| alkene | VAE (eV)[24] | LUMO (eV)[106] | $E_m$[a] (V)[107] |
|---|---|---|---|
| PCE | 0.3 | −1.689 | −0.60[b] |
| TCE | 0.59 | −1.435 | −0.67[c] |
| 1,1-DCE | 0.76 | −1.140 | −0.80[d] |
| *trans*-1,2-DCE | 0.80 | −1.200 | −0.96[e] |
| *cis*-1,2-DCE | 1.11 | −1.200 | −1.01[f] |
| VC | 1.28 | −0.761 | −1.14[g] |

[a] Estimated one electron redox potentials vs NHE from thermodynamic data.[107] [b] For the reaction PCE + $e^-$ ⇄ TCE$^\bullet$ + $Cl^-$. [c] For TCE + $e^-$ ⇄ 1,2-*trans*-DCE$^\bullet$ + $Cl^-$. For going from TCE to $Cl_2C{=}CH^\bullet$, a value of −1.0 V was estimated. [d] For 1,1-DCE + $e^-$ ⇄ $\bullet CCl{=}CH_2$ + $Cl^-$. [e] For *trans*-1,2-DCE + $e^-$ ⇄ $ClHC{=}CH^\bullet$ + $Cl^-$. [f] For *cis*-1,2-DCE + $e^-$ ⇄ $ClHC{=}CH^\bullet$ + $Cl^-$. [g] For VC + $e^-$ ⇄ $CH_2{=}CH^\bullet$ + $Cl^-$.

**Implications for $B_{12}$-Catalyzed Reductive Dechlorinations**. It is worthwhile to compare the findings in this work on cobaloxime models with the vitamin $B_{12}$-catalyzed dechlorination of PCE. In both processes the first step does not lead to detectable trichloroethenyl complexes, but vinylcobalt complexes containing one or two chlorines are detected along with the parent vinyl compounds. Available thermodynamic data may explain the change from a one-electron reductive process to the formation of these vinylcobalamins. The substrate for each subsequent dechlorination is less electron deficient, and thus electron-transfer pathways become less favorable in the series PCE, TCE, DCE, and vinyl chloride (VC). Although experimentally determined one electron reduction potentials are not available in solution, the reduced electron affinity is supported by gas-phase vertical attachment energies determined by low-energy electron scattering measurements,[106] as well as by computed energies of the LUMO's of these compounds (Table 3).[106] Also listed in Table 3 are the estimated reduction potentials for dissociative electron transfer calculated from thermodynamic data.[107] As a result of the progressively less favorable energetics for electron transfer, chlorinated ethenylcobalamins are formed via either vinylic nucleophilic substitution by cob(I)alamin or by addition to chloroacetylene. Our results with cobaloximes suggest that the observed monochlorinated vinylcobalamins in $B_{12}$-catalyzed dechlorinations are produced by the reaction of cob(I)alamin with chloroacetylene rather than DCE. Chloroacetylene formation as an intermediate during TCE dechlorination is supported by its direct

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detection by GC-MS,[8,11] and we have recently verified that cob(I)alamin reacts readily with chloroacetylene to provide (*cis*-chloroethenyl)cobalamin.[108]

## Summary

The results detailed in this work support the following conclusions. Chlorinated ethenylcobaloximes are stable compounds that are unlikely to undergo homolytic Co−C bond cleavage at a sufficient rate to support dechlorination of chlorinated alkenes. These compounds can, however, be dechlorinated via a reductive process that is promoted by cob(I)aloxime. (Trichloroethenyl)cobaloxime has not been detected, possibly because its reduction may occur under the conditions used. Direct support for such a process, however, is still lacking. The monochlorinated cobaloximes **5** and **6** are formed by reaction of cob(I)aloxime with chloroacetylene rather than with *cis*- or *trans*-DCE, and no ethynylcobaloxime was formed under the experimental conditions used. Compounds **4**−**6** all display irreversible electrochemistry with the observed peak potentials reflecting the relative electron-withdrawing nature of the vinyl ligand. This trend is also reflected in the Co−$N_{py}$ bond distances in the X-ray structures. Vinylcobaloxime **7** appears to display a reversible wave at scan rates > 1 V/s. Investigations with vitamin $B_{12}$ along the same lines as reported here for cobaloximes are in progress to probe if the conclusions reached in this work also hold for $B_{12}$ derivatives.

**Acknowledgment.** This work was supported in part by the Camille and Henry Dreyfus Foundation (Grant NF-97-078), the Petroleum Research Fund administered by the American Chemical Society (Grant 33490-G), and the Beckman Foundation (BYI award to W.A.v.d.D.). We also acknowledge funds from the Roy J. Carver Charitable Trust for part of the work reported here. The Materials Chemistry Laboratory at the University of Illinois in which the X-ray structures were determined was supported in part by the NSF (Grant CHE 95-03145). NMR data were obtained in the Varian Oxford Instrument Center for Excellence, funded in part by the W.M. Keck Foundation, NIH (Grant PHS 1 S10 RR10444), and NSF (Grant CHE 96-10502). Mass spectra were recorded on a ZAB-SE mass spectrometer funded in part by the Division of Research Resources, National Institutes of Health (Grant RR 01575), the National Science Foundation (Grant PCM 8121494), and the National Institute of General Medical Sciences (Grant GM 27029).

**Supporting Information Available:** Listings of crystallographic data as well as bond lengths and angles for complexes **4**−**7** in CIF format and tables and figures for the X-ray structures. This material is available free of charge via the Internet at http://pubs.acs.org.

IC011023X

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