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# Synthesis of (chlorovinyl)cobaloxime complexes, model complexes of proposed intermediates in the $B_{12}$-catalyzed dehalogenation of chlorinated ethylenes†

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**(Chlorovinyl)cobaloxime complexes, $(dmgH)_2(py)CoR$ (R = *cis*-dichlorovinyl, *trans*-2-chlorovinyl or 1-chlorovinyl, dmgH = dimethylglyoximate) were synthesized from the reaction of chlorinated ethylenes with *in situ* generated $(dmgH)_2Co(I)$ in the presence of pyridine.**

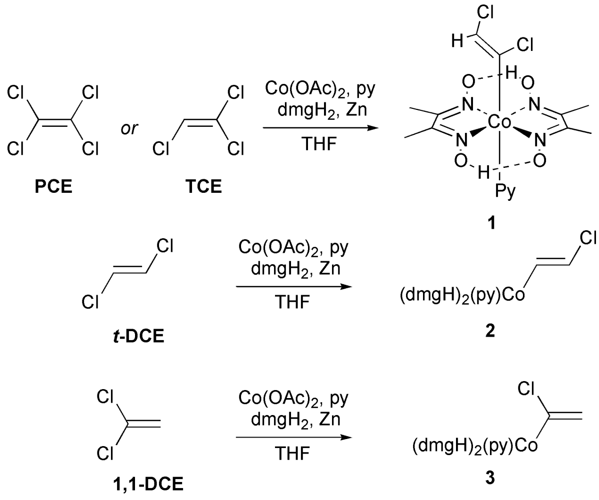
Tetrachloroethylene (PCE) and trichloroethylene (TCE) are widely used industrial solvents that have received a great deal of attention because they are commonly found drinking water contaminants.[1,2] One of the most exciting recent discoveries in the area of remediation was the observation that cobalamins (*e.g.*, vitamin $B_{12}$) and similarly structured metal cofactors such as heme and $F_{430}$ catalyze the dehalogenation of these species.[3–6]

Organometallic intermediates have been proposed in the dechlorination sequence based on UV–visible absorbance data,[5,7,8] mass spectrometry data,[9] mass balance considerations,[10] and kinetic evidence.[11] This hypothesis is bolstered by studies that report the reaction of low-valent metal complexes with halogenated ethylenes, in which chlorovinyl complexes are formed.[12–22] The importance of the putative organometallic intermediates is not known. Indeed, there is some evidence that the reduction of PCE occurs without organometallic intermediates.[7,23] Good models are needed to test their potential modes of involvement. Herein we report the synthesis of cobaloxime model complexes for the proposed chlorovinyl intermediates.

The procedure described by Pickin and Welker[24] to synthesize cobalt-sp$^2$ carbon bonds was modified in an effort to produce the chlorovinyl cobalt complexes. Each chloroethylene (PCE, TCE, *trans*- or 1,1-dichloroethylene) was added to a solution of Co(II)acetate, dimethylglyoxime, pyridine, and zinc in THF and heated to reflux under nitrogen atmosphere. After the reaction was complete, the products were purified by column chromatography (silica gel, EtOAc) and stored in air.

An interesting aspect of this preparative route is that while four chlorinated ethylenes were found to separately participate in this reaction, only three unique products were formed (Scheme 1). Both PCE and TCE reacted under these conditions to give $(dmgH)_2(py)Co(\textit{cis}\text{-}CCl{=}CHCl)$ (**1**). The isolated yield for the preparation of **1** from TCE was 45%. One possibility to explain the result that both PCE and TCE produce **1** is that PCE is reduced to TCE under the reaction conditions. Analysis of the reaction mixture by GC-MS for the PCE reduction confirmed that TCE was formed during the course of the reaction. Other workers have demonstrated that zero valent Zn can reduce PCE to TCE under certain conditions.[25,26] In the present case, however, it was found that the reduction of PCE to TCE is cobalt-mediated. When PCE was reacted with dimethylglyoxime, pyridine, and zinc under the same conditions, no conversion to TCE was observed.

The $^1$H NMR spectrum of **1** contains a prominent singlet ($\delta$ 6.46, $C_6D_6$) corresponding to the vinyl proton. The *cis* stereochemistry of the vinyl group was confirmed by comparison of the X-ray powder diffraction pattern of a sample of **1** grown from $CHCl_3$–hexanes to the pattern calculated from the unit cell parameters for the previously solved crystal structure by Jones *et al.* for the $CHCl_3$ solvate of **1**.[13] Comparison of the patterns confirms that the same material was prepared.



**Scheme 1**

*trans*-Dichloroethylene (DCE) reacts under the same conditions to give $(dmgH)_2(py)Co(\textit{trans}\text{-}2\text{-}CH{=}CHCl)$ (**2**). The isolated yield from *trans*-DCE is 21%. The $^1$H NMR spectrum of **2** contains two prominent doublets ($C_6D_6$, $\delta$ 6.08, 6.99, $J$ = 12.6 Hz), which are assigned to the *trans*-vinylic protons. The solid-state structure of **2** determined by single crystal X-ray diffraction confirms the *trans* stereochemistry assignment and is shown in Fig. 1.‡

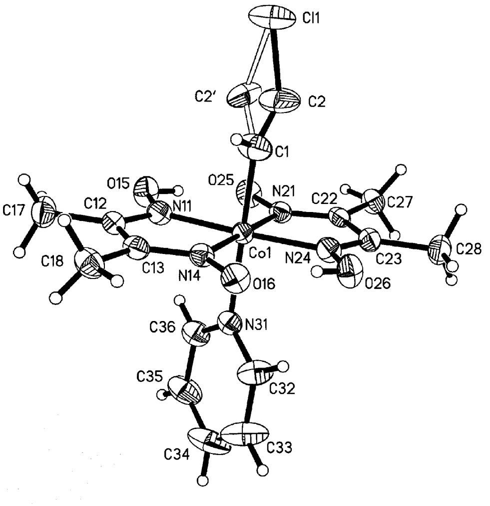


**Fig. 1** X-Ray structure of *trans*-$(dmgH)_2(py)Co(CH{=}CHCl)$ (**2**). One carbon atom (C2) of the vinyl group was found to be disordered and was modelled as occupying the two sites shown.

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† Electronic supplementary information (ESI) available: full experimental details and characterization of complexes **1**–**3**, and X-ray diffraction data. See http://www.rsc.org/suppdata/cc/b1/b109001a/

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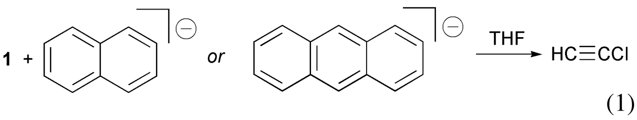
Reaction with 1,1-DCE also produced a clean, crystalline, yellow product, $(dmgH)_2(py)Co(CCl{=}CH_2)$ (**3**) in 48% yield. The $^1H$ NMR spectrum contains vinyl resonances with a small geminal coupling constant ($C_6D_6$, $\delta$ 5.61, 5.95, $J$ = 2.1 Hz).

The synthetic strategy for preparation of complexes **1–3** follows previous work in which nucleophilic Co(I) was used to prepare vinylcobalt complexes.[24,27–30] In the present case, substitution of cobalt for chlorine was accomplished. It is notable that the stereochemical fidelity that has generally been observed[28–30] was also maintained in the preparation of **2** from *trans*-DCE, and that *cis*-DCE did not react to give a chlorovinyl complex under the same conditions.

Complexes **1–3** were subjected to acidic conditions to assess whether protonolysis is a favorable pathway for the cleavage of the Co–C bond. In separate protonolysis experiments the chlorovinyl complexes were dissolved in $C_6D_6$ with benzoic acid, HCl and $H_2SO_4$. These solutions were placed into sealed NMR tubes and heated incrementally to 135 °C. The reaction progress was monitored by NMR spectroscopy. None of the acids were observed to react with complexes **1–3** to produce a free chlorinated ethylene or any other identifiable product.

Hydrogenolysis experiments were performed by exposing solutions of **1–3** dissolved in $C_6D_6$ to relatively low $H_2$ pressures ($\sim$200 mbar) in sealed NMR tubes and heating incrementally to 135 °C. NMR spectroscopy was used to monitor the reaction progress and identify the products. Only the *cis*-dichlorovinyl complex, **1**, reacted with $H_2$ after prolonged heating at 135 °C to produce a small amount of free *cis*-DCE (2% conversion after 2 d).

The reactivity of **1** toward reducing agents was also examined. Treatment of THF solutions of **1** with sodium naphthalenide or sodium anthracenide at rt resulted in immediate reaction. The volatile materials were transferred from the reaction mixtures under vacuum and were analyzed by GC-MS. It was found that chloroacetylene was the major volatile product in both cases [eqn. (1)].



(1)

Treatment of a THF solution of **1** with $NaBH_4$ also resulted in reduction of the complex and the formation of volatile products. After transferring the volatile materials from the reaction mixture under vacuum, GC-MS analysis showed that both chloroacetylene and vinyl chloride were recovered in a 1 : 1 ratio. Relevant to the wide use of Ti(III)citrate as a bulk electron donor in the study of $B_{12}$-catalyzed dechlorination reactions,[4,6–10] the reaction of **1** with Ti(III)citrate was also investigated. The reduction performed in MeOH gave *cis*-DCE as the major volatile product, while no chloroacetylene or vinyl chloride was observed.

If (chlorovinyl)cobalt complexes are indeed intermediates in the dechlorination of chlorinated ethylenes by $B_{12}$, the reactivity studies with models **1–3** indicate that protonolysis and hydrogenolysis mechanisms are not likely candidates for their decomposition. Instead, reduction appears to be a much more favorable pathway for the cleavage of the Co–C bond to yield dechlorinated products. Reduction of **1** by the radical anions of naphthalene and anthracene (2.26 and 1.76 V *vs.* NHE, respectively)[31] in THF yields chloroacetylene as the major volatile product. This is a potentially important result in light of the results of Burris *et al.*[32] and Semadeni *et al.*[10] that indicate that the acetylene produced in the dechlorination of trichloroethylene is derived from chloroacetylene. The results of this study suggest that a (*cis*-dichlorovinyl)cobalamin complex may be the direct precursor to chloroacetylene. The different product distributions obtained from $NaBH_4$ and Ti(III)citrate indicate that the products generated are likely sensitive to the nature of the reducing agent and possibly the solvent. A systematic investigation of these effects is underway.

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## Notes and references

‡ *Crystal data*: $C_{15}H_{21}ClCoN_5O_4$, $M$ = 429.75, orthorhombic, $a$ = 9.630(2), $b$ = 12.377(2), $c$ = 15.402(3) Å, $U$ = 1835.8(6) Å$^3$, $T$ = 173(2) K, space group $P2_12_12_1$ (no. 19), $Z$ = 4, $\mu$(Mo-K$_\alpha$) = 1.112 mm$^{-1}$, 9319 reflections measured, 3259 unique ($R_{int}$ = 0.037) which were used in all calculations. The final $wR(F^2)$ was 0.0935. C2 of the vinyl ligand was disordered over 2 sites, which were refined with 55:45 occupancy.CCDC 172183. See http://www.rsc.org/suppdata/cc/b1/b109001a/ for crystallographic files in .cif or other electronic format.

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