Inorg. Chem. **2006**, *45*, 2288–2295

Inorganic Chemistry
Article

Synthesis, Structure, and Unusual Reactivity of *β*-Halovinyl Cobalt Porphyrin Complexes

Joseph M. Fritsch, Noah D. Retka, and Kristopher McNeill*

Department of Chemistry, University of Minnesota, 225 Pleasant Street SE,
Minneapolis, Minnesota 55455

Received October 31, 2005

The preparation, structures, and reactivity of tetraphenylporphyrin (TPP) cobalt halovinyl complexes are reported. β-Halovinyl complexes of (TPP)Co(*E*-CHCHX) (X $=$ Br and I) were prepared from the insertion of acetylene into the cobalt halide bonds of the corresponding halide complexes. The reactivity of these compounds and of the previously reported (TPP)Co(*E*-CHCHCl), was studied in depth, and it was found that complex reactivity increased with the leaving group ability of the halide. A *trans*-dichlorovinyl cobalt porphyrin complex, (TPP)Co(*Z*-CClCHCl), was also prepared through the reaction of (TPP)CoNa and TCE. The structures of (TPP)Co(*E*-CHCHBr), (TPP)Co(*Z*-CClCHCl), and (TPP)Co(C$_2$H) are reported. The C–C bond length of the vinyl group was found to vary for the β-halovinyl complexes (TPP)Co(*E*-CHCHX) from 1.211 Å for X $=$ Br to 1.234 Å for X $=$ Cl and 1.320 Å for (TPP)Co(*Z*-CClCHCl). A comparison of these structures to many chlorovinyl cobalt complexes shows that *trans*-2-halo substitution results in a dramatically decreased vinyl C–C bond length. The mechanism of halide substitution for the β-halovinyl complexes was investigated with kinetic experiments that indicated a dissociative mechanism and supported the intermediacy of a cobalt acetylene complex.

Introduction

Chlorinated ethylenes are widespread groundwater contaminants listed on the US EPA's priority pollutant list because of their environmental presence and their adverse toxicological profile.[1−3] There has been much recent interest in the catalytic reductive dehalogenation of these compounds by cobalt catalysts, such as cyanocobalamin and tetrakis(4-carboxyphenyl) porphyrin cobalt, (TCPP)Co).[4−14] One of the key distinguishing features of these catalyst systems is the apparent involvement of Co−C-bonded intermediates, particularly chlorovinyl complexes[4−6,14−20] and, potentially, chloroethyl complexes.[6,21]

Chlorovinyl organometallic cobalt complexes have been synthesized in the native cobalamin and cobalamin model systems.[12,13,18,22−24] Many other cobalt vinyl compounds have also been prepared with various substituents.[25−30] Because

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* To whom correspondence should be addressed. Email: mcneill@chem.umn.edu.

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10.1021/ic0518834 CCC: $33.50

of our studies of (TCPP)Co, we have had a continuing interest in porphyrin cobalt chlorovinyl complexes including one that has been previously reported.[14,31] While the chemistry of halovinyl complexes of cobalt has only begun to be explored in the past decade, halovinyl complexes of other metals have been well studied. There appear to be numerous differences between halovinyl complexes of cobalt and other metal centers such as nickel, palladium, and platinum. For example, trichlorovinylmetal complexes are readily prepared for Group 10 metals, but they have remained elusive with cobalt.[32−38]

In this study, we further explore the chemistry of halovinyl cobalt complexes through the preparation of a series of complexes, an examination of their structures, and an investigation into the unusual lability of *trans*-β-halovinyl cobalt porphyrin complexes.

Experimental Section

Materials. Trichloroethylene (TCE), tetraphenylporphyrin cobalt(II) ((TPP)Co), tetrabutylammonium fluoride hydrate (TBAF), tetrabutylammonium bromide (TBABr), tetrabutylammonium iodide (TBAI), hydrobromic acid (47−49 wt %), ^{n}BuLi in hexanes (1.0 M), 1,1-dichloroethylene, vinyl chloride, 4-(dimethylamino)pyridine (DMAP), 4-cyanopyridine (4-CN-py), sodium chloride (Na^{35}Cl, 99%), lithium bromide, potassium hexamethyldisilazide (KHMDS), aluminum trichloride, and benzophenone were purchased from Aldrich. Tetrabutylammonium hexafluorophosphate (TBAPF$_6$) and tetrabutylammonium chloride (TBACl) were purchased from Fluka. Hydroiodic acid (57 wt %) was purchased from J. T. Baker. Acetylene was purchased from Minneapolis Oxygen Company (Minneapolis, MN). Both *cis*-dichloroethylene (cDCE) and *trans*-dichloroethylene (tDCE) and were purchased from TCI America. Deuterated acetylene (C_2D_2) was purchased from Cambridge Isotope Laboratories. Sodium benzophenone ketyl was prepared via the addition of 0.9 equiv of sodium metal to benzophenone in THF. Sodium mercury amalgam was prepared by dissolving up to 0.5% sodium in mercury. *tert*-Butoxide (^{t}BuOK) was prepared by reaction of excess neat *tert*-butyl alcohol (^{t}BuOH) with KH under an inert atmosphere. TBA^{35}Cl was prepared by mixing TBAPF$_6$ (132 mg, 0.34 mmol) and Na^{35}Cl (100 mg, 1.72 mmol) in methanol; the resulting solid was 26 wt % ^{35}Cl.

General Methods. ^{1}H and ^{13}C NMR spectra were collected at 300 and 75 MHz, respectively, on a Varian Inova Instrument. ESI-TOF mass spectra were collected on a Bruker BioTOF II instrument. UV−vis absorbance spectra were collected with a Jasco V530 spectrophotometer (300−700 nm) with a 4 mL septum-sealed quartz cuvette. GC-MS data were collected with an Agilent 6890 GC (column Phenomenex ZB-624, 60 m × 0.32 mm i.d., 1.8 μm film thickness) and an Agilent 5973 Mass Selective detector.

X-ray Structure Analysis. Diffraction data were collected using crystals mounted on thin glass capillaries with oil on a Siemens SMART Platform CCD diffractometer with Mo Kα radiation (graphite monochromator) at 173(2) K. The structures were solved using direct and Patterson methods using SHELXS-97 and were refined using SHELXL-97.[39] Crystallographic data for (TPP)Co(*E*-CHCHBr), (TPP)Co(*Z*-CClCHCl), and (TPP)Co(C_2H) are given in Table 1. Additional crystallographic data including tables of bond lengths and angles are presented in the Supporting Information.

(*trans*-2-Bromovinyl)(tetraphenylporphyrin) Cobalt(III), (TPP)Co(*E*-CHCHBr), 1. The methods from Sakurai and Setsune were adapted for the preparation of compound **1**.[14,31,40] (TPP)CoBr was prepared by two methods. **Method A**. (TPP)CoBr was prepared through reaction of (TPP)Co (300 mg, 0.45 mmol) with HBr (47−49 wt %, 4 mL, 24 mmol) in methanol (300 mL) with 4 days of stirring at room temperature. The solution was vacuum filtered, and the solvent was removed from the filtrate in vacuo to near dryness. The (TPP)CoBr solid was isolated with vacuum filtration and washed with 2:1 H_2O/MeOH. (TPP)CoBr was isolated in a 49% yield. **Method B**. (TPP)CoBr was also prepared from (TPP)CoCl through halide exchange; lithium bromide (10 equiv) was added to (TPP)CoCl in THF, and then the mixture was washed with H_2O, and extracted into $CHCl_3$. The combined extracts were washed with H_2O and dried over $MgSO_4$. (TPP)CoBr was isolated in a 95% yield.

(TPP)Co(*E*-CHCHBr) was prepared from the reaction of (TPP)CoBr (100 mg, 0.14 mmol) and C_2H_2 (200 mL, 1 atm, 8 mmol) in CH_2Cl_2 (30 mL) in a sealed tube with stirring for 4 days. The solvent was removed in vacuo. Purification was performed by column chromatography (SiO_2, 60:40 hexane/$CHCl_3$), and the yield was 60%. X-ray quality crystals were obtained by slow cooling of a saturated solution (4:1 hexane/CH_2Cl_2) to −35 °C. UV−vis (CH_2Cl_2): λ_{max} 410, 527 nm. ^{1}H NMR (CD_2Cl_2): δ 8.91 (s, 8H), 8.13 (d, $J = 6.3$ Hz, 8H), 7.75 (m, 12H), −0.25 (d, $J = 11.7$ Hz, 1H), −0.97 (d, $J = 11.4$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 145.5, 141.4, 133.6, 133.3, 128.1, 127.1, 122.1, 82.9. ESI-TOF MS (MeOH): m/z observed $M^+ = 776.10$, $[M + K]^+ = 815.07$. ESI-TOF high-resolution mass spectrometry (HRMS) with polypropylene glycol standard: m/z 776.098, −3.2 ppm error.

For compound **1** prepared with (TPP)CoBr from Method A, a brominated porphyrin impurity, (Br$_1$-TPP)Co(*E*-CHCHBr), was identified with ^{1}H NMR spectroscopy and mass spectrometry analysis at approximately the 10% level. This was also observed in the crystal structure of **1** which showed a single Br replacement of H, modeled at 6% incorporation, at the β-pyrrole position on the porphyrin ring. No bromoporphyrin impurity was observed with (TPP)CoBr prepared by Method B.

(*trans*-2-Iodovinyl)(tetraphenylporphyrin) Cobalt(III), (TPP)Co(*E*-CHCHI), 2. The methods from Sakurai and Setsune were

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Table 1. Crystallographic Data and Details of the Structural Refinements for (TPP)Co(*E*-CHCHBr), **1**, (TPP)Co(*Z*-CClCHCl), **3**, and (TPP)Co(C_2H), **4**

	1	**3**	**4**
empirical formula	$C_{46}H_{29.94}Br_{1.06}CoN_4$	$C_{46}H_{29}Cl_2CoN_4$	$C_{46}H_{29}CoN_4$
fw	777.58	767.56	696.17
cryst syst	triclinic	triclinic	tetragonal
space group	$P\bar{1}$	$P\bar{1}$	$I4/m$
a (Å)	11.251(2)	12.2370(15)	13.2500(9)
b (Å)	13.175(3)	12.3804(15)	13.2500
c (Å)	14.369(3)	13.7944(17)	9.7890(7)
α (deg)	103.136(3)	67.209(2)	90
β (deg)	107.623(3)	86.051(2)	90
γ (deg)	102.179(3)	66.063(2)	90
V (Å^3)	1884.9(7)	1751.3(4)	1789.3(13)
Z	2	2	2
ρ_{calcd} (g cm^{-1})	1.370	1.456	1.293
μ (cm^{-1})	15.53	6.84	5.18
F(000)	792	788	720
cryst color	red-purple	purple	purple
ind. reflns	6642	6184	7990
obsd reflns	5534	5339	820
R_{int}	0.0284	0.0232	0.0257
GOF on F^2	1.076	1.064	1.254
R1^a, wR2^b(%) [$I > 2\sigma(I)$]	4.47, 11.91	3.91, 10.06	3.60, 11.26
R1^a, wR2^b(%) all data	5.32, 12.42	4.73, 10.52	3.70, 11.34

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

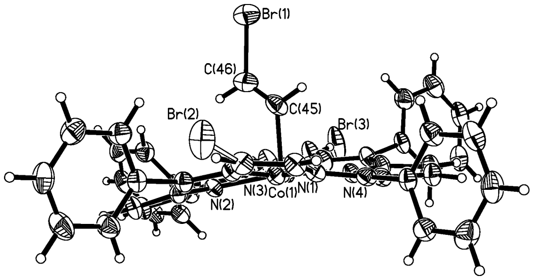

Figure 1. ORTEP drawing of **1** with thermal ellipsoids drawn at the 50% probability level. Porphyrin bromination refined to be present at 6% total occupancy over two symmetric positions.

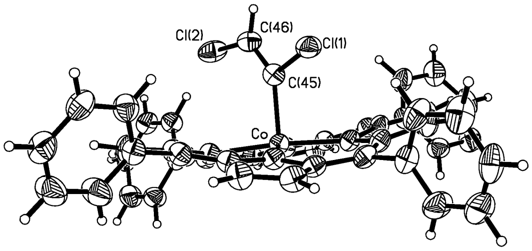

Figure 2. ORTEP drawing of **3** with thermal ellipsoids drawn at the 50% probability level. The disordered dichlorovinyl group was refined at an occupancy of 77:23 into two conformers at 180° from one another. For clarity, only the major conformer is shown.

adapted for preparing compound **2**.[14,31,40] (TPP)CoI was prepared by reaction of (TPP)Co (300 mg, 0.45 mmol) with HI (57 wt %, 5 mL, 22 mmol) in methanol (300 mL) with 4 days of stirring. The solution was vacuum filtered, and the solvent was removed from the filtrate in vacuo to near dryness. The (TPP)CoI solid was isolated with vacuum filtration and washed with 2:1 H_2O/MeOH. (TPP)CoI was isolated in an 83% yield.

(TPP)Co(*E*-CHCHI) was prepared by reaction of (TPP)CoI (100 mg, 0.13 mmol) and C_2H_2 (200 mL, 1 atm, 8 mmol) in CH_2Cl_2 (30 mL) in a sealed tube with stirring for 4 days. The solvent was removed in vacuo. Purification was performed by column chromatography (SiO_2, 60:40 hexane/$CHCl_3$); the yield was 43%. UV−vis (CH_2Cl_2): λ_{max} 409, 527 nm. ^{1}H NMR (CD_2Cl_2): δ 8.94 (s, 8H), 8.13 (d, J = 6.9 Hz, 8H), 7.75 (m, 12H), −0.04 (d, J = 11.4 Hz, 1H), −1.06 (d, J = 11.4 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 145.6, 141.5, 133.7, 133.3, 128.1, 127.2, 122.1, 72.1, 52.4. ESI-TOF MS (MeOH): m/z observed M$^+$ = 824.2. ESI-TOF HRMS with polypropylene glycol standard: m/z 824.0839, 0.4 ppm error.

(*trans*-Dichlorovinyl)(tetraphenylporphyrin) Cobalt(III), (TPP)Co(*Z*-CClCHCl), 3. Compound **3** was prepared through reaction of (TPP)Co^{I}Na with TCE (Method A) and via reaction of (TPP)Co^{III}Cl and the tDCE anion (Method B).[41−43] **Method A**. (TPP)Co (100 mg, 0.155 mmol) was dissolved in THF and reduced with sodium benzophenone ketyl (10 mL of a 69 mM THF solution) under an inert atmosphere. (An alternate reduction method utilized excess sodium amalgam with 4 h of stirring followed by decanting the (TPP)Co^{I}Na solution from the amalgam.) The red porphyrin solution turned dark green upon reduction. TCE (0.5 mL, 5 mmol) was added to (TPP)Co^{I}Na. The mixture was stirred for 1 h, and the solvent was removed in vacuo. The residue was extracted with CH_2Cl_2 and purified by column chromatography (SiO_2, 70:30 hexane/toluene); the yield was 23%. **Method B**. Chlorinated ethylene deprotonation methods were adapted from Köebrich.[41−43] TCE (100 μL, 1.4 mmol, dried over molecular sieves) was added to a 100 mL Schlenk flask in 15 mL of 1:1:1 (v/v/v) THF/Et_2O/hexanes. The solution was cooled to −110 °C in a liquid nitrogen−ethanol bath. Either ^{n}BuLi (500 μL, 1.25 mmol, 2.5 M in hexanes) or KHMDS (70 mg, 0.33 mmol in THF solution) was added to the Schlenk flask via syringe under a nitrogen atmosphere. The reaction was allowed to proceed for 20 min. The reaction mixture was transferred via cannula to a solution of (TPP)Co^{III}Cl (50 mg, 0.072 mmol, cooled to −110 °C in a liquid nitrogen−ethanol bath) in 15 mL of THF. The reaction was held at −110 °C for 4 h, then slowly warmed to −35 °C overnight. The solvent was removed in vacuo. Purification was performed by column chromatography (SiO_2, 60:40 hexane/$CHCl_3$); the yield was 85%.

X-ray quality crystals of **3** were obtained via slow evaporation from a hexane/CH_2Cl_2 (5:1) mixture. UV−vis (CH_2Cl_2): λ_{max} 393, 422, 531 nm. ^{1}H NMR (CD_2Cl_2): δ 8.94 (s, 8H), 8.13 (d, J = 5.7 Hz), 7.75 (m, 12H), 2.51 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 146.0,

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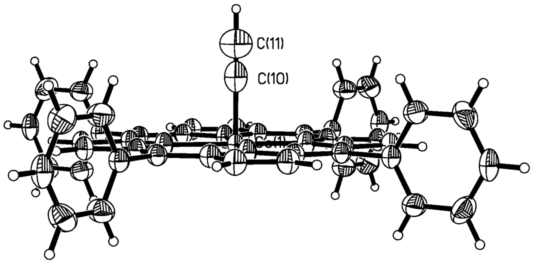


Figure 3. ORTEP drawing of **4** with thermal ellipsoids drawn at the 50% probability level. The acetylide moiety was refined with disordered partial occupancy in "up" and "down" conformations in a 61:39 ratio.

141.2, 133.4, 128.1, 127.2, 122.2, 122.1, 81.6, 29.9. ESI-TOF MS (MeOH): *m/z* observed $M^+ = 766.11$, $[M + Na]^+ = 789.10$, $[M + K]^+ = 805.20$. ESI-TOF HRMS with polypropylene glycol standard: *m/z* 766.1106, −1.3 ppm error.

(Acetylide)(tetraphenylporphyrin) Cobalt(III), (TPP)Co-(C_2H), 4. Compound **4** was prepared through the reaction of (TPP)-$Co^{III}Cl$ and the vinyl chloride anion generated with methods adapted from Köebrich.[41−43] Vinyl chloride (80 mL, 1 atm, 3.2 mmol) was added via vacuum transfer to a 100 mL Schlenk flask containing 15 mL of 1:1:1 (v/v/v) THF/Et_2O/hexanes. The solution was cooled to −110 °C in a liquid nitrogen−ethanol bath. Either ^{n}BuLi (500 μL, 1.25 mmol, 2.5 M in hexanes) or KHMDS (70 mg, 0.33 mmol in THF solution) was added to the Schlenk flask via syringe under a nitrogen atmosphere. The reaction was allowed to proceed for 70 min. The reaction mixture was transferred via cannula to a solution of (TPP)$Co^{III}Cl$ (50 mg, 0.072 mmol, cooled to −110 °C) in 15 mL THF. The reaction was held at −110 °C for 4 h, then slowly warmed to −35 °C overnight. The solvent was removed in vacuo. Purification was performed by column chromatography (SiO_2, 60:40 hexane/$CHCl_3$); the yield was 42%. X-ray quality crystals were obtained by slow diffusion of hexane/CH_2Cl_2 (5:1). UV−vis (CH_2Cl_2): λ_{max} 377, 421, 526 nm. ^1H NMR ($CDCl_3$): δ 8.97 (d, $J = 2.0$, 8H), 8.20 (dm, $J = 7$ Hz, 8H), 7.75 (m, 12H), −1.67 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 146.0, 141.4, 133.53, 133.51, 128.2, 127.24, 122.9, 92.10. ESI-TOF MS (MeOH): *m/z* observed $M^+ = 696.17$, $[M + Na]^+ = 719.3$. ESI-TOF HRMS with polypropylene glycol standard: *m/z* 696.1713, 0.8 ppm error.

Halogen Substitution. Approximately 10 mg (~10 μmol) of each β-halovinyl complex was dissolved in $CDCl_3$ and transferred to an NMR tube. Excess TBAX (X= F, Cl, Br, I) was added to the tube, dissolved, and mixed. Spectral features of interest are the α-carbon vinyl proton doublet at −0.1 ppm for the iodovinyl complex, **2**, −0.25 ppm for the bromovinyl complex, **1**, and −0.4 ppm for the chlorovinyl complex (TPP)Co(*E*-CHCHCl), **5** (previously reported).[14] Halogen substitution was carried out at room temperature and was monitored at regular intervals by ^1H NMR spectroscopy for 72 h.

Compound **5** (10 mg, 13 μmol) was treated with a $TBA^{35}Cl$/$NaPF_6$ mixture (33.1 mg, 26 wt % Cl, 230 μmol) in refluxing $CHCl_3$ for 5 days. In separate trials, the reaction was heated to reflux both with an open condenser and in a sealed tube, monitored with ^1H NMR, purified by column chromatography (SiO_2, 70:30 hexane/$CHCl_3$), and analyzed with ESI-TOF MS.

Kinetic Halogen Substitution Experiments. The kinetics of the conversion of **1** (8 mg, 10 μmol) to **5** at 35 °C were monitored by ^1H NMR spectroscopy in $CDCl_3$. The reaction proceeded with a constant amount of TBACl (25 μL of 0.5 M TBACl in $CDCl_3$, 13.5 μmol) and varying amounts of TBABr (12.5, 25, 50, 125, and 250 μL of 0.5 M TBABr in $CDCl_3$, 6.8, 13.5, 27, 54, and 135 μmol; 85 and 183 mg TBABr, 270 and 570 μmol) and $TBAPF_6$ to hold the ionic strength constant (0, 100, 150, 180, 195, 200, and 205 mg $TBAPF_6$ in $CDCl_3$, 0, 260, 400, 470, 500, 525, and 530 μmol). Total NMR solution volume was 700 μL in each tube. Time points were collected at time = 0, 2, 5, 12, 24, 36, 51, and 72 h. The α-carbon proton peak areas of **1** and **5** were compared to quantify the extent of conversion from **1** to **5**.

Reaction with Pyridines. Approximately 10 mg of each β-halovinyl complex was dissolved in $CDCl_3$ for ^1H NMR analysis. A spectrum was collected and then 1 drop of pyridine (approximately 20 μL) was added to each tube. Spectra were collected after the pyridine addition. In a similar manner, reactions between **5** with excess DMAP and **1** with excess 4-CN-py were monitored with ^1H NMR.

Reaction with a Lewis Acid. Approximately 10 mg of **5** was dissolved in C_6D_6 for ^1H NMR analysis. Under an inert atmosphere, excess $AlCl_3$ was added to each tube. ^1H NMR spectra were collected before and after addition.

Reaction with Strong Bases. Approximately 10 mg of each β-halovinyl complex was dissolved in C_6D_6 for ^1H NMR analysis. Under inert atmosphere, excess KHMDS was added to each tube. To each β-halovinyl complex, excess ^{t}BuOK in ^{t}BuOH was added to each tube. ^1H NMR spectra were collected before and after addition.

Reactions with Aqueous Acid and Base Solutions. Approximately 10 mg of each β-halovinyl complex was utilized in each experiment. For H_2O, the β-halovinyl compounds were dissolved in THF-d_8. For HCl and NaOH, the β-halovinyl complexes were dissolved in $CDCl_3$ for ^1H NMR analysis. Spectra were collected before and after the addition of 1 drop of H_2O, HCl (2 M), or NaOH (1 M) to each tube. Spectra were collected at regular time intervals. In the case of HCl, the volatile materials were isolated via vacuum transfer and characterized with GC-MS.

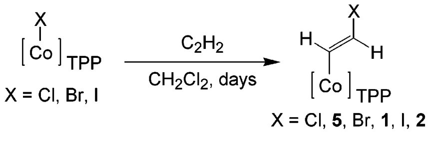
Approximately 10 mg of compound **4** was dissolved in $CDCl_3$ for ^1H NMR analysis. Spectra were collected before and after the addition of 1 drop of HCl (2 M). The volatile materials were isolated via vacuum transfer and characterized with GC-MS.

Solution Stability. The stability of the β-halovinyl complexes to the loss of C_2H_2 was tested by sparging halovinyl complex solutions in *p*-xylenes with N_2. Approximately 10 mg of each β-halovinyl in $CDCl_3$ was diluted into 50 mL of *p*-xylene. The solutions were N_2-sparged for various time intervals and monitored with ^1H NMR. The xylenes were removed *in vacuo*, and the residue dissolved in $CDCl_3$.

C_2D_2 Replacement of C_2H_2. Approximately 10 mg of iodovinyl **2** (12 μmol) was dissolved into $CDCl_3$ and transferred to an NMR tube. A known volume bulb was used for quantitative gas transfer of 25 μmol C_2D_2. The NMR tubes were flame-sealed and the reaction mixture was analyzed by ^1H NMR spectroscopy at regular time intervals. At the completion of the experiment, the solution was analyzed with ESI-TOF MS.

Results

Preparation of Halovinyl and Acetylide Cobalt Complexes. An acetylene insertion reaction (eq 1) was used to prepare the halovinyl compounds (TPP)Co(*E*-CHCHX) (X = Cl, Br, I) **5**, **1**, and **2** in good yields.[14,31]



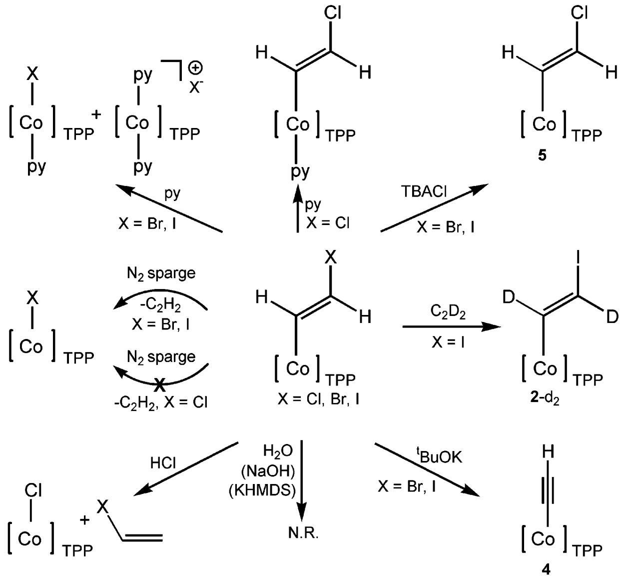
(1)

Acetylene insertion into M−Cl bonds yielding chlorovinylmetal complexes has been observed in a number of systems including metal chlorides (M = As, Sb, Pt, Hg)[44−51] and transition metal porphyrin complexes (M = Co, Rh).[14,31,52] All three *β*-halovinyl complexes are air stable and were handled on the benchtop. In the case of **1**, it was prepared in a 60% yield with a 6−10% (Br_1-TPP)Co(*E*-CHCHBr) impurity. This impurity resulted from the bromination of the porphyrin during the (TPP)Co^{II} oxidation to (TPP)Co^{III}Br with HBr. The replacement of *β*-pyrrole H atoms by Br has been previously reported for bromination with Br_2 (a possible contaminant in HBr or generated under the reaction conditions) and *N*-bromosuccinimide.[53,54] The presence of (Br_1-TPP)CoBr in (TPP)CoBr was observed with ESI-TOF MS. X-ray quality crystals of **1** were isolated, and during the refinement, the (Br_1-TPP)Co(*E*-CHCHBr) impurity, which cocrystallized, was modeled as disorder and found to be present at a 6% level (see Supporting Information). Compound **1** was also prepared free of the bromoporphyrin impurity by bromide exchange of the chloride in (TPP)CoCl, followed by acetylene insertion.

Compound **2** was prepared from (TPP)CoI in a 43% yield and was characterized with ^{1}H NMR, ^{13}C NMR, UV−vis, and ESI-TOF HRMS. Attempts to obtain crystals suitable for X-ray analysis were unsuccessful. Compound **2** is unstable toward acetylene deinsertion in solution over several days under ambient conditions, but is stable as a solid under inert atmosphere at −35 °C. A *β*-fluorovinyl cobalt porphyrin complex could not be prepared through an acetylene insertion reaction from either (TPP)CoF, prepared with HF, or by F^- exchange with (TPP)CoCl. The product isolated from the reaction of (TPP)CoF and C_2H_2 was compound **4**, the acetylide.

Compound **3**, (TPP)Co(*Z*-CClCHCl), was the only halovinyl complex isolated from the reaction of (TPP)Co^INa and chlorinated ethylenes (TCE, cDCE, tDCE, CH_2CCl_2, or CH_2CHCl). Compound **3** was isolated from the reaction of (TPP)Co^INa and TCE in a 23% yield. The ^{1}H NMR spectrum of this complex gives little stereochemical information, but X-ray crystallography indicates a Z configuration, with the two chlorine substituents trans to one another. The stereochemistry of **3** as the product of reaction of Co^I and TCE was surprising. This complex has *trans*-dichloro stereochemistry in stark contrast to the observed products in the aqueous phase reductive dehalogenation of TCE by (TCPP)Co, where cDCE is the major observed product.[14] The crystal structure of **3** was modeled with disorder at the vinyl group resulting in two conformations oriented at 180° from one another in a ratio of 77:23 (see Supporting Information).

Scheme 1. Reactivity Summary for the *β*-Halovinyl Tetraphenylporphyrin Cobalt Complexes



The tetraphenylporphyrin ligand is symbolized by brackets.

Another synthetic route to chlorovinyl cobalt complexes was also explored through the deprotonation of chlorinated ethylene substrates and reaction with (TPP)Co^{III}Cl. Compound **3** was the only chlorovinyl complex isolated from this synthetic procedure and was isolated in an 85% yield from the reaction of (TPP)Co^{III}Cl and the anion derived from tDCE. The characterization of **3** was consistent with the isolated products of (TPP)Co^INa and TCE. Also, through the deprotonation reaction procedure, compound **4** was obtained through of the reaction of deprotonated vinyl chloride and (TPP)Co^{III}Cl (compound **4** has been previously reported).[55] It was characterized with ^{1}H NMR, ^{13}C NMR, UV−vis, and ESI-TOF HRMS.

The structure of **4** was solved in the space group $I_{4/m}$, but suitable solutions were also obtained with I_4 and I_{-4}. This space group was chosen because it yielded the most reasonable solution for the acetylide C−C and C−H bond distances and for the thermal parameters of the ellipsoids. Although there were favorable structure solutions for a diacetylide complex based on symmetry operations, we do not think this is the case because Co^{IV} is not a viable oxidation state and no lithium counterion was observed in the structure; therefore we believe the compound to be a monoacetylide. This is also supported by ^{1}H NMR and ESI-TOF MS data and in comparison to available literature data.[55] The acetylide moiety was refined for partial occupancy and found to be present in a 61:39 ratio of the two conformations (see Supporting Information).

***β*-Halovinyl Cobalt complex Reactivity.** The reactivity of the *β*-halovinyl complexes was explored (Scheme 1) and

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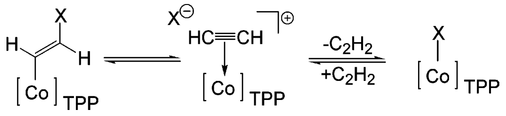
contributes to previous work regarding the reactivity of *β*-chlorovinylmetal complexes.[47,56] Aspects of the observed reactivity can be understood by considering the equilibrium described by Setsune[31] (eq 2) which includes a coordinated acetylene *π* complex previously proposed in a number of transition metal systems.[31,51,52,57−60]



(2)

The bromovinyl **1** and iodovinyl **2** complexes were found to be much more reactive than the chlorovinyl **5**. Both **1** and **2** were converted to **5** by reaction with excess TBACl. In contrast, **5** could not be converted to either **1** or **2** through the addition of excess TBABr or TBAI, respectively. Preparation of the analogous *β*-fluorovinyl cobalt complex through halide exchange with **1**, **2**, or **5** and TBAF was not successful. When **5** was treated with TBA^{35}Cl, no changes in the M$^+$ ion isotope pattern of **5** were observed. A decomposition product, (TPP)CoCl, was formed after prolonged heating of **5** at 60 °C, indicating that acetylene deinsertion is possible at higher temperature.

To determine the mechanism of halide exchange among the *β*-halovinyl complexes, the conversion of **1** to **5**, using varying amounts of bromide (TBABr) in the presence of constant chloride (TBACl) concentration, was monitored with ^{1}H NMR through integration of their respective vinyl proton signals. The loss of **1** was correlated to an increase in **5**. Slower rates of conversion from **1** to **5** were observed with increasing bromide concentration (Figure 4).

The reaction of *β*-halovinyl complexes with pyridine had varied results depending on the *β*-halogen substitution. Simple complexation of pyridine to **5** giving a 6-coordinate complex was observed by ^{1}H NMR spectroscopy and ESI-TOF MS. The vinyl proton resonances shifted downfield from −0.46 and −1.00 ppm to 0.14 and −0.96 ppm (where the signal at −0.46 ppm corresponds to the proton bound to the α-carbon and the resonance at −1.00 ppm is the proton on the *β*-carbon). In the case of **1** and **2**, no vinyl group signals were observed in the ^{1}H NMR spectrum following pyridine addition, and mass spectrometry data indicated the loss of acetylene and formation of a mixture of (TPP)(py)-CoX and (TPP)(py)$_2$Co$^+$ in both reactions. In the reaction of **5** with DMAP, a 6-coordinate complex was observed with a similar shift in the ^{1}H NMR as described above for pyridine. Simple coordination to give a 6-coordinate *β*-bromovinyl cobalt complex was achieved through the reaction of **1** with the more weakly donating 4-cyanopyridine.

The reactivity of the halovinyl complexes with H$_2$O, H$^+$, and OH$^-$ was tested. In the case of H$_2$O, no degradation of the halovinyl compounds was observed after 2 days. In the case of HCl addition, within 1 day the halovinyl complexes were completely degraded, and the emergence of vinyl halide peaks consistent with vinyl chloride, vinyl bromide, and vinyl iodide were observed by ^{1}H NMR spectroscopy. Isolation of the volatile materials via vacuum transfer followed by ^{1}H NMR and GC-MS analysis identified the products as (TPP)CoCl and the corresponding vinyl halide (i.e., vinyl chloride, vinyl bromide, or vinyl iodide). In the case of NaOH addition, no changes to the halovinyl protons were observed within 2 days. Compound **4** was also treated with HCl and yielded vinyl chloride as the major product.

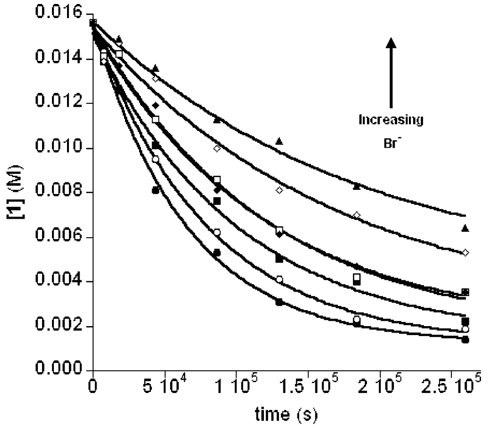


Figure 4. Concentration of **1** at time points along the kinetic time course for the conversion of **1** to **5** at different [Cl$^-$]/[Br$^-$] ratios. Curve fits represent an exponential fitting of the concentration data yielding the observed rate constant (k_{obs}) for each experiment. Time points were collected at 2, 5, 12, 24, 36, 51, and 72 h.

The reaction of *β*-chlorovinyl complex **5** with AlCl$_3$ was explored. Upon addition of AlCl$_3$ to a benzene-*d*$_6$ solution of **5**, an immediate color change from red to green-black was observed. The resulting ^{1}H NMR spectrum was consistent with [(TPP)Co^{III}][AlCl$_4$]. Subsequent treatment of the reaction mixture with pyridine yielded (TPP)Co(py)$^+$ and (TPP)Co(py)$_2$$^+$, on the basis of mass spectrometry results, confirming the loss of the chlorovinyl group.

The reaction of *β*-halovinyl complexes with strong bases was also explored. All of the *β*-halovinyl complexes were determined to be unreactive toward KHMDS as there were no observed changes to the halovinyl proton signals. Treatment with ^{t}BuOK yielded no reaction with **5**, but it reacted with both **1** and **2** slowly to yield the acetylide complex, **4**.

The lability of the C$_2$H$_2$ moiety was also investigated. Sparging solutions of the *β*-halovinyl complexes with N$_2$ yielded no change in **5** after several days, complete loss of acetylene from **1** in 6 days, and complete loss of acetylene from **2** in 1 day. Further evidence of the lability of the C$_2$H$_2$ component of the *β*-halovinyl complexes was the replacement of C$_2$H$_2$ with C$_2$D$_2$. Complete replacement for complex **2** was observed within 2 days as observed by ^{1}H NMR spectroscopy and confirmed with ESI-TOF MS, which had an increase of two mass units for the M$^+$ ion.

Discussion

***β*-Halovinyl Complex Structures.** Characterization of the halovinyl cobalt complexes identified new complexes with

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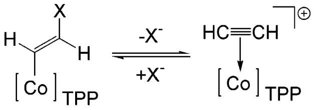
Table 2. Halovinyl Bond Lengths and Angles of Interest for (TPP)CoR (**1**, R = *E*-CHCHBr; **3**, R = *Z*-CClCHCl; **5**, R = *E*-CHCHCl)

metric	**1**	**3**	**5**[a]
Co−C (Å)	1.925(4)	1.929(4)	1.9246(4)
C═C (Å)	1.211(6)	1.320(7)	1.234(5)
C−X (Å)	1.927(4)	1.757(7)[b] 1.735(4)[c]	1.752(4)
∠Co−C═C (deg)	126.9(3)	134.0(5)	126.7(3)

[a] Ref 14. [b] C45−Cl1 [c] C46−Cl2.

Scheme 2. General Summary of the Reactivity of *β*-Halovinyl Complexes



Stability: Cl >> Br > I

Promoted by
1. better leaving group
2. addition of Lewis acid ($AlCl_3$)
3. coordination of pyridine

varying stability. The crystallographic data shows the C−C bond of the vinyl group to be very short in the *β*-halovinyl complexes (see Table 2); the bond distance for the vinyl carbons of *β*-halovinyl cobalt complexes (compound **1** = 1.211 Å, compound **5** = 1.234 Å) strongly resembles that measured for acetylene with a C−C bond distance of 1.181 Å.[61] It is interesting to compare the metrical parameters for the *trans*-*β*-halovinyl complexes and the dichlorovinyl complex **3**, in which the Cl substituents are *trans*, as the C−C bond distances are very different (Table 2).

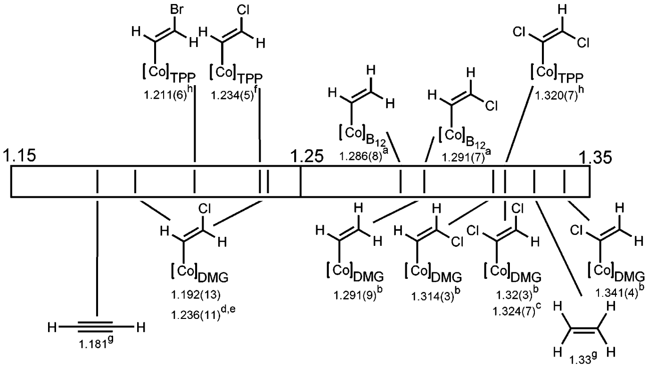
In complex **3**, the Co−C and C−Cl bond distances are also consistent with the chlorovinyl bond distances for other complexes (see Supporting Information), but the Co−C═C (134°) is significantly distorted from an idealized sp^2 carbon bond angle presumably because of steric interactions between Cl2 and the porphyrin ring.

A number of cobalt halovinyl structures have appeared recently. It is instructive to compare the C−C bond distance results across the ligand sets and halogen substitution patterns for the chlorovinyl and vinyl complexes (see Figure 5).

Such comparison emphasizes that trans-*β*-halo substitution leads to a very short C═C bond, consistent with the resonance structures shown in Figure 6.

This resonance model is not new. Indeed, it was put forth 65 years ago to explain infrared absorbance data for *β*-halovinyl Hg complexes that were consistent with intermediate bonding between double and triple.[47] While the short vinyl C−C bonding was inferred for complexes of this type on the basis of spectroscopic and reactivity data, the crystallographic data presented here give the first structural support for this model.

Unsubstituted cobalt vinyl complexes have intermediate bond lengths, while other chlorovinyl complexes have C−C bond lengths approaching those of ethylene. It is apparent that the location of the halogen substituents plays an important role in the C−C bond length of the vinyl group, and these structural trends are reflected in the reactivity of the *β*-halovinyl complexes.



[a] reference 18, [b] reference 13, [c] reference 24, [d] reference 23, [e] Disordered vinyl group, [f] reference 14, [g] reference 61, 62, [h] This work.

Figure 5. Comparison of C−C vinyl bond distances in angstroms for selected Co vinyl complexes with corrin, dimethylglyoximate, and porphyrin ligand sets.

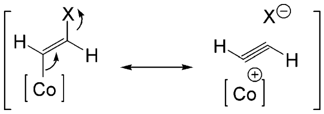
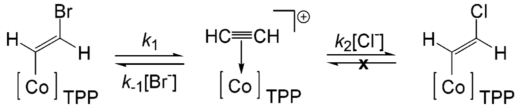


Figure 6. Contributing resonance structures for *E*-*β*-halovinyl complexes.

Reactivity of *trans*-*β*-Halovinyl Complexes. The reactivity of *β*-halovinyl complexes can largely be summarized by the equilibrium shown in Scheme 2.

Evidence for this equilibrium was obtained through the kinetics of the halogen substitution experiments. In these experiments, support for a dissociative substitution mechanism was obtained through inhibition of the conversion of **1** to **5** by added bromide ion (eq 3).



(3)

The diminished rate constant for the conversion to **5** in the presence of increasing Br^- concentrations is consistent with a competition between Br^- and Cl^- for addition to the coordinated acetylene. The kinetic data were interpreted using the scheme presented in eqs 3−5. The rate constants at

$$k_{\mathrm{obs}} = \frac{k_1 \dfrac{[\mathrm{Cl}^-]}{[\mathrm{Br}^-]}}{\dfrac{k_{-1}}{k_2} + \dfrac{[\mathrm{Cl}^-]}{[\mathrm{Br}^-]}} \tag{4}$$

$$\frac{-\mathrm{d}[\mathbf{1}]}{\mathrm{d}t} = k_{\mathrm{obs}}\,[\mathbf{1}] \tag{5}$$

35 °C for Br^- loss (k_1) and the ratio of Cl^- and Br^- attachment (k_2/k_{-1}) were determined to be 1.39×10^{-5} s^{-1} and 11.6, respectively (see Figure 7). The intermediacy of the cobalt-coordinated C_2H_2 has been previously invoked and our results support the existence of such a complex.[31,59,60]

In general, **5** appears to be very stable on the basis of the inability to yield halogen substitution with excess Br^-, I^-, or $^{35}Cl^-$. Chloride loss could only be observed with

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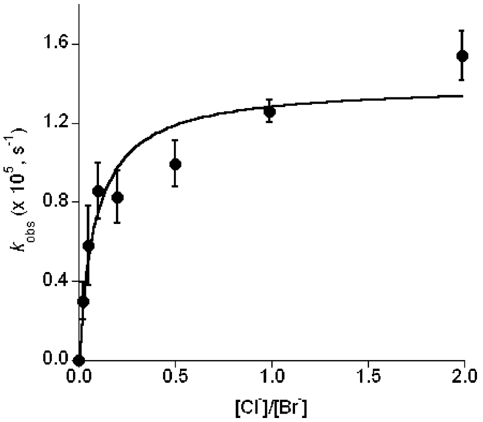

Figure 7. Observed rate constants for the conversion of **1** to **5** at different ratios of [Cl⁻]/[Br⁻]. The curve fit represents a saturation fit of k_{obs}, eq 4. Error bars represent the error of the exponential fit of [**1**] vs time plots.

prolonged heating or following the addition of $AlCl_3$, yielding [(TPP)Co][$AlCl_4$].

The reactivity of the *β*-halovinyl complexes was further explored, and **1** and **2** shared many properties. On the basis of the reactions, the stability of the complexes follows the trend **5** $\gg$ **1** > **2** and agrees with each halide's propensity to act as a leaving group. Acid hydrolysis of the Co−C bond in *β*-halovinyl compounds yielding (TPP)CoCl and the corresponding vinyl halide was a different result than that observed in the chlorovinyl cobaloximes, which were shown to be stable to acid.[23]

The lability of acetylene varied across the *β*-halovinyl complexes. Since halide substitution was not possible for **5**, it was expected that the acetylene would not be displaced by sparging with N_2. The results with bromovinyl complex **1** demonstrated a trend toward increasing reactivity in that the halide could be replaced and the C_2H_2 could be displaced with N_2 sparging. The iodovinyl complex **2** complex was found to be the most reactive since the halide could be replaced, C_2H_2 could be removed by the sparging in 1 day, and C_2H_2 could be replaced with C_2D_2. This observed complex instability provides a rationale for the inability to obtain suitable crystals of **2**.

Conclusions

This study furthers our understanding of cobalt halovinyl complexes, demonstrating that the trans-*β*-halovinyl substitution pattern leads to an unusual reactivity pattern. This work confirms and amplifies Setsune and co-workers view that *β*-halo substituents are susceptible to dissociation, leading to overall lability of the C_2H_2 moiety. The reactivity trend follows the leaving group ability: I > Br $\gg$ Cl. Finally, the distinct reactivity of *β*-halovinyl cobalt complexes is reflected in their structures, which display significantly shortened vinyl C−C bonds.

Acknowledgment. This work was funded in part by the EPA STAR Fellowship program (U-91610701-1) and the National Science Foundation (CHE-0239461). We thank Victor G. Young, Jr. and Ben Kucera from the X-ray Crystallographic Laboratory for help solving the crystal structures.

Supporting Information Available: Table comparing structure details for many vinyl and halovinyl cobalt complexes of porphyrin, dimethylglyoximate, and corrin ligands and crystallographic information for (TPP)Co(*E*-CHCHBr), **1**, (TPP)Co(*Z*-CClCHCl), **3**, and (TPP)Co(C_2H), **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0518834