Further loss of carbon monoxide from III should lead to the formation of clusters with still more metal–metal bonds. These studies are now in progress.

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Registry No. Ia, 80399-46-8; Ib, 79790-55-9; IIa, 80409-94-5; IIb, 80409-95-6; III, 80409-96-7.

Supplementary Material Available: Tables of final fractional atomic coordinates, bond distances and angles, and structure factors (35 pages). Ordering information is given on any current masthead page.

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Direct Observation of a Cationic Intermediate in the Acid-Catalyzed Decomposition of (2-Hydroxy-, (2-Ethoxy-, and (2-Phenoxyethyl)cobaloximes

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Summary: The kinetics of the acid-catalyzed decomposition of the title compounds to form ethylene and cobaloxime(III) have been studied by UV and visible spectroscopy as well as manometrically in both weakly and strongly acidic H_2SO_4/H_2O mixtures. Compelling kinetic evidence has been obtained for formation of a cationic intermediate (upon loss of the β-leaving group) which accumulates in strongly acidic media where the activity of water is low. The ^1H NMR spectrum of the intermediate and its temperature dependence are consistent with its assignment as a cobaloxime(III)–ethylene π complex with two preferred conformations, although a σ-bonded ethylcobaloxime carbonium ion cannot be ruled out.

Cobalt(III) olefinic π complexes and/or electronically equivalent σ-bonded alkylcobalt carbonium ions have been suggested as intermediates in the alcoholysis of (2-acetoxyalkyl)cobaloximes,[1–4] in the acid-catalyzed rearrangements of (2-hydroxy-*n*-propyl)- and (2-hydroxyisopropyl)cobaloximes[5,6] and decomposition of (2-hydroxyethyl)cobaloxime[6] as well as in the synthesis of organo-

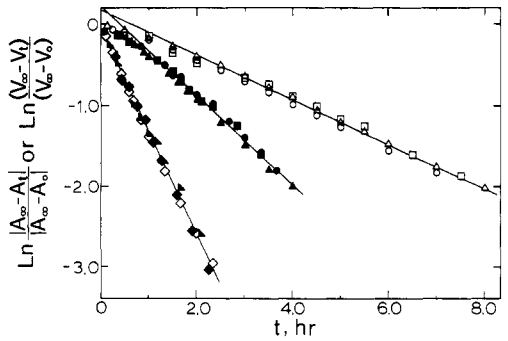
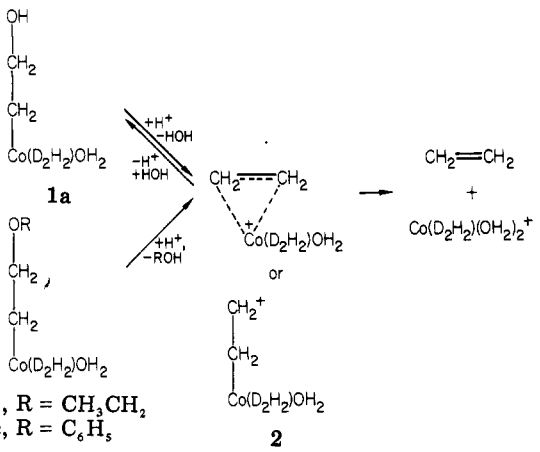


Figure 1. Normalized, semilogarithmic plots of the UV (255 nm), visible (445 nm), and manometric kinetics of the decomposition of **1a**, **1b**, and **1c** at $H_o = 1.70 \pm 0.01$, 25.0 ± 0.1 °C: **1c**, UV (○), visible (△), manometric (□), $k_{obsd} = (7.65 \pm 0.18) \times 10^{-5}$ s^{-1}; **1b**, UV (●), visible (▲), manometric (■), $k_{obsd} = (1.53 \pm 0.04) \times 10^{-4}$ s^{-1}; **1a**, UV (♦), visible (◇), manometric (◣), $k_{obsd} = (3.53 \pm 0.05) \times 10^{-4}$ s^{-1}.

Scheme I



cobalt complexes from vinyl ethers and cobalt(III) complexes in nucleophilic solvents.[4,7–9] To date, all evidence presented for the existence of such intermediates has been indirect. We would now like to report firm kinetic evidence for the existence of an intermediate in the acid-catalyzed decomposition of (2-hydroxyethyl)cobaloxime to cobaloxime(III) and ethylene[10] and direct observation of this intermediate by ^1H NMR spectroscopy.

The decomposition of (2-hydroxyethyl)aquocobaloxime (**1a**)[11] in weakly acidic H_2SO_4/H_2O mixtures ($H_o = 1.70 \pm 0.01$)[14–16] (Figure 1) was found to be a strictly first-order process when monitored by UV or visible spectroscopy, as well as manometrically. In contrast, the decomposition of (2-ethoxyethyl)-(**1b**) and (2-phenoxyethyl)aquocobaloxime (**1c**) in the same media shows a distinct lag followed by a first-order decay using the same three techniques. The observed first-order rate constants decrease markedly

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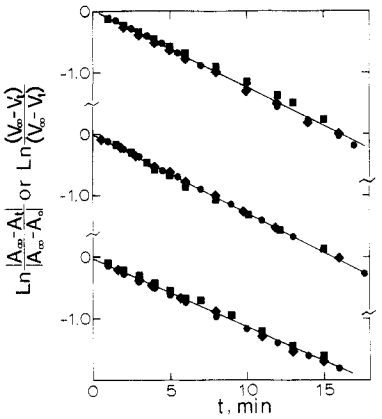
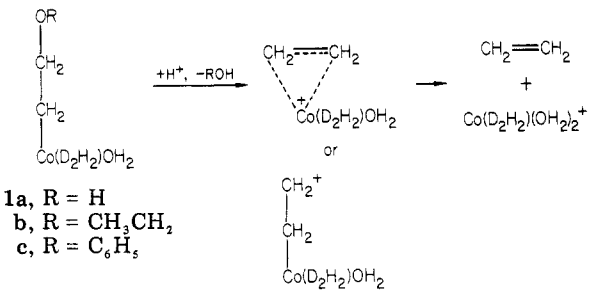


Figure 2. Normalized, semilogarithmic plots of the kinetics of decomposition of **1a** (●), **1b** (♦), and **1c** (■), at H_0 ca. −5.0, 25.0 ± 0.1 °C. Upper plot: UV (255 nm), $H_0 = -5.02 \pm 0.02$, $k_{obsd} = (2.08 \pm 0.03) \times 10^{-3}\ s^{-1}$. Center plot: visible (445 nm), $H_0 = -4.99 \pm 0.02$, $k_{obsd} = (2.12 \pm 0.03) \times 10^{-3}\ s^{-1}$. Lower plot: manometric, $H_0 = -5.06 \pm 0.03$, $k_{obsd} = (1.85 \pm 0.03) \times 10^{-3}\ s^{-1}$.

Scheme II



1a, R = H
b, R = CH_3CH_2
c, R = C_6H_5

2

in the order **1a** > **1b** > **1c** (Figure 1). These results suggest a mechanism such as that shown in Scheme I in which the decomposition of the three complexes is linked via a common cationic intermediate (**2**). Further evidence for such a scheme comes from the following observations. (i) The kinetics of decomposition of **1b** and **1c** in such media are unaffected by the presence of added alcohol leaving group over the concentration range ca. 3.7×10^{-5} to 3.7×10^{-2} M. (ii) Both the duration and severity of the lag as well as the observed first-order rate constant for decomposition of **1b** and **1c** are substantially altered by initiation of the reaction with various mixtures of **1b** or **1c** with **1a**. (iii) Complex **1a** may be obtained, after neutralization, from the partial decomposition of **1b** or **1c** at $H_0 = 1.50$.[17]

This situation is substantially altered in much more strongly acidic H_2SO_4/H_2O mixtures (Figure 2). At H_0 ca. −5.0 (ca. 9.95 M H_2SO_4) spectrophotometric observations of the decomposition of all three complexes show a rapid "burst" of absorbance change (too fast to quantitate under these conditions) followed by a much slower first-order decay which is identical for all three compounds. Significantly, manometric measurements of the rate of ethylene evolution are also identical for all three compounds under these conditions and are in excellent agreement with the spectrophotometric results (Figure 2). These observations require a common intermediate in the decomposition of all three complexes and suggest that in such strongly acidic media the activity of water is sufficiently reduced[18,19] to prevent the hydration of the intermediate to form **1a** and that Scheme II now applies.[20]

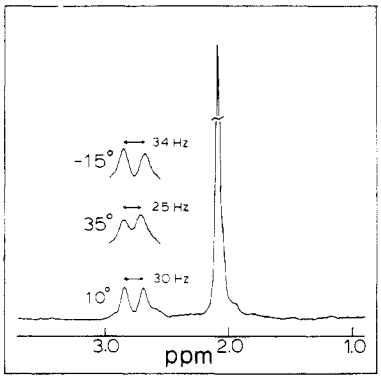


Figure 3. ^1H NMR spectrum of the intermediate formed from **1a** in ca. 13.0 M D_2SO_4/D_2O at 10 °C (insets 35 and −15 °C) using a JEOL JNM-FX200 FT NMR spectrometer operating at 199.5 MHz. The chemical shifts indicated are relative to external Me_4Si.

Because of the relatively slow rate of decomposition of the intermediate in such strongly acidic media, it is possible to observe it directly by Fourier transform ^1H NMR spectroscopy. Figure 3 shows the ^1H NMR spectrum observed at 199.5 MHz and 10 °C as soon as possible after makeup of a sample of **1a** in ca. 13.0 M D_2SO_4/D_2O (D_0 ca. −6.6).[21,22] The spectrum is characterized by a 12.0 proton singlet resonance at 2.06 ppm (relative to external Me_4Si) representing the cobaloxime equatorial methyls and two rather broad singlets of approximately equal intensity at 2.66 and 2.81 ppm integrating to a total of four protons. Similar spectra may be observed at D_0 ca. −6, as well as in samples of **1b** and **1c** in similar media.[23] When the intermediate is observed at 60 MHz, the organic ligand gives a broad singlet ($w_{1/2}$ ca. 15 Hz) centered at 2.74 ppm. Figure 3 also shows the temperature dependence of the two organic ligand resonances (at 199.5 MHz). The separation between the two resonances can be seen to decrease from 34 Hz at −15 °C to 25 Hz at 35 °C while the relative intensity of the two resonances changes such that the upfield member increases at the expense of the downfield member as the temperature is increased. These observations are consistent with the formulation of the intermediate as a cobaloxime(III)–ethylene π complex in which rotation about the π bond axis is relatively slow (on the NMR time scale) and two different preferred conformations exist, presumably one in which the ethylene hydrogens point toward the equatorial oxime oxygens and one in which the ethylene hydrogens point toward the equatorial methyls, leading to a chemical shift difference of about 0.15 ppm for the ethylene hydrogens in the two conformations. However, as the temperature-dependent change in intensity of the two organic ligand resonances is quite small, it is not possible to rule out a σ-bonded ethylcobaloxime carbonium ion undergoing relatively slow topomerization (on the NMR time scale) as the intermediate.

Acknowledgment. This research was supported by the Robert A. Welch Foundation, Houston, Texas, Grant

(17) E.g., decomposition of 4.46 mmol of **1b** for 50 min at 25.0 °C in 500 mL of 0.0217 M H_2SO_4 (H_0 = 1.50) provided, after neutralization, reaction with pyridine, concentration, and workup by silica gel chromatography, 0.84 mmol of unreacted starting material (18.8%) and 0.25 mmol (5.7%) of (2-hydroxyethyl)(pyridine)cobaloxime.

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Y-749. We are grateful to the Chemistry Department of The University of Texas at Dallas for the use of the JEOL JNM-FX200 FT-NMR spectrometer and particularly to Dr. Dean Sherry for his assistance with the FT NMR measurements.

Registry No. 1a, 15218-80-1; **1b**, 80422-34-0; **1c**, 64707-51-3; **2**, 80422-35-1.

Catalytic Polymerization of Acetylenes and Olefins by Tetrakis(acetonitrile)palladium(II) Bis(tetrafluoroborate)

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Summary: The cationic Pd(II) compound $[Pd(CH_3CN)_4](BF_4)_2$ was found to catalyze the polymerization of H—C≡C—R (R = Ph, COOMe), styrene, α-methylstyrene, 1,3-cyclohexadiene, norbornylene, and norbornadiene under very mild conditions. The polyacetylenes are highly colored and have relatively high molecular weights. The poly(phenylacetylene) has a trans configuration around the C=C bond. The polymerization of 1,3-cyclohexadiene leads predominantly to the 1,2 polymer with only minimal cross-linking. The norbornane framework is retained during the polymerization of norbornylene. The poly(norbornadiene) is a highly cross-linked material.

We wish to report that the cationic Pd(II) compound $[Pd(CH_3CN)_4](BF_4)_2$, 1,[1] is a versatile catalyst for the polymerization of a wide range of acetylenes and olefins under relatively mild conditions. Except for a few halides of transition metals in high oxidation states, e.g., $TiCl_4$ and $FeCl_3$, transition-metal compounds in general have not been found to catalyze the cationic polymerization of olefins.[2] This is particularly true for the "softer" transition metals belonging to the second and third period of group 8. However, we have recently presented evidence for the generation of carbonium ions by the interaction of olefins with 1.[3] Therefore, it should be expected that 1 would act as a good initiator for cationic polymerization reactions. Indeed, we find this to be true, and our results are summarized in Table I. These reactions all involved the addition of 100 equiv of the monomer to a 1×10^{-2} M solution of 1 and were carried out under air- and moisture-free conditions by using standard vacuum line techniques. Consistent with a cationic polymerization mechanism, we found that compared to phenylacetylene, the polymerization of the electron-deficient methyl propiolate took place only at a significantly higher temperature and led to a polymer with lower molecular weight. Similarly, no polymerization was observed for the electron-deficient olefins, acrylonitrile and methyl acrylate.

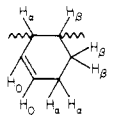
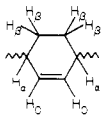
The polyacetylenes are soluble in organic solvents and are highly colored, consistent with the presence of extensive conjugation. The poly(phenylacetylene) shows a maxima at 237 nm (ϵ 1.8×10^6 M^{-1} cm^{-1}, mol wt 9000) with a shoulder at 339 nm (ϵ 6.4×10^5 M^{-1} cm^{-1}) in THF. The corresponding maxima and shoulder for poly(methyl propiolate) are at 232 nm (ϵ 1.85×10^5 M^{-1} cm^{-1}, mol wt 3000) and 291 cm (ϵ 9×10^4 M^{-1} cm^{-1}), respectively. The poly(phenylacetylene) that we have obtained has one of the highest molecular weights recorded thus far.[4] Its infrared spectrum (KBr pellet) exhibits an absorption at 1595 cm^{-1}, indicating the presence of polyconjugated C=C bonds. Two strong bands appear at 755 and 695 cm^{-1}, and these correspond to the C–H out-of-plane deformations of monosubstituted benzene rings. The region between 2000 and 1700 cm^{-1} also exhibits the characteristic absorption of monosubstituted benzenes. In addition, a band at 910 cm^{-1} indicates a trans configuration around C=C bond.[5] When $CHCl_3$, instead of CH_3CN, was used as the solvent, a slightly different polymer exhibiting infrared bands at both 910 and 870 cm^{-1} was obtained. The latter band can be ascribed to a cis configuration around the C=C bonds.[5] Thus the stereostructure of the poly(phenylacetylene) obtained appears to be solvent dependent—in acetonitrile predominantly trans polymer

Table I. Catalytic Polymerization of Olefins and Acetylenes by $[Pd(CH_3CN)_4](BF_4)_2$ [a]

monomer	solvent	temp, °C	time	yield,[b] %	$\bar{M}_n$[c]
H—C≡C—Ph	CH_3CN	25	5 min	30	9000
H—C≡C—CO_2Me	CH_3CN	70	12 h	>90	3000
CH_2=CHPh	CH_3CN	25	5 min	>90	70000
CH_2=C(Me)Ph	CH_3NO_2	0	5 min	75	8000
	CH_3CN	25	30 min	40	2000
	CH_3NO_2	25	5 min	>90	*d*
	CH_3NO_2	25	60 min	>90	*d*

[a] A monomer to catalyst ratio of 100:1 was used in all cases. [b] Yields reported are those of isolated pure materials. [c] Molecular weights of polymers were determined by gel permeation chromatography using solutions of polymers in tetrahydrofuran. A 500-Å microstyragel column was used. The weights reported are those of standard polystyrene samples having GPC traces similar to those observed. [d] The polymer was insoluble in THF.

Table II. Expected ^1H NMR Data for Poly(1,3-cyclohexadiene)

	1,2-polycyclohexadiene	1,4-polycyclohexadiene
		
$H_o/(H_\alpha + H_\beta)$	1/3	1/3
H_α/H_β	1/1	1/2

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