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Electrochemistry Studies of a Metallacyclobutene Complex: Synthesis of a Furan Product by Oxidation of a Cobaltacyclobutene

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Summary: Two-electron oxidation of a cobaltacyclobutene, under electrochemical or chemical oxidizing conditions, produces a furan in high yield. Reaction of the cobaltacyclobutene or the furan with iron(III) chloride produces a butenolide.

Metallacyclobutenes have been proposed as intermediates in numerous transformations catalyzed by transition-metal complexes,[1−7] including the linear oligomerization and polymerization of alkynes promoted by transition-metal carbene complexes,[2] the Dötz reaction,[3] ring-closing metathesis reactions of dienynes,[4] metal-catalyzed cyclopropenation of alkynes with diazo carbonyl compounds,[5] the conversion of metal carbenes and alkynes to furans,[6] and the transition-metal-mediated conversion of cyclopropenes to furans.[7] Despite the fact that mechanistic proposals involving metallacyclobutene intermediates often invoke changes in metal oxidation state, no reports on the electrochemistry of metallacyclobutenes have previously appeared in the literature.[8,9] Recently we reported the reaction of a cobalt alkyne complex with ethyl diazoacetate to give a cobaltacyclobutene complex (**1**; see Scheme 1).[10] As part of our efforts toward defining the chemistry of late-metal metallacyclobutenes[11,12] and the electrochemistry of metallacycles[8,9] we have now examined the behavior of **1** toward electrochemical and chemical oxidation. Herein we report the first electrochemistry studies of a metallacyclobutene and demonstrate that either electrochemical or chemical oxidation of a cobaltacyclobutene leads to formation of a furan product in high yield.[13]

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[13] We previously reported the reaction of **3** with carbon monoxide to give an η^4-vinylketene complex, which in turn was converted to furan **5** upon heating in the presence of carbon monoxide.[11c]

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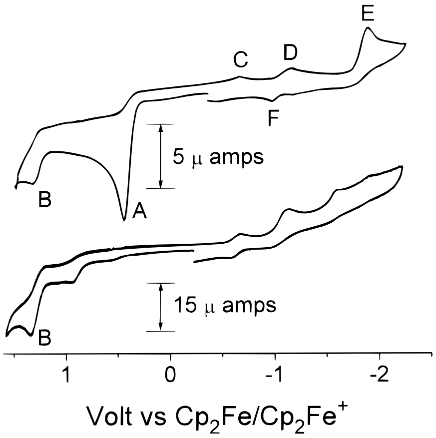
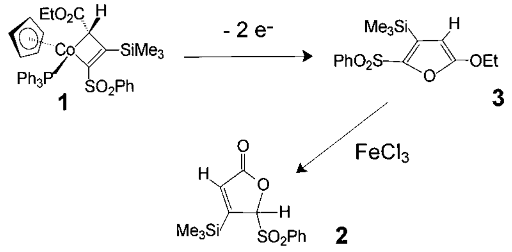


Figure 1. (Top) Cyclic voltammetry scan of 0.94 mM **1** in acetonitrile solution containing 0.1 M tetrabutylammonium hexafluorophosphate. The scan was initiated in the positive potential direction (platinum-disk working electrode, scan rate 100 mV/s). (Bottom) Cyclic voltammetry scan after bulk electrochemical oxidation of 0.59 mM **1**: (glassy-carbon-disk working electrode, scan rate 100 mV/s).

Scheme 1



In a preliminary attempt at metallacyclobutene oxidation we examined the reaction of **1** (0.07 mmol) with iron(III) chloride (0.44 mmol) in diethyl ether (16 mL) and found that after complete consumption of **1** the only organic product recovered from the reaction mixture was 4-(trimethylsilyl)-5-(phenylsulfonyl)furan-2(5*H*)-one (**2**), which was isolated as a white analytically pure powder in 31% yield.[14] In principle, butenolide **2** could be formed from the corresponding ethoxy-substituted furan **3** by an acid-catalyzed hydrolysis. When acetonitrile is employed as solvent in an attempted reaction of **1** with iron(III) chloride, no organic products were obtained from the chromatographic workup, and 75% of starting material **1** was recovered.

A cyclic voltammetry (CV) scan of **1** in acetonitrile solution is shown in the top portion of Figure 1.[15] This voltammogram, initiated in the positive potential direction, shows the presence of six waves labeled A−F; waves A ($E_{p_a} = +0.44$ V)[16] and B ($E_{p_a} = +1.34$ V) are of foremost importance to this study. Wave A arises from the oxidation of **1**. The chemical irreversibility of this wave, which persists at a scan rate of 5 V/s, indicates that oxidation of the cobaltacycle results in a rapid homogeneous reaction.[17,18] We will demonstrate that wave A represents a two-electron-oxidation process in which furan **3** is generated and that wave B arises from the oxidation of **3**.[20,21]

Exhaustive bulk electrochemical oxidation of a red solution of **1** required only 15 min and an average of 2.3 F/equiv to come to completion.[23] A CV scan of the resulting yellow solution was obtained immediately after completion of the electrolysis and is displayed in the bottom portion of Figure 1. The absence of waves A and E indicates complete consumption of **1** by the electrolysis process. Removal of solvent followed by chromatographic workup of the residue afforded a yellow product, identified as furan **3**, which was isolated in 82% yield.[14,24] CV scans of the anodic window of isolated **3** show only the presence of wave B, which arises from oxidation of **3**.[25] Hence, the appearance of waves in addition to B after exhaustive oxidation of **1** (Figure 1, bottom) indicates that the electrolysis generates minor products in addition to the furan.[26]

The conversion **1** → **3** was also accomplished by chemical means.[27] Chemical oxidation studies were initially conducted in acetone-d_6 solutions in NMR tubes. Treatment of **1** with 2 equiv of silver tetrafluoroborate for 4 h resulted in 86% yield of **3** (95% conversion of **1**). The rate of the reaction was slower

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(14) For butenolide **2**: mp 102−103 °C; IR (NaCl, neat) 1794, 1761 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.41 (s, 9H), 5.85 (d, 1H, $J = 1.5$ Hz), 6.47 (d, 1H, $J = 1.5$ Hz), 7.58−7.97 (m, 5H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.5 MHz) δ −1.46, 96.8, 129.4, 129.8, 134.3, 135.0, 136.0, 165.9, 170.1. Anal. Calcd for $C_{13}H_{16}O_4SSi$: C, 52.68; H, 5.44. Found: C, 52.61; H, 5.23. For 2-(phenylsulfonyl)-3-(trimethylsilyl)-5-ethoxyfuran (**3**): IR (C_6D_6) 1587 cm^{-1}; ^1H NMR (C_6D_6) δ 0.46 (s, 9H, $SiMe_3$), 0.80 (t, $J = 7.2$ Hz, 3H, CH_3), 3.30 (q, $J = 7.2$ Hz, 2H, OCH_2), 4.94, (s, 1H, =CH), 6.84−8.08 (m, 5H, C_6H_5); $^{13}C\{^1H\}$ NMR (C_6D_6) δ −0.3, 14.1, 67.1, 88.2, 127.8, 129.1, 132.6, 132.8, 142.1, 142.4, 163.4; MS (EI) *m*/*z* (relative intensity) 324 (34, M^+); high-resolution MS calcd for $C_{15}H_{20}O_4SSi$ 325.0930, found 325.0935. Anal. Calcd for $C_{15}H_{20}O_4SSi$: C, 55.53; H, 6.21. Found: C, 55.91; H, 6.39.

(15) All potentials are reported vs the ferrocene/ferrocenium (Fc/Fc^+) couple, which has an $E_{1/2}$ value of +0.39 V vs SCE in acetonitrile/0.1 M $TBAPF_6$ solution.

(16) E_{p_a} = anodic peak potential. E_{p_c} = cathodic peak potential.

(17) For a discussion of electrode reactions with coupled homogeneous chemical reactions, see: Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; pp 429−483.

(18) Plots of the peak current for wave A vs (scan rate)$^{1/2}$ failed to exhibit linearity over an order of magnitude increase in scan rate for any solvent (CH_3CN, THF, CH_2Cl_2) or working electrode material (platinum, glassy carbon, or gold disk) employed in this study. This indicates weak adsorption of the cobaltacycle to the electrode surface and accounts for the significantly larger current observed for wave A compared to wave E in CV scans of **1**.[19] The least amount of adsorption was observed when either a glassy-carbon or platinum electrode was used in acetonitrile solution.

(19) For a discussion of adsorption in cyclic voltammetry experiments, see: Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; pp 525−532.

(20) The minor waves C ($E_{p_c} = -0.67$ V) and D ($E_{p_c} = -1.16$ V) are product waves of B and A, respectively.

(21) The cobaltacyclobutene also undergoes a two-electron, chemically irreversible reduction at wave E ($E_{p_c} = -1.90$ V). Wave F ($E_{p_a} = -0.97$ V) is a product of E. The two-electron nature of E was confirmed by bulk electrolysis studies. For example, bulk electrochemical reduction of 0.0228 g of **1** at an applied potential of −2.20 V using a platinum-basket electrode required 5.983 C (1.92 faraday/equiv).

(22) The electrolysis was conducted in acetonitrile solution using a platinum-basket working electrode.

(23) The number of faradays per equivalent ranged from 2.12 to 2.66 when the applied potential was set in the range 0.44−0.69 V. Typically 21−25 mg of **1** was used in the bulk electrolysis experiments.

(24) Isolation of the furan from electrolysis experiments was conducted as follows. After the acetonitrile solvent was removed, toluene was added to the residue and the resulting mixture was filtered, thereby separating most of the supporting electrolyte from the product. Chromatography of the toluene solution was conducted under a nitrogen atmosphere on a silica gel column using 5% ethyl acetate−95% benzene (v/v) as the eluting solution.

(25) The cathodic window CV scan of **3** shows only the presence of a chemically irreversible reduction wave at $E_{p_c} = -2.66$ V on a glassy-carbon working electrode. This wave is not shown in the potential window of Figure 1.

(26) CV scans of the butenolide **2** under the same experimental conditions show a chemically irreversible reduction wave at −1.96 V. This wave is not present in CV scans obtained after oxidation of **1**.

(27) All chemical oxidations were conducted under a nitrogen atmosphere.

and the yield of **3** was lower when similar experiments were conducted using diacetylferrocenium as the oxidizing agent. For example, treatment of **1** with 2 equiv of diacetylferrocenium resulted in a 47% yield of **3** (56% conversion of **1**) after 4 h and a 58% yield of **3** (70% conversion of **1**) after 24 h. When 3 equiv of diacetylferrocenium was used, a 74% yield of **3** (82% conversion of **1**) was observed after 4 h. The butenolide product **2** was not observed in these NMR-scale experiments. Chemical oxidation studies were also conducted in acetonitrile solution. Reaction of **1** with 4 equiv of $AgBF_4$ in acetonitrile solution afforded 63% of **3** and 28% of recovered **1**; butenolide **2** was not observed in this experiment.

The results of the electrochemistry studies and the chemical oxidation experiments using silver tetrafluoroborate or diacetylferrocenium shed light on the reaction of **1** with iron(III) chloride: two-electron oxidation of **1** by chemical or electrochemical means affords furan **3**. To determine whether iron(III) chloride promotes the conversion **3** → **2**, a reaction between **3** and iron(III) chloride was conducted in diethyl ether solution. After the reaction was allowed to proceed for 2.5 h, solvent was removed and the residue chromatographed to afford **2** in 58.4% yield; no furan starting material was observed.

The reactions described here are the first reported oxidation reactions of metallacyclobutenes. Although oxidation of the cobaltacycle affords the same product observed upon treatment of **1** with CO,[9a] the electrochemical route affords the most rapid route to the furan. We are currently exploring the reactivity patterns of cobaltacyclobutenes and are investigating the redox-promoted reactions of other metallacyclobutene complexes.

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