Carbon-Sulfur Bond Cleavage of Benzothiophene by $\text{Cp}^*\text{Co}(\text{C}_2\text{H}_4)_2$

Natalie H. Chan, James H. Roache, and William D. Jones*

Department of Chemistry, University of Rochester, Rochester, NY 14627

*email: jones@chem.rochester.edu

ABSTRACT:

$\text{Cp}^*\text{Co}(\text{C}_2\text{H}_4)_2$ was reacted with benzothiophene and C–S activation of the vinyl-sulfur bond was observed. The resulting product, $[\text{Cp}^*\text{Co}]_2(\mu\text{-}\kappa^2\text{-C,S-C}_8\text{H}_6\text{S})$ was characterized by ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, ^{13}C DEPT-135 NMR, and ^1H - ^{13}C 2D HSQC spectroscopies. The broad Cp^* methyl peaks in these spectra suggested a fluxional structure.

Keywords: desulfurization; cobalt; C–S cleavage

Introduction

The removal of sulfur from natural gas and refined petroleum products is commonly referred to as hydrodesulfurization (HDS). This process prevents sulfur from poisoning catalysts in automobiles and reduces the emission of SO_2 in combusting fossil fuels. Recently, the U.S. Environmental Protection Agency finalized their regulations in Tier 3 Vehicle Emissions and Fuel Standards Program that federal gasoline will be required to meet an annual average standard of 10 ppm of sulfur by 2017 [1]. Therefore, there is a pressing need to develop catalysts containing inexpensive and abundant metal centers for C–S bond activation in organosulfur compounds, which is the elementary step in HDS. First row transition metals are thus attractive choices for serving as models for C–S bond activation from this perspective.

Most of the research in this area focuses on homogeneous modeling of the HDS process using various metal catalysts. The sulfur compounds of interest are aromatic heterocycles such as thiophene, benzothiophene, and dibenzothiophene due to their lower reactivity as compared to thiols, sulfides, and disulfides. The end result in most of these reactions is metal insertion into the carbon-sulfur bond either through oxidative addition or migration of the α -carbon forming a metalthiobenzene ring with the transition metal. Bianchini, et al., discovered an unprecedented coordination pathway for benzothiophene leading to the metal inserted metallocycle product using $[(\text{triphos})\text{Ir}(\text{C}_6\text{H}_6)]\text{BPh}_4$ as a precursor [2]. Upon reaction of this complex with an excess of benzothiophene at 25 °C, they observed the formation of an η^3 bound benzothiophene complex

with the evolution of benzene (Scheme 1). Benzothiophene was coordinated to the iridium complex through the sulfur atom and the unsubstituted carbon-carbon double bond. Heating this complex in THF above 40 °C led to iridium insertion into the carbon-sulfur bond. Based on ^{31}P and ^1H NMR spectroscopy, no intermediates were observed in either the coordination of the benzothiophene or the metal insertion step. X-ray diffraction analysis of the iridium inserted product showed a planar metallocycle similar to metallocycles observed with other metal complexes [3], and the bond lengths within the metallocycle are indicative of a delocalized π -system. The relatively low temperature at which the metal insertion occurs can be accounted for by considering the η^3 bound benzothiophene complex to be on the pathway to C–S bond cleavage. This example illustrates that the coordination pathway is dependent on the transition-metal complex used, but, the end result remains the same, metal insertion into the carbon-sulfur bond.

Earlier studies in our group demonstrate that reactions of $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{Ph})\text{H}$ with thiophene, benzothiophene, and dibenzothiophene at 65 °C lead to products arising from oxidative addition at the carbon-sulfur bond (Scheme 2) [4]. Mechanistic studies with deuterated thiophenes have shown that the reaction proceeds through η^1 -S bound and η^2 -C,C bound intermediates [5]. Further experiments provided insight into the steric and electronic effects that control insertion of rhodium into one C–S bond vs. another [6-8] DFT studies of the selectivity seen in these insertions provided evidence for an η^2 -C,S species prior to C–S cleavage [9,10]. An

analogous dimethylthiophene insertion product with iridium was reported by Angelici, $\text{Cp}^*\text{Ir}(\kappa^2\text{-C,S-C}_4\text{H}_2\text{Me}_2)(\text{PMe}_3)$, which forms by reaction of $\text{Cp}^*\text{Ir}(\eta^4\text{-thiophene})$ with PMe_3 [11].

Our group has also investigated the activation of thiophene using precursors for the reactive $[\text{M}(\text{dippe})]$ fragment where $\text{M} = \text{Ni}$ [12,13], Pd [14,15], and Pt [14]. The $[\text{Pt}(\text{dippe})]$ fragment showed unique reactivity in that it was observed to insert into the hindered C–S bond of 4,6-dimethyldibenzothiophene (eq 1) [16]. DFT studies of substituted thiophenes were also carried out, showing good agreement with experimental regioselectivities [17-19]. Reactions of the nickel and palladium fragments with benzothiophene and dibenzothiophene have also been reported [12-14].

Our group also reported carbon–sulfur cleavage by a cobalt complex. Reaction of $(\text{C}_5\text{Me}_5)\text{Co}(\text{C}_2\text{H}_4)_2$ with thiophene at 70 °C results in the formation of a dinuclear cobalt species in which the carbon-sulfur bond of thiophene was cleaved (eq 2) [20]. ^1H NMR studies of this dinuclear molecule revealed a fluxional structure with a broad C_5Me_5 resonance which separated into two distinct peaks upon cooling to -50°C . This same cobalt complex was also reacted with

dibenzothiophene yielding a similar dinuclear complex (eq 3) [21]. Unfortunately, upon cooling to $-80\text{ }^{\circ}\text{C}$, the broad C_5Me_5 resonance could not be resolved. It has been postulated that these reactions occur through the loss of ethylene followed by insertion into the carbon–sulfur bond. The carbon–sulfur inserted product then reacts with another cobalt fragment forming the dinuclear adduct.

In this report, the C–S bond cleavage in benzothiophene, a common constituent of petroleum-related deposits, by $\text{Cp}^*\text{Co}(\text{C}_2\text{H}_4)_2$ is investigated and the activation product is characterized by ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, ^{13}C DEPT-135 NMR, and ^1H - ^{13}C 2D HSQC spectroscopies, and by single crystal X-ray analysis.

Benzothiophene C–S Bond Activation

Three equivalents of benzothiophene was reacted with $\text{Cp}^*\text{Co}(\text{C}_2\text{H}_4)_2$ for 95 h at $100\text{ }^{\circ}\text{C}$ in benzene. The reaction yielded a black crude product $(\text{Cp}^*\text{Co})_2(\mu\text{-}\kappa^2\text{-C,S-C}_8\text{H}_6\text{S})$, **1**, in 80 % yield. Based on the NMR spectra recorded and previous work on similar organosulfur compounds, we propose an analogous structure to that seen with thiophene and dibenzothiophene (eq 4).

A single crystal X-ray structure of **1** was determined. The molecule crystallizes in space group $P2_1/n$ with $Z = 2$, indicating that the molecule lies on a special position. Solution of the structure revealed that **1** lies on a 2-fold axis, with the κ^2 -benzothiophene being disordered over two orientations. The 2-fold lies perpendicular to the Co–Co axis. Figure 1 shows the resulting

structure. Even with the disorder present, one can see differences in the binding of the two cobalt atoms to sulfur. The Co1-S1 bond is substantially shorter (2.073 Å) than the Co1A-S1 bond (2.209 Å). Similarly, the Co1-C18 bond is shorter (1.91 Å) than the Co1A-C18 bond (2.05 Å). The Co1A-C17 bond is also long (2.19 Å), consistent with the formulation of the complex as Co1 being in the +3 oxidation state, with Co1A in the +1 oxidation state. This same type of disorder was observed in the thiophene and dibenzothiophene X-ray structures [20,21].

Fig. 1. Structure of $(\text{Cp}^*\text{Co})_2(\kappa^2\text{-S,C-C}_8\text{H}_6\text{S})$, **1**. Ellipsoids are shown at the 50% level.

The ^1H NMR spectrum of the product was recorded (Figure 2). The Cp^* resonance integrates as 30 protons to the 6 hydrogens of the benzothiophene ligand, in agreement with the dinuclear structure. The Cp^* peak was unusually broad, suggesting a dynamic exchange which gives an apparent symmetry in the averaged NMR spectrum. This process was assigned as a fluxional process in which the η^2 -coordinated double bond has interchanged cobalt atoms (eq 5). In the ^1H NMR spectrum, the resonances at δ 4.10 and 9.27 are assigned to the vinylic protons of the ring-opened benzothiophene. The resonance at δ 4.10 was believed to be H_a , as it is shielded by its proximity to two cobalt centers, but this assignment is tentative (*vide infra*). The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** was also examined, and showed a broad resonance at δ 88.90 that was presumed to be the central Cp^* carbons and two singlets at δ 178.1 and 86.66 for the $\text{C}_{\alpha/\beta}$ or $\text{C}_{\beta/\alpha}$ carbons of the κ^2 -benzothiophene (Figure 3).

Fig. 2. ^1H NMR spectrum of **1** in benzene- d_6 .

To determine the vinylic carbon assignments, ^1H - ^{13}C HSQC and $^{13}\text{C}\{^1\text{H}\}$ DEPT spectra were recorded (Figures 4 and 5). Using the data from the 2D HSQC spectrum, the aromatic peaks and the broad Cp* methyl peak in the ^{13}C NMR spectrum could be assigned. The pairs of upfield/downfield signals for the vinylic hydrogens in the ^1H and ^{13}C spectra could be correlated, but we were once again unsure of assigning the peaks at δ [9.27, 178.14] and [4.10, 86.72] to $\text{H}_\alpha/\text{C}_\alpha$ and $\text{H}_\beta/\text{C}_\beta$ or vice versa. Since C_α and the Cp* ring carbons are both attached to cobalt centers, both of them have the potential to give a broad peak in the ^{13}C NMR spectrum due to quadrupolar relaxation from the cobalt. A ^{13}C DEPT-135 spectrum differentiated between these peaks (Figure 4). The absence of the peak at δ 89.90 in the ^{13}C DEPT-135 spectrum confirms that this peak is due to the quaternary Cp* ring carbons. The two resonances at δ 178 and 86 are present in both ^{13}C NMR and the DEPT-135 spectra, implying that these are the vinylic peaks. In both ^{13}C and DEPT-135 spectra, the resonance at δ 86.7 has a significantly higher intensity than

= 340 vs. 110 Hz).

Fig. 3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** in benzene- d_6 .

Fig. 4. ^1H - ^{13}C HSQC spectrum of **1** in benzene- d_6 .

Fig. 5. $^{13}\text{C}\{^1\text{H}\}$ DEPT spectrum of **1** in benzene- d_6 .

Since C_α is bonded to two quadrupolar cobalt atoms, it would be expected to have a much shorter relaxation time and be broadened more than C_β . Therefore, the $^1\text{H}/^{13}\text{C}$ resonances at δ 9.27/178.14 are assigned to $\text{H}_a/\text{C}_\alpha$ and those at δ 4.10/86.72 are assigned to $\text{H}_b/\text{C}_\beta$.

Conclusions

$\text{Cp}^*\text{Co}(\text{C}_2\text{H}_4)_2$ was synthesized from $\text{Co}_2(\text{CO})_8$ and reacted with benzothiophene. The resulting product, $[\text{Cp}^*\text{Co}]_2(\mu\text{-}\kappa^2\text{-C,S-C}_8\text{H}_6\text{S})$ was characterized by ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, ^{13}C DEPT-135 NMR and ^1H - ^{13}C 2D HSQC. The broad Cp^* methyl peaks in these spectra are consistent with a fluxional structure, as seen with the DBT analog [21].

Experimental

General Considerations. Dry and deoxygenated dichloromethane and hexanes were collected from an Innovative Technology PS-MD-6 solvent purification system. Dry and oxygen-free benzene- d_6 , THF and ethyl ether were vacuum distilled from purple solutions of Na and benzophenone under a nitrogen atmosphere. CDCl_3 and xylenes was used without further purification. $\text{Cp}^*\text{Co}(\text{C}_2\text{H}_4)_2$ was synthesized from $\text{Co}_2(\text{CO})_8$ as reported in the literature [22]. NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer. Chemical shift values

in NMR spectra were referenced internally to the residual solvent resonances. Elemental analysis was obtained from the CENTC Elemental Analysis Facility at the University of Rochester.

Reaction of (C₅Me₅)Co(C₂H₄)₂ with Benzothiophene. (C₅Me₅)Co(C₂H₄)₂ (0.8 mmol, 200 mg) and three equivalents of benzothiophene (2.4 mmol, 324 mg) were dissolved in 50 mL of benzene. The orange-brown solution was placed in a 100 °C oil bath for 4 d. A ¹H NMR spectrum of the crude reaction mixture revealed that the cobalt starting material had been consumed. The benzene was removed under vacuum, and the crude product was transferred to a sublimation vessel. The crude product was sublimed at 60 °C for 3.5 h to remove any excess benzothiophene starting material. The sample was recrystallized from CH₂Cl₂/toluene/hexane to yield 170 mg product (80%). ¹H NMR (500 MHz, benzene-*d*₆, 25 °C) of crude [Cp*Co]₂(μ-η²,η³-C₈H₆S): δ 9.27 (d, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 7.4 Hz, 1H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.55 (t, *J* = 7.4 Hz, 1H), 4.10 (d, *J* = 8.0 Hz, 1H), 1.68 (s, 30H). ¹³C{¹H} NMR (125 MHz, benzene-*d*₆, 25 °C): δ 178.14 (s, CH_α), 149.99 (s, C), 138.45 (s, C), 126.85 (s, CH), 125.62 (s, CH), 124.54 (s, CH), 124.07 (s, CH), 88.90 (br s, C₅Me₅), 86.66 (s, CH_β), 10.59 (br s, C₅Me₅). ¹³C DEPT-135 NMR (125 MHz, benzene-*d*₆, 25 °C): δ 178.19 (s, CH_α), 126.87 (s, CH), 125.64 (s, CH), 124.56 (s, CH), 124.09 (s, CH), 86.68 (s, CH_β), 10.62 (br s, C₅Me₅). A ¹H-¹³C 2D HSQC NMR spectrum (500 MHz, benzene-*d*₆, 25 °C) of crude product was recorded. Anal. Calcd. (found) for Co₂C₂₈H₃₆S·1/4CH₂Cl₂: % C, 62.40 (62.73); % H, 6.77 (7.10); % N, 0.00 (0.044).

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Supporting Information Available.

Supporting information give preparative details for Cp*Co(C₂H₄)₂ and X-ray structural data for **1**. A listing of crystallographic information including data collection parameters, bond lengths, fractional atomic coordinates, and anisotropic thermal parameters (PDF) for complex **1** (CCDC deposition #1408675).

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Graphical Abstract

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