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Cleavage of Carbon−Sulfur Bonds of Benzothiophene and Dibenzothiophene Mediated by Trinuclear Pentahydride Complex of Ruthenium $\{(\eta^5\text{-}C_5Me_5)Ru\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$

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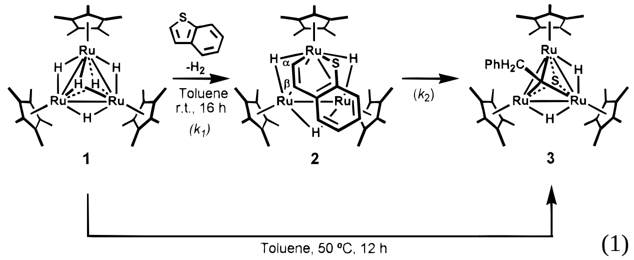
In recent years, the hydrodesulfurization (HDS) process has attracted a great deal of interest of a number of inorganic and organometallic chemists. Most of the investigations in this field have been directed toward understanding how organosulfur compounds interact with transition metal sites on catalyst surfaces and are activated in ways that result in desulfurization. Among organosulfur compounds found in petroleum feedstock, the broad class of thiophenes is most difficult to desulfurize due to the stabilization by their aromatic character. Thus many inorganic and organometallic chemists have devoted a considerable amount of effort to open a path to the HDS of thiophenes in these 10 years.[1] Thus far, only several successful examples of the carbon−sulfur bond cleavage of benzothiophene and dibenzothiophene by mono- and dinuclear transition metal complexes have been reported,[2] while there is a vast chemistry of organosulfur-transition metal complexes. In the course of our study of substrate activation on multimetallic sites by using the trimetallic hydride cluster $(Cp'Ru)_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ (**1**) ($Cp' = \eta^5$ -C_5Me_5),[3] we achieved a consecutive cleavage of two carbon−sulfur bonds in benzothiophene and dibenzothiophene. We shall describe, herein, a new approach to hydrodesulfurization of benzothiophene and dibenzothiophene giving ethylbenzene and biphenyl, respectively, with the aid of the trimetallic hydride cluster **1**.

Treatment of **1** with 3 equiv of benzothiophene in toluene at 50 °C for 12 h quantitatively afforded μ_3-sulfido−μ_3-alkylidyne complex $(Cp'Ru)_3(\mu\text{-}H)_2(\mu_3\text{-}S)(\mu_3\text{-}CCH_2C_6H_5)$ (**3**) as a result of the successive cleavage of two carbon−sulfur bonds (eq 1).



(1)

Compound **3** was unequivocally characterized on the basis of ^{1}H and ^{13}C NMR spectra and elemental analysis. The signal for the three C_5Me_5 ligands was observed as a single peak (δ 1.82) at room temperature due to a rapid site-exchange of the two hydrides on the edges of the Ru_3 triangle.[4] In the ^{13}C NMR spectrum, a characteristic signal for the μ_3-alkylidyne carbon appeared at δ 309.1 as a singlet.

An X-ray study using a single-crystal obtained from cold (−30 °C) tetrahydrofuran revealed product **3** to have triply bridging sulfide and alkylidyne ligands on the opposite side of the Ru_3 plane (Figure 1).[5]

Two carbon−sulfur bonds of benzothiophene were cleaved stepwise by the cooperative action of three ruthenium centers. When we monitored the reaction of **1** with 3 equiv of benzothiophene in toluene-d_8 at 40 °C by means of ^{1}H NMR spectroscopy, an intermediary thiaruthenacyclohexadiene complex **2**, formed as a result of the oxidative addition of the carbon−sulfur bond toward one of three ruthenium centers, could be observed together with a singlet peak (δ 4.5) due to the liberated dihydrogen in the initial stage of the reaction. After 90 min, the signals due to the starting complex **1** completely disappeared, and the yield of **2** reached about 90%. Thiaruthenacycle **2** could be isolated as spectroscopically pure black-green solids from the resulting mixture at −30 °C. Complex **2** could be definitely characterized on the basis of the ^{1}H and ^{13}C NMR and ^{1}H−^{13}C HSC spectra. The ^{1}H NMR spectrum displayed two doublet resonances at δ 9.38 (J = 8.5 Hz, 1H) and 6.32 (J = 8.5 Hz, 1H)

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(4) The variable-temperature ^{1}H NMR spectra of the C_5Me_5 region demonstrated the fluxionality of **3**. In the ^{1}H NMR spectrum measured in tetrahydrofuran-d_8 at −80 °C, two resonance signals for C_5Me_5 ligands were observed at δ 1.84 and 1.66 in the intensity ratio of 2:1. These signals coalesced into one signal (δ 1.79) at −55 °C.

(5) Complex **3** crystallized in the triclinic system, space group $P\bar{1}$ (# 2). In a unit cell, four molecules are included, and one of two independent molecules is illustrated in Figure 1.

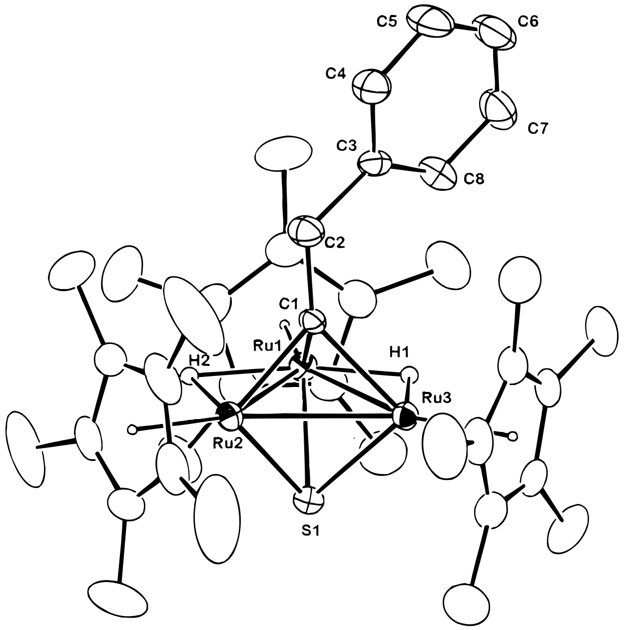


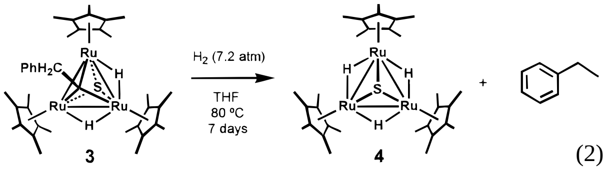
Figure 1. Molecular structure of $[(\eta^5\text{-}C_5Me_5)Ru]_3(\mu\text{-}H)_2(\mu_3\text{-}S)(\mu_3\text{-}CCH_2C_6H_5)$ (**3**). The thermal ellipsoids correspond to 30% probability. Selected bond length (Å) and angles (deg) are as follows: Ru1−Ru2 2.7459(9), Ru1−Ru3 2.7331(6), Ru2−Ru3 2.7478(7), Ru1−S1 2.293(2), Ru2−S1 2.277(1), Ru3−S1 2.288(2), Ru1−C1 2.079(4), Ru2−C1 2.016(6), Ru3−C1 2.063(5), C1−C2 1.500(9), C2−C3 1.529(9); Ru2−Ru1−Ru3 60.20(2), Ru1−Ru2−Ru3 59.67(2), Ru1−Ru3−Ru2 60.13(3), Ru1−C1−C2 130.5(3), Ru2−C1−C2 123.8(3), Ru3−C1−C2 133.1(4), C1−C2−C3 120.6(4).

assignable to the methine protons bonded to C_α and C_β, respectively, of the metallacycle moiety of **2**. The ^{13}C resonance signals for C_α and C_β appeared at δ 176.0 (d, $J = 144.0$ Hz) and 70.1 (d, $J = 144.0$ Hz), respectively. The substantial downfield shift of the H_α and C_α resonances to the μ-carbene region unambiguously indicates that C_α is σ-bonded to a ruthenium atom and π-bonded to another ruthenium atom. This clearly shows that the cleavage of the C(*olefinic*)−S bond predominates over that of the C(*aromatic*)−S bond.

The reaction of **1** with excess (30 equiv) of benzothiophene to give **2** is pseudo first-order in **1** ($k_1 = \{-d[\mathbf{1}]/dt\}[\mathbf{1}]^{-1} = 1.28(2) \times 10^{-4}\ s^{-1}$ at 9.8 °C) with $\Delta H^\ddagger = 11.2(29)$ kcal mol^{-1} and $\Delta S^\ddagger = -36.7(9)$ cal mol^{-1} deg^{-1}. The large negative value of $\Delta S^\ddagger$ is characteristic of the reactions which proceed on the trimetallic site of **1** surrounded by three C_5Me_5 ligands and indicates that fitting into the size and shape between the substrate and the reaction site is essential for the reaction to proceed.

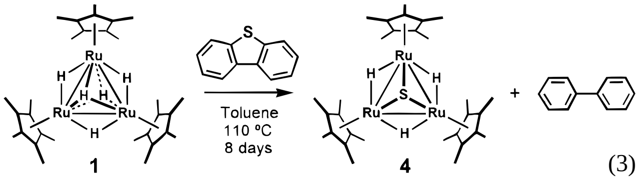
Thiaruthenacycle **2** isolated from the reaction between **1** and benzothiophene was quantitatively converted to **3** upon heating in toluene at 50 °C. A kinetic study applied to the isolated **2** showed that **2** was transformed into **3** in a first-order manner ($k_2 = \{-d[\mathbf{2}]/dt\}[\mathbf{2}]^{-1} = 5.35(14) \times 10^{-5}\ s^{-1}$ at 49.9 °C) with activation parameters of $\Delta H^\ddagger = 24.7(10)$ kcal mol^{-1} and $\Delta S^\ddagger = -1.9(29)$ cal mol^{-1} deg^{-1}. The value of activation entropy is consistent with the intramolecular mechanism for the cleavage of the C−S bond incorporated in thiaruthenacycle **2**.

The μ_3-alkylidyne−μ_3-sulfido complex **3** underwent hydrogenolysis by the treatment of **3** with hydrogen (7.2 atm) in tetrahydrofuran to produce ethylbenzene and the μ_3-sulfido complex **4** in 96% and 84% yields,[6] respectively (eq 2).



(2)

Complex **1** shows activity for the cleavage of the carbon−sulfur bonds in dibenzothiophene as well as benzothiophene. The reaction of **1** with dibenzothiophene proceeds at 110 °C for 8 days to form **4** and biphenyl in yields of 67% and 64%, respectively (eq 3).



(3)

Steric bulk around the sulfur atom in dibenzothiophene is much greater than that in benzothiophene. Therefore, these reaction paths seem very likely to be different from each other. Despite several attempts, we have not succeeded in isolating nor characterizing any intermediate species so far. However, in summary, we have demonstrated that the trimetallic hydride cluster **1** can effectively activate benzothiophene and dibenzothiophene under relatively mild conditions to cleave their C−S bonds selectively due to the cooperative action of the metal centers.

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Supporting Information Available: Table of ^1H and ^{13}C NMR spectral assignments of **2**−**4** and ORTEP diagram, text describing X-ray procedures, and tables of X-ray data, positional and thermal parameters, and distances and angles for **3** (10 pages). See any current masthead page for ordering and Web access instructions.

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[6] The μ_3-sulfido complex **4** was alternatively synthesized and characterized by the X-ray diffraction studies. Matsubara, K.; Suzuki, H.; Tanaka, M. To be published.