

A New Pathway for Thiophene Ring Opening by Transition Metals

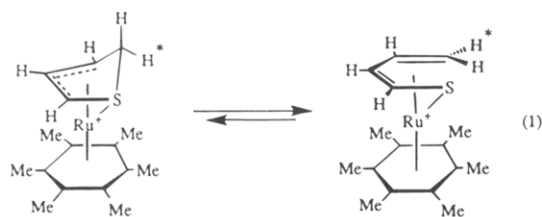
Karen M. Koczaja Dailey,[†] Thomas B. Rauchfuss,^{*,†}
Arnold L. Rheingold,^{*,‡} and Glenn P. A. Yap[‡]

School of Chemical Sciences
University of Illinois
Urbana, Illinois 61801
Department of Chemistry
University of Delaware
Newark, Delaware 19711

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Metal ion-promoted degradation of thiophenes is central to industrial processes aimed at the hydrogenolytic removal of organosulfur impurities from fossil fuels.^{1,2} The C–S cleavage step is especially crucial; three general types of ring-opened thiophene complexes have been identified (Chart 1). Simplest are those species in which only the sulfur atom and one carbon atom are coordinated, the result of oxidative addition of a C–S bond. Two versions of this structure (I and II in Chart 1) can be distinguished on the basis of the planarity, electron count, and degree of delocalization of the MSC₄ ring.^{3,4} Ring-opened thiophenes are also known to span two metals via sulfur and two carbon atoms (III in Chart 1). In the catalytic process, it is plausible that bonding modes I–III are related mechanistically such that loss of ligand from II gives I, which is electronically suited for binding a second metal to give III,⁵ which in turn is known to be susceptible to hydrogenolysis.^{5b} In this report we describe a fourth bonding mode for ring-opened thiophene (structure IV) that extends this series and is suggestive of a pathway for extrusion of the S atom.

The reduced thiophene complexes (C₆Me₆)Ru(η⁴-C₄R₄S) (R = Me or H) were found to readily protonate at carbon.⁶ Subsequent work⁷ showed that the protonated complex of thiophene, (C₆Me₆)Ru(η⁴-C₄H₅S)⁺, reversibly undergoes C–S scission to give a thiapentadienyl derivative (eq 1). This finding



shows that the sequence of reduction (to generate the η⁴-thiophene complex) followed by protonation can effect C–S cleavage. We were, however, disappointed to find that proto-

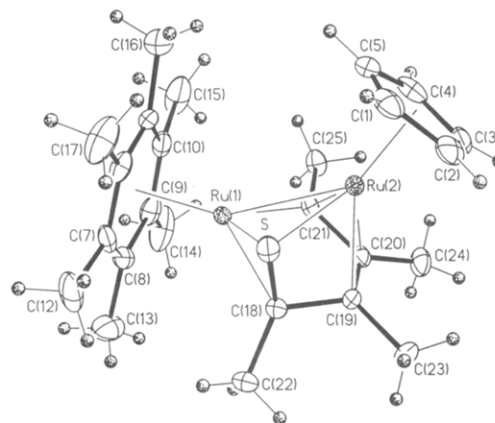
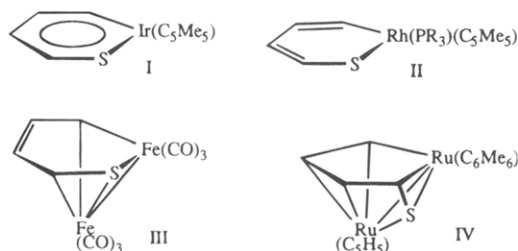


Figure 1. Structure of the cation in [(C₆Me₆)(C₅H₅)Ru₂(C₄Me₄S)]PF₆ (**2aPF₆**). Important distances (Å): Ru(1)–Ru(2), 2.728(1); Ru(1)–S, 2.268(1); Ru(2)–S, 2.314(2); Ru(1)–C(18), 2.127(4); Ru(1)–C(21), 2.071(5); Ru(2)–C(19), 2.231(4); Ru(2)–C(20), 2.209(4); Ru(2)–C(21), 2.150(4); S–C(18), 1.776(4); C(18)–C(19), 1.521(8); C(19)–C(20), 1.379(7); C(20)–C(21), 1.444(6); Ru(1)–C(21), 2.071(5); Ru(2)–C(21), 2.150(4).

Chart 1



nation did not promote the cleavage of C–S bonds in complexes of 2,5-dimethylthiophene or tetramethylthiophene.⁸ We have found that a metal ion can serve as an auxiliary electrophile,⁹ in place of a proton, to effect C–S cleavage reactions.

Treatment of (C₆Me₆)Ru(η⁴-C₄Me₄S) with [(C₅H₅)Ru(MeCN)₃]-PF₆ (MeCN solution, 25 °C, 2 h) afforded a 53% yield of [(C₅H₅)(C₆Me₆)Ru₂(SC₄Me₄)]PF₆ (**2aPF₆**), after recrystallization from THF–hexanes.¹⁰ Single-crystal X-ray diffraction¹¹ showed that the complex is asymmetric (Figure 1), in accord with the ¹H and ¹³C NMR spectra. The Ru atoms are mutually bonded (2.82 Å), and the thiapentadienediyl group is coordinated in η⁴ and η³ modes to Ru(C₅H₅) and Ru(C₆Me₆), respectively. The species is structurally related to the thiaferrole motif (III in Chart 1). However, there is no free olefin, and the sulfur atom is strongly twisted out of the C₄ plane, while remaining bound to both metals. The remaining C–S bond is 1.77 Å (vs 1.718 Å in thiophene²).

It is reasonable to assume that **2a**⁺ arises via an initial attack of the unsaturated electrophile (C₅R₅)Ru(MeCN)₂⁺ on (C₆-Me₆)Ru(η⁴-C₄Me₄S), presumably at sulfur.¹² Subsequent loss

[†] University of Illinois.

[‡] University of Delaware.

(1) Angelici, R. J. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; J. Wiley and Sons: New York, 1994; Vol. 3, p 1433. Gates, B. C. *Catalytic Chemistry*; John Wiley: New York, 1992. Reynolds, J. G. *Chem. Ind. (London)* **1991**, 570.

(2) Rauchfuss, T. B. *Prog. Inorg. Chem.* **1991**, 39, 259.

(3) For 4e⁻ ring-opened thiophenes, see: Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, 112, 199.

(4) For 2e⁻ ring-opened thiophenes, see: Chen, J.; Angelici, R. J. *Polyhedron* **1990**, 9, 1883. Selna, H. E.; Merola, J. S. *Organometallics* **1993**, 12, 1583. Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Herrera, V.; Sanchez-Delgado, R. A. *J. Am. Chem. Soc.* **1993**, 115, 2731. Jones, W. D.; Chin, R. M.; Crane, T. W.; Baruch, D. M. *Organometallics* **1994**, 13, 4448.

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(8) For the influence of methyl substituents on C–S scission, see: Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1991**, 113, 559.

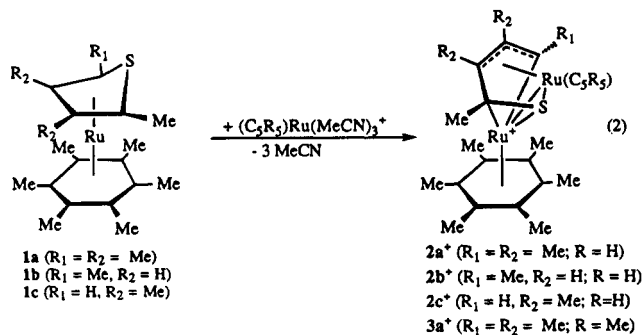
(9) For η⁴-thiophene complexes form S-bound complexes with low-valent metal fragments (Fe(CO)₄, Mo(CO)₅) resulting in eventual desulfurization, see: (a) Luo, S.; Ogilvy, A. E.; Rauchfuss, T. B.; Rheingold, A. L.; Wilson, S. R. *Organometallics* **1991**, 10, 1003. (b) Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, 113, 2544.

(10) **2aPF₆**: 53% yield; ¹H NMR (acetone-*d*₆) δ 4.88 (s, 5H), 3.07 (s, 3H), 2.32 (s, 18H), 1.90 (s, 3H), 1.89 (s, 3H), 1.24 (s, 3H); ¹³C{¹H} NMR (CD₃NO₂) δ 188.7, 115.3, 108.8, 99.2, 85.0, 84.1, 34.4, 30.9, 21.6, 17.6, 15.4; FAB-MS, M⁺. Anal. CHPS.

(11) For C₂₅H₃₅F₆PRu₂S: monoclinic P2₁/n, a = 17.097(4), b = 9.111(3), and c = 17.992(5) Å, β = 108.01(2)°, Z = 4, V = 2666 Å³, T = 224 K, D_{calc} = 1.781 g/cm³, R(F) = 4.03% for 8384 independent reflections (4.0° ≤ 2θ ≤ 62.0°). The PF₆⁻ was partially disordered.

(12) Chen, J.; Angelici, R. J. *Organometallics* **1990**, 9, 849.

of two other MeCN ligands would be compensated by C–S cleavage and Ru–Ru bond formation (eq 2). The ruptured thiophene serves as an $8e^-$ fragment (six π electrons, two σ electrons), vs 2, 4, and $6e^-$ SC_4R_4 ligands seen previously (Chart 1).



It is noteworthy that the $2e^-$ process of C–S oxidative addition is promoted by the attachment of a redox inactive electrophile. The ability of electrophiles to control the redox state of sulfur ligands is well known (induced redox reaction¹³) and may be related to the catalytic activity of metal–sulfido ensembles. These results parallel and extend the previously observed proton-induced C–S cleavage,⁷ with the advantage that the metal electrophile activates a more encumbered substrate (see eq 1). This is relevant to the fact that thiophenes in fossil fuels are typically highly substituted.¹⁴

The generality of the new reaction was tested by variations in both the metal electrophile and the thiophene substrate, illustrated by examples $3a^+$ and $2b^+$,^{15,16} although the latter was only identified spectroscopically. The trimethylthiophene case^{17,18}

(13) Young, C. J.; Kocaba, T. O.; Yan, X. F.; Tiekink, E. R. T.; Wei, L.; Murray, H. H., III; Coyle, C. L.; Stiefel, E. I. *Inorg. Chem.* **1994**, *33*, 6252 and references therein.

(14) *Geochemistry of Sulfur in Fossil Fuels*; Orr, W. L., White, C. M., Eds; American Chemical Society: Washington, DC, 1990.

(15) $3aPF_6$: 10% yield; 1H NMR (acetone- d_6) δ 2.83 (s, 3H), 2.26 (s, 18H), 1.72 (s, 15H), 1.66 (s, 3H), 1.62 (s, 3H), 1.26 (s, 3H); FAB-MS, M^+ . Anal. CHPS.

afforded only a single regioisomer, as indicated by 1H and ^{13}C NMR studies. Single-crystal X-ray diffraction showed that $2c^+$ is structurally similar to $2a^+$ and that C–S cleavage occurs at the less hindered C–S bond.¹⁹

Summarizing, C–S bonds of alkyl-substituted thiophenes are easily cleaved by the combined action of reducing and electrophilic metal centers. In a slightly different approach, a 51% yield of $2a^+$ results when a solution of $(C_5H_5)Ru(MeCN)_3^+$ and the oxidized tetramethylthiophene complex, $(C_6Me_6)Ru(C_4Me_4S)^{2+}$, is treated with cobaltocene. That is, the reduced metal center can be generated *in situ* for attack by the electrophile. The fact that these chemically distinct metal reagents cooperate in solution suggests that analogous processes could describe a surface reaction, as might be found in heterogeneous hydrodesulfurization catalysis.

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Supplementary Material Available: Crystallographic and characterization data for $2aPF_6$ and $2cPF_6$ (20 pages); listing of observed and calculated structure factors (30 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(16) $2bPF_6$: ~30% yield; 1H NMR (acetone- d_6) δ 5.12 (d, 1H), 5.02 (s, 5H), 3.60 (d, 1H), 3.00 (s, 3H), 2.30 (s, 18H), 1.26 (s, 3H); FAB-MS, M^+ .

(17) The trimethylthiophene complexes are new; $1c$ was prepared according to the methods in ref 6 from $[(C_6Me_6)Ru(\eta^5-2,3,4-Me_3C_4HS)]-(OTf)_2$ in 52% yield: 1H NMR (C_6D_6) δ 4.24 (s, 1H), 1.84 (s, 3H), 1.79 (s, 3H), 1.77 (s, 18H), 1.27 (s, 3H).

(18) $2cPF_6$: 28% yield; 1H NMR (acetone- d_6) δ 9.88 (s, 1H), 4.99 (s, 5H), 2.34 (s, 18H), 1.93 (s, 3H), 1.86 (s, 3H), 1.25 (s, 3H); $^{13}C\{^1H\}$ NMR (CD_3NO_2) δ 176.85, 115.2, 107.9, 100.2, 83.7, 83.7, 31.4, 20.6, 20.0, 17.3; FAB-MS, M^+ . Anal. CHPS.

(19) For $C_{24}H_{33}F_6PRu_2$: triclinic $P\bar{1}$, $a = 9.361(6)$, $b = 11.244(6)$, and $c = 12.849(6)$ Å, $\alpha = 96.96(4)^\circ$, $\beta = 90.09(4)^\circ$, $\gamma = 102.58(4)^\circ$, $V = 1310(1)$ Å³, $Z = 2$, $T = 297$ K, $D_{calc} = 1.777$ g cm⁻³, $R(F) = 5.36\%$ for 3680 observed [$I > 2\sigma(I)$] independent reflections ($4^\circ \leq 2\theta \leq 52^\circ$). The largest remaining peak in the electron density difference map (1.0 eÅ⁻³) occurs at a chemically unreasonable position [0.8 Å from C(19)] and was considered as random noise. The C–S bond distance is 1.773(7) Å.