A New Pathway for Thiophene Ring Opening by Transition Metals

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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 I). 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 I) can be distinguished on the basis of the planarity, electron count, and degree of delocalization of the MSC, ring.3,4 Ring-opened thiophenes are also known to span two metals via sulfur and two carbon atoms (III in Chart I). 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 (C,Me6)Ru(η5-C5R5S) (R = Me or H) were found to readily protonate at carbon.6 Subsequent work7 showed that the protonated complex of thiophene, (C,Me6)Ru(η5-C5H5S)2, reversibly undergoes C-S scission to give a thiapentadienyl derivative (eq 1). This finding shows that the sequence of reduction (to generate the η6-thiophene complex) followed by protonation can effect C-S scission. We were, however, disappointed to find that protonation of the η5-thiophene complex 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 (C,Me6)Ru(η5-C5Me5S) with [(C,H5)Ru(MeCN)2]-PF6 (MeCN solution, 25 °C, 2 h) afforded a 53% yield of [(C,H5)Ru(SC,Me2)]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 thiapentadienyl group is coordinated in η5 and η6 modes to Ru(C5H5) and Ru(C5Me5), respectively. The species is structurally related to the thiaferrole motif (III in Chart I). 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 thiophene).12

It is reasonable to assume that 2a+ arises via an initial attack of the unsaturated electrophile (C,R3)Ru(MeCN)+ on (C6- Me5)Ru(η5-C5Me5S), presumably at sulfur.12 Subsequent loss

Figure 1. Structure of the cation in [(C,Me6)(C,H5)Ru(MeCN)2]PF6 (2aPF6).

Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν(C-S)</th>
<th>ν(C=S)</th>
<th>ν(C=O)</th>
<th>ν(C≡C)</th>
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<tr>
<td>C5Me5S</td>
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<tr>
<td>C5Me5H3S</td>
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<tr>
<td>(C,Me6)Ru(η5-C5R5S)</td>
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References

(1) For the influence of methyl substituents on C-S scission, see: Jones, W. D.; Dong, L. J. Am. Chem. Soc. 1991, 113, 559.
(4) Figure 1. Structure of the cation in [(C,Me6)(C,H5)Ru(MeCN)2]PF6 (2aPF6). Important distances (Å) are: Ru(1)–Ru(2), 2.728 (1); Ru(1)–S, 2.286 (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).

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(10) 2aPF6: 53% yield, 1H NMR (acetone-d6) δ = 4.88 (s, 5H), 3.07 (s, 3H), 2.32 (s, 18H), 1.30 (s, 3H), 1.89 (s, 3H), 2.14 (s, 3H), 1/C/H NMR (CD3NO2) δ = 188.7, 115.3, 108.9, 92.0, 85.4, 31.9, 23.4, 17.6, 15.4; FAB-MS, M+. Anal. CHPS.

(11) For C5(H2)3P2ReS2: monochlorine C24H18, 4 = 17.997(4), c = 9.111(3), and c = 17.992(5) Å, β = 108.10(2)°, Z = 4, V = 2666 Å3, T = 224 K. 

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afforded only a single regioisomer, as indicated by $^1$H 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 \((\text{CsH}_5)\text{Ru}(\text{MeCN})_3^+\) and the oxidized tetramethylthiophene complex, \((\text{CMe}_3)_2\text{Ru}(\text{C}_2\text{Me}_3\text{S})^2^+\), is treated with cobaltocene. That is, the reduced metal center can be generated \textit{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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\textbf{Supplementary Material Available:} Crystallographic and characterization data for 2aPF$_6$ and 2ePF$_6$ (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; $^1$H NMR (acetone-d$_6$) $\delta$ 5.12 (d, 1H), 5.02 (s, 5H), 5.60 (d, 1H), 3.00 (s, 3H), 2.30 (s, 18H), 1.26 (s, 3H); FAB-MS, M$^+$.  
(17) The trimethylthiophene complexes are new; IC was prepared according to the methods in ref 6 from \([(\text{CsMe}_3)_2\text{Ru}(\text{Me})(\text{C}_5\text{H}_8\text{S})]=\) (GT)$_2$ in 52% yield: $^1$H NMR (CD$_3$NO$_2$) $\delta$ 4.24 (s, 1H), 1.84 (s, 3H), 1.79 (s, 3H), 1.77 (s, 18H), 1.27 (s, 3H).  
(18) 2ePF$_6$: 28% yield; $^1$H NMR (acetone-d$_6$) $\delta$ 3.98 (s, 1H), 4.99 (s, 5H), 2.34 (s, 18H), 1.93 (s, 3H), 1.86 (s, 3H), 1.25 (s, 3H); $^{13}$C($^1$H) NMR (CD$_3$NO$_2$) $\delta$ 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 \((\text{CsH}_5)\text{Ru}(\text{Me})(\text{C}_5\text{H}_8\text{S})$ triclinic P1, $a = 9.361(6)$, $b = 11.244(6)$, and $c = 12.849(6)$ Å, $\alpha = 96.96(4)^\circ$, $\beta = 90.09(4)^\circ$, $\gamma = 102.58(4)^\circ$, $V = 1310(1)$ Å$^3$, $Z = 2$, $T = 297$ K. $D_{\text{calc}} = 1.777$ g cm$^{-3}$, $R(\text{F}) = 5.36\%$ 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.