A New Mechanism for Metal-Catalyzed Thiophene Hydrogenolysis: Proton-Induced C–S Cleavage of Coordinated Thiophene in Solution and in the Solid State

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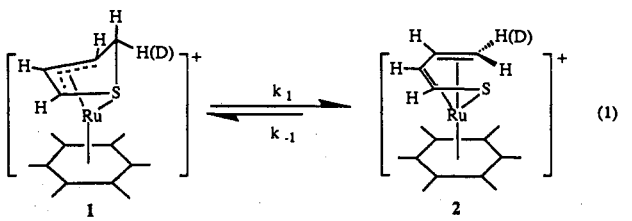
Metal centers are widely involved in the cleavage of carbon–sulfur bonds in both bioorganic[1] and industrial settings.[2] Particularly relevant in the latter context is large scale use of metal sulfide catalysts for the hydrogenolytic removal of sulfur from crude fossil fuels. Mechanistic investigations of this process have focused especially on the interaction of soluble metal complexes with thiophenes, a particularly abundant family of organosulfur compounds in fossil fuels.[3,4] Lacking thus far are mechanistic features of the C–S hydrogenolysis event itself.[5] This report describes a system where one can observe proton-induced C–S scission and its reverse, in real time, allowing complete determination of the key mechanistic details.

We have previously described that $(C_6Me_6)Ru(\eta^4\text{-}C_4H_4S)$ undergoes protonation by weak acids (e.g., NH_4^+) to give $(C_6Me_6)Ru(\eta^4\text{-}2\text{-}H\text{-}C_4H_4S)^+$ (**1**).[6] This process defines a new pathway by which hydrogen can be transferred to the heterocycle. We have found that **1** undergoes spontaneous C–S bond cleavage (acetone solution, 55 °C, $t_{1/2}$ = 2.58 h) to give the ring-opened product **2** (Figure 1, eq 1).



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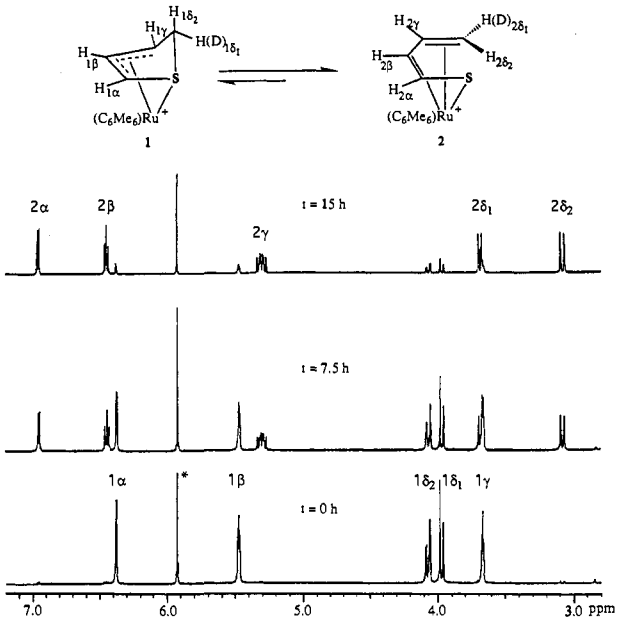

Figure 1. ^1H NMR spectra (400-MHz) for the conversion of **1** to **2** (CD_3COCD_3, 55 °C), showing the region of protons from the C_4H_5S ligand. The peak at 5.92 ppm (labeled with an asterisk) is for the internal standard Cp_2Co^+.

Compounds similar to **2** have been previously described in important work by Angelici and co-workers, who studied the complementary hydride reduction of species of the type $[(C_5R_5)Ru(C_4R_4S)]^+$.[7]

Before presenting our analysis of reaction 1, it is relevant to review the data that supports the structures of **1** and **2**. The spectroscopy for **1** has recently been reported by us together with the crystallographic characterization of its analog $[(C_6Me_6)Ru(2\text{-}H\text{-}C_4Me_2H_2S)]PF_6$ which features a particularly long S–C(sp^3) bond of 1.92 Å (vs 1.78 Å in C_4H_4S).[6] By virtue of its low solubility in $CHCl_3$, the ring-opened isomer **2** can be cleanly isolated from the equilibrium mixture. Its formulation is supported by microanalytical and fast atom bombardment mass spectra (simulation of the positive ion envelope). Key structural data are provided by ^1H and ^{13}C NMR spectroscopic studies including a complete set of homonuclear $^1H\{^1H\}$ decoupling experiments.[8] The NMR data compare favorably with the results for the related ring-opened $(C_5H_5)Ru(\eta^5\text{-}C_4H_5S)$.[7]

The equilibrium constant for eq 1 is 4.38 (±0.32, 45 °C, CD_3COCD_3), determined by approaching the equilibrium from both directions. The rates of approach to equilibrium, k_1 and k_{-1}, were both first order, with $k_1 = 1.71(\pm0.12) \times 10^{-5}$ and $k_{-1} = 3.90(\pm0.28) \times 10^{-6}$ s^{-1}.[9] The temperature dependence of the rates and equilibrium constants for the C–S cleavage were examined over the range 35–65 °C. The enthalpies of activation

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(6) Luo, S.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1992**, *114*, 8515. Careful inspection of Figure 2 in this paper shows that traces of **2** are also evident.

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(8) Anal. Calcd (found) for $C_{16}H_{23}F_6PRuS$: C, 38.94 (38.81); H, 4.70 (4.69); S, 6.50 (6.32). ^1H NMR (CD_2Cl_2): 2.44 (s, C_6Me_6), 6.68 (dd, J = 5.5, 1.0 Hz, $H_{2\alpha}$), 6.12 (t, J = 6.5, 5.5, 1.0 Hz, $H_{2\beta}$), 4.96 (dddd, J = 11.5, 9.0, 6.5, 1.2, 1.0 Hz, $H_{2\gamma}$), 3.41 (dd, J = 9.0, 1.5 Hz, $H_{2\delta_1}$), 3.14 (ddd, J = 11.5, 1.5, 1.0 Hz, $H_{2\delta_2}$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 107.75 (C_6Me_6), 113.33 ($C_{2\alpha}$), 99.62 ($C_{2\beta}$), 97.24 ($C_{2\gamma}$), 60.33 ($C_{2\delta}$), 16.75 (C_6Me_6). FAB-MS (positive ion): m/e = 349.

(9) The solution conversion from **1** to **2** was monitored by quantitative ^1H NMR spectroscopy. The signals of the 2-H-C_4H_4S ligand of **1** were integrated vs the internal standard Cp_2CoOTf. The equilibrium concentrations of both **1** and **2** were measured on NMR samples that had been stored for 10× longer than $t_{1/2}$ of the conversion process. Plots of the disappearance of **1** obeyed first-order, reversible kinetics. Following the Eyring equation, $\ln(k/T)$ was plotted vs $1/T$ for both forward and reverse reactions. Isotope effect studies were conducted on the deuterium-labeled $[(C_6Me_6)Ru(\eta^4\text{-}2\text{-}D\text{-}C_4H_4S)]PF_6$ (**1**-d_1).[6]

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($\Delta H^{\ddagger}$) for the forward and reverse reactions are 93.8 (±3.6) and 103.1 (±3.9) kJ/mol while the entropies of activation ($\Delta S^{\ddagger}$) for the forward and reverse reactions are −41.4 (±13) and −24 (±8) J/mol·K, respectively. The temperature dependence of K_{eq} confirms that the conversion is primarily enthalpically driven with $\Delta H = -9.3$ (±0.4) kJ/mol and $\Delta S = 17.2$ (±5.6) J/mol·K. The equilibrium constant governing C–S scission reflects the competition between attack of Cδ at thiolato sulfur vs ruthenium.

Further insight into the C–S cleavage event is provided by studies of the monodeuterated complex **1**-d_1, wherein the deuterium is located in the equatorial position.[6] The rate constant for ring opening of this species (k_1) is subject to virtually no isotope effect ($k_H/k_D < 1.05$). Thus C–S cleavage occurs without the intermediacy of metal hydrides. The ^{2}H NMR spectrum of **1**-d_1 consists of only one ^{2}H signal (3.84 ppm) which correlates very well with the ^{1}H NMR shift for the $1\delta_1$ site (see Figure 1 for labeling scheme). In the equilibrated mixture, a new ^{2}H signal appears at 3.41 ppm. Thus the ring opening is stereospecific. The distinction between C–S cleavage with retention vs inversion at carbon rests on the proper assignment of the 3.41 ppm signal. This assignment was unambiguously provided by ^{1}H NMR difference NOE measurements, which shows that the deuterium is situated in the $2\delta_1$ site since it is cis to $H_{2\gamma}$.[10] Thus the equatorial deuterium in **1** converts to the anti position of the terminal methylene in **2** (eq 1). C–S cleavage occurs with retention of configuration at the Cδ center.[11,12]

The ring-opening process depicted in eq 1 was originally uncovered during a routine reexamination of a microcrystalline sample of **1** that had been stored for several weeks. Further experiments confirm that the conversion of **1** to **2** occurs in the solid state. The conversion was monitored by solid-state CP/MAS ^{13}C NMR spectroscopy (Figure 2).[13] The resonances in the solid-state ^{13}C NMR spectrum of freshly prepared **1** (B in Figure 2) show one-to-one correlation to the solution spectrum (A in Figure 2). Microcrystalline **1** gradually converts to **2** over the course of 25 h at 55 °C. Again signals from the product correlate well to the CP/MAS ^{13}C NMR data for pure **2** (F in Figure 2). The rate of the solid-state conversion is qualitatively similar to that of the solution process; however, the equilibrium constant is larger by a factor of 2. Measurements on [(C_6-Me_6)Ru(2-H-$C_4Me_2H_2S$)]PF_6 failed to show any evidence for C–S cleavage in solution and as a solid.

To summarize, we have found that protonation of a reduced thiophene ligand leads to C–S cleavage. This result suggests that thiophene hydrogenolysis could proceed via a pathway wherein H_2 serves both as a reductant and as a source of protons. The finding that C–S cleavage in our model also occurs in the solid state makes even more clear the relationship of these results to heterogeneous catalytic processes.[14]

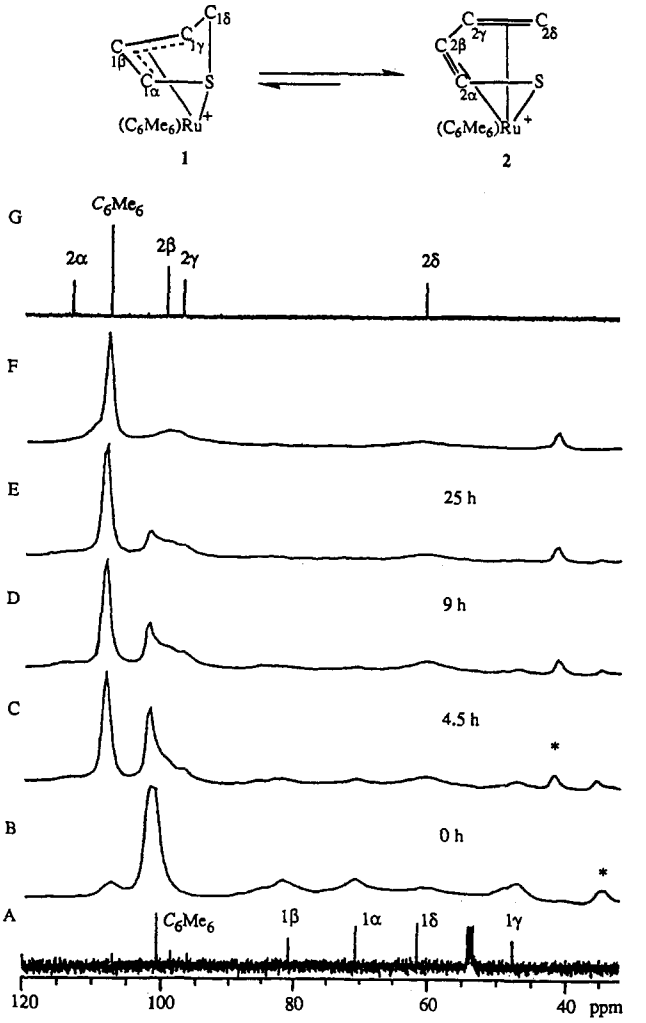

Figure 2. Solution and solid-state ^{13}C NMR spectra for the solid-state conversion of **1** to **2**. Spectra A and G are solution ^{13}C NMR spectra of **1** (75 MHz, CD_2Cl_2) and **2** (100 MHz, CD_3COCD_3), respectively. Traces B–G are CP-MAS 75-MHz ^{13}C NMR spectra for the conversion of **1** to **2**. Spectrum B is for a freshly prepared sample of **1**. Spectrum F is for pure **2**. Peaks labeled with an asterisk are spinning sidebands from the C_6Me_6 resonances.

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Supplementary Material Available: Experimental procedure of kinetic studies for the conversion of **1** to **2** and the isolation of **2**, the ^{1}H COSY spectrum of **2**, ^{1}H NMR difference NOE spectra of **2**, ^{2}H{^{1}H} NMR spectra of **1**-d_1 and the equilibrium mixture of **1**-d_1 and **2**-d_1, and kinetic plots for the conversion of **1** to **2** (5 pages). Ordering information is given on any current masthead page.

(10) The ^{1}H NMR NOE measurements were conducted on a CD_3COCD_3 solution of **2** (0.01 M). Upon the irradiation of $H_{2\gamma}$, a positive NOE was observed at $H_{2\delta_1}$ (5.6%) and $H_{2\beta}$ (6.0%), respectively, while a negative NOE (<1%) was also observed at $H_{2\delta_2}$ and $H_{2\alpha}$.

(11) Reduction of [CpRu(C_4H_4S)]$^+$ with D$^-$ sources stereospecifically affords the ring-opened product with the D$^-$ at the $2\delta_2$ position.[7] This result could arise via H$^-$ (D$^-$) addition to an axial position of the C_4H_4S ligand as observed for other nucleophiles,[5c,12] followed by C–S cleavage with retention.

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(13) The solid-state conversions were conducted by heating a solid sample of **1** in a thermostat oven (ca. ±0.5 °C) at 55 °C. The sample was removed from the oven for recording the CP/MAS ^{13}C NMR spectra on a General Electric GN-300 NMR spectrometer equipped with a CP/MAS probe from Chemagnetics (spinning rate ca. 5 kHz) at room temperature. A 42-kHz-rf field strength was used for proton decoupling.

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