# Base Hydrolysis of Coordinated Thiophene: A Route from Thiophenes to Furans and the Preparation of $[(C_5Me_5)RhS]_4$

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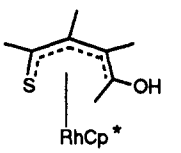
*Summary:* The tetramethylthiophene (TMT) complex $[Cp^*Rh(TMT)]^{2+}$ ($Cp^* = C_5Me_5$) undergoes hydrolytic cleavage of the C–S bond upon treatment with aqueous KOH. The product has the formula $Cp^*Rh(MeCOC_3Me_3S)$. A single-crystal X-ray diffraction study, as well as spectroscopic methods, showed that the compound contains $Cp^*Rh$ bound to an $\eta^4$-acetylpropenethiolate group. $HOSO_2CF_3$ reverses the hydrolysis. Thermolysis of the ring-opened complex gives tetramethylfuran together with the cubane cluster $[Cp^*RhS]_4$. The hydrolysis reaction was shown to apply to $[Ru(TMT)_2](OTf)_2$ and $[Ru(2,5\text{-}Me_2H_2C_4S)(cymene)](OTf)_2$, which also gave acetylpropenethiolate complexes.

Transition-metal cations are well-known to facilitate the hydrolysis of many organic substrates, e.g. esters, amides, and nitriles.[1] Herein we extend this reaction into the organometallic realm, the site of attack being the C–S bond in thiophene. Since thiophenes are normally immune to hydrolysis, our results demonstrate an unusual degree of electrophilic activation conferred by $\pi$-coordination of thiophene to a dicationic metal center. The present work defines some novel approaches to the synthesis of both heterocycles and metal cluster compounds.

Salts of $[Cp^*Rh(TMT)]^{2+}$ ($[1]^{2+}$; $Cp^* = \eta^5\text{-}C_5Me_5$; TMT = 2,3,4,5-tetramethylthiophene) and analogues[2] have been of recent interest as precursors to the corresponding $\eta^4$-thiophene complexes, e.g. $[1]^0$.[3,4] Otherwise the reactivity of dicationic thiophene complexes has been little studied. Addition of 3 equiv of KOH as a 0.03 M aqueous solution to solid $[1](OTf)_2$ ($OTf = OSO_2CF_3$) resulted in initial dissolution, followed minutes later by the precipitation of analytically pure red-orange crystals of $Cp^*Rh(MeCOC_3Me_3S)$ (81% yield).[5,6] The 300-MHz $^1H$ NMR spectrum of the product (**2**) exhibits five methyl resonances in the ratio 1:1:1:5:1. An acyl group is indicated by a $^{13}C$ NMR resonance at 202 ppm and a strong IR absorption at 1667 $cm^{-1}$.

A single-crystal X-ray diffraction study established the structure of **2**.[7] The structure is comprised of three crystallographically independent but structurally similar molecules (Figure 1). Compound **2** is formally a derivative of an $\alpha,\beta$-unsaturated thione, previous examples of which were prepared by the oxidative addition of thiacyclobutenes (thietes).[8] Interpreting the crystallographic results is complicated by the severe disorder found for one of the three independant molecules. However, the C–C and C–S distances in the well-behaved molecules of **2** lead us to favor the description of the $MeCOC_3Me_3S$ ligand as a 3-propene-1-thiolate.

The formation of **2** is proposed to proceed via $[Cp^*Rh(\eta^5\text{-}4\text{-hydroxybutadienethiolate})]^+$:




The same intermediate is also invoked for the reverse of the hydrolysis: the addition of ~2.1 equiv of HOTf to an acetone solution of **2** afforded $[1](OTf)_2$ (80–85% yield). Analogous to the proposed 4-hydroxybutadienethiolate intermediate are the compounds $[(C_5H_5)Ru(\eta^5\text{-}4\text{-Nu-}1,3\text{-butadienethiolate})]$ recently prepared by nucleophilic additions to $[(C_5H_5)Ru(C_4R_4S)]^+$ ($Nu^- = H^-$, $OMe^-$, $SEt^-$, $CH(CO_2Me)_2^-$).[9]

Vacuum pyrolysis of solid **2** (110 °C) gave a colorless distillate of tetramethylfuran (TMF), which was pure by $^1H$ NMR spectroscopy[10,11] (Scheme I). The 300-MHz analysis of the nonvolatile residue from the pyrolysis showed a single resonance corresponding to $[Cp^*RhS]_4$,[12] a cubane cluster.[13] Heating (110 °C, 16 h) a toluene

(1) Sutton, P. A.; Buckingham, D. A. *Acc. Chem. Res.* **1987**, *20*, 357. Buckingham, D. A. In *Biological Aspects of Inorganic Chemistry*; Addison, A. W., Cullen, W. R., Dolphin, D., James, B. R., Eds.; Wiley-Interscience: New York, 1977.

(2) Russell, M. J. H.; White, C.; Yates, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 857.

(3) Ogilvy, A. E.; Skaugset, A. E.; Rauchfuss, T. B. *Organometallics* **1989**, *8*, 2739.

(4) Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 199. Chen, J.; Angelici, R. J. *Organometallics* **1989**, *8*, 2277.

(5) Anal. Calcd (found) for $C_{18}H_{27}ORhS$: C, 54.82 (54.68); H, 6.90 (7.00). $^1H$ NMR ($C_6D_6$): $\delta$ 2.28 (br s, 3 H), 2.091 (s, 3 H), 1.493 (s, 3 H), 1.450 (s, 15 H), 1.295 (s, 3 H). $^{13}C\{^1H\}$ NMR (75.48 MHz, $C_6D_6$): $\delta$ 202 (s), 107.3 (d, $J$ = 7.85 Hz), 96.40 (d, $J$ = 6.19 Hz), 92.08 (sl br s), 75.44 (sl br s), 28.03 (s), 23.98 (s), 19.65 (s), 13.77 (s), 9.28 (s). IR (KBr): 1667 $cm^{-1}$.

(6) Compound **2** is a structural isomer of the sulfoxide $Cp^*Rh(\eta^4\text{-TMTO})$, which was recently described by us: Skaugset, A. E.; Rauchfuss, T. B.; Stern, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 2432.

(7) Compound **2**, $Rh(C_8H_{12}OS)(C_{10}H_{15})$: red, translucent, platelike crystal, 0.1 × 0.3 × 0.4 mm, triclinic space group $P\bar{1}$ with $a$ = 13.549 (2) Å, $b$ = 15.391 (2) Å, $c$ = 15.508 (2) Å, $\alpha$ = 64.577 (3)°, $\beta$ = 70.684 (3)°, $\gamma$ = 80.190 (3)°, $V$ = 2755 (1) Å$^3$, and $\rho_{calc}$ = 1.426 g/cm$^3$ for $Z$ = 6 at 26 °C. Diffraction data: Syntex $P2_1$ automated four-circle diffractometer, Mo radiation (K$\alpha$, 0.71073 Å), graphite monochromator, range $2.0 < 2\theta < 44.0°$ for $+h,\pm k,\pm l$, 7336 reflections ($R_i$ = 0.042), 4242 observed ($I > 2.58\sigma(I)$); corrected for anomalous dispersion and polarization effects. Solution and refinement: direct methods (SHELXS-86) gave Rh positions; difference Fourier syntheses revealed three independent molecules, one with disordered ligands; hydrogen atoms were not included in the structure factor calculations; least-squares refinement (SHELX-76) of 510 variables blocked in combinations of molecules per cycle against 4242 data converged with conventional agreement factors $R$ = 0.062 and $R_w$ = 0.082 ($p$ = 0.03); final difference Fourier map located the maximum density (0.8 e/Å$^3$) in the vicinity of the Rh atoms.

(8) Parker, E. J.; Bodwell, J. R.; Sedergau, T. C.; Dittmer, D. C. *Organometallics* **1982**, *1*, 517. Dittmer, D. C.; Takahashi, K.; Iwanami, M.; Tsai, A. I.; Chang, P. L.; Blidner, B. B.; Stamos, I. K. *J. Am. Chem. Soc.* **1978**, *98*, 2795.

(9) Hachgenei, J.; Angelici, R. J. *J. Organomet. Chem.* **1988**, *355*, 359. Spies, G. H.; Angelici, R. J. *Organometallics* **1987**, *6*, 1897.

(10) $^1H$ NMR ($C_6D_6$): $\delta$ 2.035 (s, 6 H), 1.702 (s, 6 H). $^1H$ NMR ($CCl_4$, TMS): $\delta$ 2.091 (s, 6 H), 1.772 (s, 6 H). $^{13}C\{^1H\}$ NMR ($CCl_4$): $\delta$ 142.86 (s), 113.70 (s); literature (Kiewiet, A.; de Wit, J.; Weringa, W. D. *Org. Magn. Reson.* **1974**, *6*, 461) values $\delta$ 142.6 (s), 113.5 (s). High-resolution EIMS: $m/z$ 124.088020 (calcd for $C_8H_{12}O$ $m/z$ 124.088815). The identification of TMF was confirmed by comparison with the $^1H$ NMR spectrum of an independently prepared sample.

(11) Organotransition-metal chemistry of furans: de Boer, E. J. M.; de With, J. *J. Am. Chem. Soc.* **1986**, *108*, 8271. Chaudret, B.; Jalon, F. A. *J. Chem. Soc., Chem. Commun.* **1988**, 711.

(12) Orange crystals. Anal. Calcd (found) for $C_{40}H_{60}Rh_4S_4$: C, 44.45 (44.62); H, 5.60 (5.57); Rh, 38.09 (37.99); S, 11.87 (11.79). $^1H$ NMR ($C_6D_6$): $\delta$ 1.72 ppm (s). FDMS: $m/z$ 1080 ($M^+$).

(13) The $Cp_4Co_4S_4$ cubane is also known: Simon, G. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1973**, *95*, 2164.

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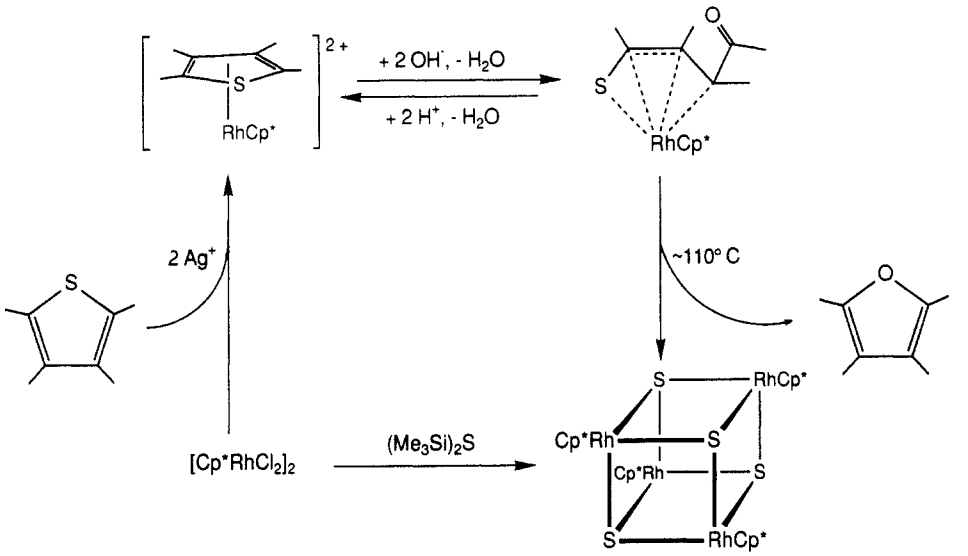
**Scheme I**



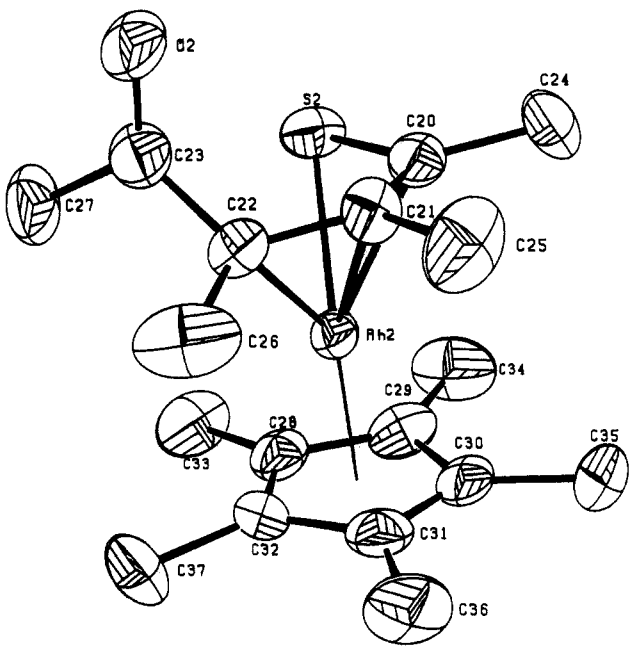




**Figure 1.** ORTEP drawing of one of the three crystallographically independent molecules of Cp*Rh($MeCOC_3Me_3S$). The hydrogen atoms have been omitted for clarity. Bond distances (Å): Rh–S, 2.383 (4); Rh–C20, 2.14 (1); Rh–C21, 2.14 (1); Rh–C22, 2.14 (1); S2–C20, 1.76 (1); C20–C21, 1.39 (2), C21–C22, 1.45 (2); C22–C23, 1.49 (2); C23–O, 1.22 (2); range for (C28–32)–Rh, 2.18 (1)–2.27 (1). Bond angles (deg): S2–C20–C21, 117.4 (10); C20–C21–C22, 117 (1); C21–C22–C23, 121 (1).

solution of **2** (1.19 g/20 mL) afforded a 79% yield of an analytically pure black-red precipitate of the cluster. Under similar conditions (sealed NMR tube, $C_6D_6$, 70 °C, 2 weeks) the yield of TMF was 77%. In contrast to the thermal lability of **2**, the $\pi$-thiophene complex $[1]^{2+}$ is stable at 120 °C for 24 h. The $Rh_4S_4$ cluster has been prepared independently by the reaction of $(Me_3Si)_2S$ and $[Cp^*RhCl_2]_2$.[14]

The hydrolysis of $[Ru(TMT)_2](OTf)_2$[15] to [Ru($MeCOC_3Me_3S$)(TMT)] was also straightforward (3 equiv of KOH, 210 min, 79% yield).[16] This reaction demonstrates preferential double attack of $OH^-$ at one TMT vs single addition of $OH^-$ at each of the two TMT ligands. This hydrolysis can also be reversed cleanly by the addition of HOTf. Compared to **2**, the ruthenium acyl complex is noticeably more thermally labile (70 °C, ~24 h, $^1H$ NMR analysis), giving TMF and TMT in a ratio of 1:2.6. The formation of TMT suggests that clusters of the type $[(TMT)RuS]_n$ are not stable under these conditions, in contrast to the case for the electronically related $[Cp^*RhS]_4$. Base hydrolysis of [(*p*-cymene)Ru(2,5-$Me_2H_2C_4S$)]$(OTf)_2$[17] (*p*-cymene is 4-isopropyltoluene), under conditions identical with those for the preparation of **2**, gave approximately equal amounts of two products. One of these products was identified as the acyl complex [(*p*-cymene)Ru($MeCOC_3H_2MeS$)] after purification by column chromatography on silica gel.[15]

In summary, dicationic thiophene complexes are sufficiently electrophilic to undergo base hydrolysis of a C–S bond by the addition of 2 equiv of hydroxide. Since thiophenes are normally stable to strong base, this work suggests a new strategy for metal-assisted thiophene desulfurization. The new reactivity may prove applicable to the synthesis of other heterocycles as well as metal cluster compounds.

**Acknowledgment.** This research was supported by the National Science Foundation. Johnson Matthey is thanked for the loan of the rhodium and ruthenium. Dr. Vera Mainz (School of Chemical Sciences Molecular Spectroscopy Laboratory) provided expert assistance in some of the $^{13}C$ NMR measurements.

**Supplementary Material Available:** Tables of bond angles and distances, positional parameters, and thermal parameters (9 pages); a table of structure factors (29 pages). Ordering information is given on any current masthead page.

(14) Lockemeyer, J. R.; Rheingold, A. L.; Rauchfuss, T. B. Unpublished results on $[Cp^*RhS]_4^{0/+/2+}$.

(15) Lockemeyer, J. R.; Rauchfuss, T. B.; Rheingold, A. L.; Wilson, S. R. *J. Am. Chem. Soc.* **1989**, *111*, 8828. The preparation of these dicationic ruthenium sandwich compounds will be described in a forthcoming full report: Ganja, E. A.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics*, in press.

(16) Orange crystals. Anal. Calcd (found) for $C_{16}H_{24}ORuS$: C, 48.34 (48.18); H, 6.08 (6.16). $^1H$ NMR ($C_6D_6$): $\delta$ 2.43 (br s, 3 H), 2.108 (s, 3 H), 1.475 (s, 3 H), 1.425 (s, 3 H), 1.415 (s, 3 H), 1.398 (s, 3 H), 1.132 (s, 3 H), 1.029 (s, 3 H). FDMS: $m/z$ 398 ($M^+$; $^{102}Ru$). IR (KBr): 1654 $cm^{-1}$.

(17) Orange oil. $^1H$ NMR ($C_6D_6$): $\delta$ 5.58 (d, 1 H, $J$ = 6.9), 4.88 (d, 1 H, $J$ = 5.7), 4.72 (d, 1 H, $J$ = 5.7), 4.51 (d, 1 H, $J$ = 5.7), 4.40 (d, 1 H, $J$ = 5.7), 2.38 (d, 1 H, $J$ = 6.9), ~2.32 (m, 1 H), 2.325 (s, 3 H), 1.986 (s, 3 H), 1.667 (s, 3 H), 1.016 (d, 6 H, $J$ = 6.9 Hz). FDMS: $m/z$ 364 ($M^+$; $^{102}Ru$). IR ($CCl_4$): 1657 $cm^{-1}$.