Base Hydrolysis of Ruthenium(II) Thiophene Complexes and Reactions of the Coordinated Ligands

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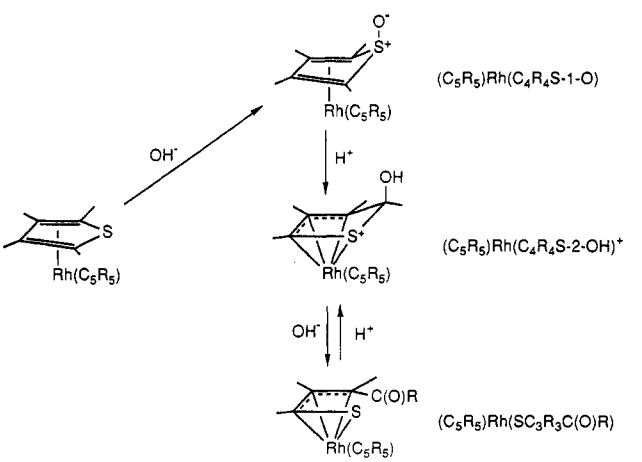
Described are reactions of aqueous base with dicationic thiophene complexes of the type $[Ru(C_6R_6)(C_4R_4S)]^{2+}$ (**1**) and the acid/base reactivity of these products. Attack of OH^- on $[Ru(C_6R_6)(C_4R_4S)]^{2+}$ (**1**) occurs at sulfur to give $[Ru(C_6R_6)(C_4R_4S\text{-}1\text{-}OH)]^+$ ($2H^+$) which was observed by ^1H NMR spectroscopy. This species displays two forms of reactivity: (i) further reaction with OH^- to give the *S*-oxides (sulfoxides) $Ru(C_6R_6)(C_4R_4S\text{-}1\text{-}O)$ (**2**) and (ii) rearrangement to give 2-hydroxythiophene-yl derivatives $[Ru(C_6R_6)(C_4R_4S\text{-}2\text{-}OH)]^+$ (**3**). In solution the *S*-oxides rearrange to give acyl thiolate complexes such as Ru(cymene)(SC_3MeH_2-COMe) (**4d**). The acyl thiolato complexes exist in two isomeric forms which were separated in the case of **4d** and are labeled $\mathbf{4d}_{kin}$ and $\mathbf{4d}_{therm}$. The conversion of $\mathbf{4d}_{kin}$ to $\mathbf{4d}_{therm}$ proceeds via a first order process with $t_{1/2}$ = 4.5 h and $K_{eq} \sim 30$. In contrast the acyls derived from tetramethylthiophene are dynamic on the NMR time scale until low temperatures. [Ru(cymene)-($MeSC_3Me_3COMe$)]$^+$ prepared by methylation of **4a** is static. Similarly, methylation of the two isomers of **4d** gave the corresponding S-methylated isomers $\mathbf{4d}_{therm}Me^+$ and $\mathbf{4d}_{kin}Me^+$ whose isomerization is catalyzed by HOTf. Solutions of $H\mathbf{4d}_{therm}Me^{2+}$ react with dimethylthiophene to regenerate **1d**. Base hydrolysis of $[Ru(arene)(C_4H_4S)]^{2+}$ affords a pair of isomeric formyl thiolates Ru(arene)(SC_3H_3CHO), which were shown not to undergo H/D exchange with aqueous base. The isomerization of the species with arene = cymene isomerized very slowly ($t_{1/2}$ = 84 h) vs **4d**. Basification of $[Ru(C_4Me_4S)(C_4R_4S)]^{2+}$ (R_4 = Me_4, 2,5-Me_2H_2) results in the addition of O^{2-} to one ring, in the case of the mixed thiophene complex the addition occurs at the less methylated ring. The base hydrolysis reactions are reversible such that reprotonation affords the starting dicationic thiophene sandwich complexes. However it was found that protonation of $\mathbf{4d}_{therm}$ affords the vinyl-thiolato complex $[Ru(C_6R_6)(\mu\text{-}SCMe{=}CHCH_2COMe)]_2^{2+}$, not thiophene complex **1d**. Deprotonation of this diruthenium species with KOH gives the dimetallic thioaldehyde complex $[Ru(C_6R_6)(\mu\text{-}S{=}CMeCH{=}CHCOMe)]_2$ which rapidly (minutes, 25 °C) isomerizes to $\mathbf{4d}_{therm}$. Treatment of $\mathbf{4d}_{therm}$ with $BH(OMe)_3^-$ affords one stereoisomer of Ru(cymene)($SC_3MeH_2CHOHMe$).

Introduction

Interest in thiophene complexes is motivated by the utility of metal catalysts in desulfurization catalysis. A more immediate reward however comes from the intrinsic novelty of the thiophene ligand system itself.[1] Thiophenes adopt diverse bonding modes and display high reactivity which can differ sharply from the behavior of the free heterocycle. Relevant to the present investigation is the finding that cationic η^5-thiophene complexes are rather electrophilic, allowing a range of nucleophilic additions,[2] which in selected cases can result in C–S cleavage.

This paper describes the acid/base reactivity of a series of ruthenium thiophene complexes. In the "acid form" the starting compounds (ring)$Ru(C_4R_4S)^{2+}$ are reactive toward 2 equiv of aqueous base, first as an OH^- acceptor and next as a proton donor. The first and the second conjugate bases exist in at least two isomeric forms whose interconversions we have examined. The present results are related to previous work where we showed that one C–S bond in $(C_5Me_5)Rh(C_4R_4S)^{2+}$ (Scheme I) undergoes base hydrolysis by attack of 2 equiv of OH^-.[3] C–S cleavage occurs upon deprotonation of the intermediate $[(C_5Me_5)$-$Rh(\eta^4\text{-}C_4R_4S\text{-}2\text{-}OH)]^+$, giving rise to a neutral acyl thiolato complex. Furthermore NMR measurements indicated that the resulting acyl thiolates were dynamic in a manner that was poorly understood. We also showed that the *initial* attack of (excess) base results in formation of the thiophene 1-oxide complex $[(C_5Me_5)Rh(\eta^4\text{-}C_4R_4S\text{-}1\text{-}O)]$, but intermediates in the formation of this S-oxide were not observed.

Scheme I



Our studies of related ruthenium systems have uncovered the following: (i) evidence that *S*-hydroxythiophene complexes are precursors to the thiophene 1-oxides and C_4R_4S-2-OH complexes, (ii) an explanation of the dynamic

(1) Rauchfuss, T. B. *Prog. Inorg. Chem.* **1991,** *39,* 259.
(2) Angelici, R. J. *Acc. Chem. Res.* **1988,** *21,* 387.
(3) Skaugset, A. E.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1992,** *114,* 8521.

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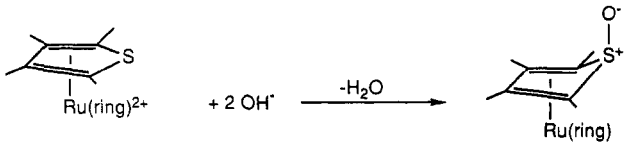
properties of the acyl thiolates, (iii) the stereochemical course of the protonation of the acyl thiolates. The present ruthenium complexes are of mechanistic use since they and several of their hydrolysis products are water soluble, thereby allowing examination of reactions in homogeneous solution. Aside from questions of economy (Ru vs Rh, cyclohexadienes vs C_5Me_5H), a further advantage of the (arene)Ru^{2+} system is that it forms complexes with a variety of thiophene ligands.[4]

Results

Detection of Thiophene 1-Oxide Intermediates in the Base Hydrolyses of $[(C_6R_6)Ru(C_4R_4S)]^{2+}$. The study began with an examination of the reactivity of $[(ring)Ru(C_4R_4S)]^{2+}$ (**1a–f**) with strong aqueous base. The addition of 3 equiv of KOH to an aqueous solution of these thiophene sandwich complexes results in only a slight color change of the yellowish solution. ^1H NMR analysis of the fresh reaction solutions indicated the formation of single products of C_s symmetry. For example the product derived from **1a** features one doublet for the $CH(CH_3)_2$ groups and three methyl singlets in a ratio of 2:2:1. On the basis of the collective spectroscopic data and their reactivity (see below), the products were assigned as Ru(ring)(η^4-C_4R_4S-1-O) (eq 1).



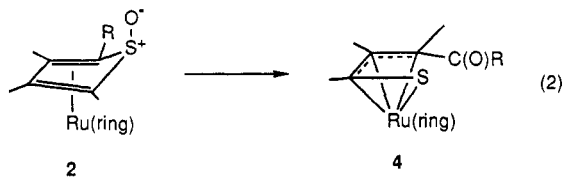
2a-f (1)

	ring	C_4R_4S
1a	cymene	C_4Me_4S
1b	C_4Me_4S	C_4Me_4S
1c	C_4Me_4S	2,5-$C_4H_2Me_2S$
1d	cymene	2,5-$C_4H_2Me_2S$
1e	cymene	C_4H_4S
1f	C_6Me_6	C_4H_4S

The hydrolysis of **1d** was studied in greatest detail. Treatment of D_2O solutions of these dications with 2.5, 10, and 25 equiv of KOH gave the thiophene 1-oxide **2d**, followed by the slower formation of the acetylpropenethiolate **4d**. This pattern of reactivity was also demonstrated for several other cases where the formation of the thiophene 1-oxide products was monitored by ^1H NMR spectroscopy. Extraction of these species from the aqueous reaction mixture with CH_2Cl_2 affords moderately stable solutions which convert to the acetylpropenethiolates **4a–f** over the course of several hours. Chromatography of these CH_2Cl_2 solutions on silica accelerates the conversion to the acyls without inducing isomerization of the acyls themselves (see below). Kinetically stable 1-oxides of the type $(C_5R_5)Rh(C_4Me_4S$-1-O) had been characterized previously.[5,6]

Our attempts to obtain IR spectra of **2d** provided some insights as to the lability of these species. Grinding a sample of **2d** with KBr caused a rapid color change to the orange η^4-acetylpropenethiolate complex **4d**, identified by its IR spectrum. Similarly, the thiophene 1-oxide **2d** was observed to convert to the acyl in minutes when its CH_2Cl_2 solutions were simply evaporated onto NaCl plates. Hypothesizing that contact with the salt crystal induces the rearrangement, a solution of the 1-oxide was evaporated onto a film of polyethylene, in this case we did observe the expected strong ν_{so} band at 1011 cm^{-1}.

Isomerization of the Coordinated Thiophene 1-Oxides to Acetylpropenethiolate Complexes. As mentioned above, it was found that the 1-oxides **2** cleanly converted to acyl thiolato complexes **4** upon standing in aqueous or nonaqueous solutions (eq 2). These conversions



2 **4** (2)

are complete in hours at room temperature. It was further found that the acyl thiolates **4** exist in two isomeric forms. The rates of isomerization vary over several orders of magnitude, depending on the substituents on the thiophene and the coligands. Again, the most detailed studies focused on the acyls derived from **1d**. We observed that the disappearance of the 1-oxide **2d** is accompanied by the formation of the kinetic isomer of the acyl $\mathbf{4d}_{kin}$ which in turn converts to a second acyl isomer $\mathbf{4d}_{therm}$ (Figure 1). The isomeric acyls were isolated in pure form by chromatography. Since the rate of the isomerization is slow, the reaction can be optimized for the purpose of isolating either the kinetic or the thermodynamic isomer. The equilibrated mixture consists of a ~97:3 ratio (25 °C) of the two isomers. The isomerization of benzene solutions of $\mathbf{4d}_{kin}$ to $\mathbf{4d}_{therm}$, as monitored by ^1H NMR spectroscopy (35 °C), was found to be first order with $k = 4.25 \times 10^{-5}$ s^{-1} ($t_{1/2}$ = 4.5 h).

The assignment of the two forms of **4d** as isomeric acyl thiolates is supported by their field desorption mass spectra, IR spectra, and microanalysis. The previous crystallographic characterization of $(C_5Me_5)Rh(SC_3Me_3$-COMe) indicated that these complexes can be viewed as allyl–thiolato chelates. The IR spectra of the acyls **4a–f** show ν_{co} bands at ~1655 cm^{-1}, which occur at somewhat low frequencies in comparison with conventional organic ketones. We interpret this frequency shift as reflecting the electron releasing tendencies of the metalated carbon center adjacent to the carbonyl. Bergman et al. report IR data for Mo and W complexes with C-bound enolates where the carbonyl bands are in the range 1640–1700 cm^{-1}.[7] In the specific case of $\mathbf{4d}_{kin}$ and $\mathbf{4d}_{therm}$ we observed ν_{co} bands at 1661 and 1654 cm^{-1}. The ^1H NMR spectra for the two forms of **4d** (Figure 1, spectra C and D) can be fully assigned to two asymmetric structures. For each isomer one observes four $C_6H_4Me(i$-Pr) resonances and, in CD_2Cl_2 and Me_2CO, two $CH(CH_3)_2$ doublets. The SC_3MeH_2COMe resonances appear as pairs of doublets, although the chemical shift difference for $\mathbf{4d}_{therm}$ is particularly large at 3.2 ppm. The ^{13}C NMR spectra of the isomers of **4d** showed resonances at ca. 206 ppm, in the range associated with ketones. Otherwise the spectra could be assigned in a self-consistent manner.

(4) Ganja, E. A.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **1991**, *10*, 270.
(5) Skaugset, A. E.; Rauchfuss, T. B.; Stern, C. A. *J. Am. Chem. Soc.* **1990**, *112*, 2432.
(6) Robust complexes of the type (cymene)$Os(C_4Me_4S$-1-O) have been prepared: Skaugset, A. E. Ph.D. Thesis, University of Illinois at Urbana—Champaign, 1992. Feng, Q.; Krautscheid, H.; Rauchfuss, T. B.; Skaugset, A. E.; Venturelli, A. Manuscript in preparation.
(7) Burkhardt, E. R.; Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 2022.

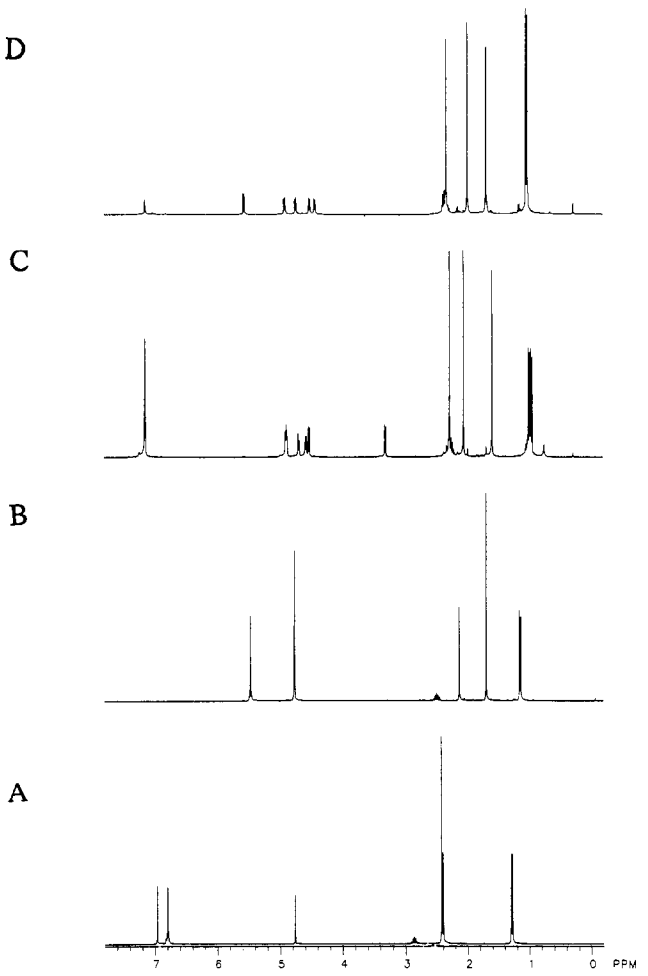


Figure 1. 300-MHz ^{1}H NMR spectra for [(cymene)Ru($C_4H_2Me_2S$)]$^{2+}$ (**1d**) and its hydrolysis products: (A) **1d** in D_2O; (B) [(cymene)Ru($C_4H_2Me_2S$-1-O)] (**2d**) in D_2O; (C) [(cymene)-Ru(SC_3MeH_2COMe)] (**4d**$_{kin}$) in C_6D_6; (D) [(cymene)Ru(SC_3-MeH_2COMe)] (**4d**$_{therm}$) in C_6D_6.

The acyl thiolates arising from base hydrolysis of the tetramethylthiophene complexes **1a,b** isomerize faster than the derivatives of dimethylthiophene and thiophene. Thus the ^{1}H NMR spectrum of **4a** consists of both broadened and sharp signals at room temperature while at −60 °C (200 MHz) the spectrum features signals for an 82:18 pair of isomeric acetyl thiolates. At +60 °C the spectrum was again sharp, apparently as the result of dynamic averaging. The multiplicity of the ^{1}H NMR signals for $C_6H_4MeCH(CH_3)_2$ indicates that even in the fast exchange limit the molecule lacks a plane of symmetry. The ^{13}C NMR spectrum (−60 °C) of **4a** confirmed the presence of two isomers.

Experiments were conducted on complexes of unsubstituted thiophene [(arene)Ru(C_4H_4S)]$^{2+}$ (arene = cymene (**1e**), C_6Me_6 (**1f**)[8]) in order to probe the possible involvement of the α protons in the base hydrolysis. Solutions of **1f** in D_2O were observed to undergo two competing processes, dissociation of thiophene to give [(cymene)-Ru($H_2O)_3$]$^{2+}$ and H/D exchange at the low field site on the thiophene. Previous work has shown that the 2,5 protons absorb at lower fields than the 3,4 protons. Angelici and co-workers had shown that basic CD_3OD solutions of [(C_5H_5)Ru(C_4H_4S)]$^+$ undergo regioselective H/D exchange in the 2,5 positions[9] while the present case is noteworthy since it requires no added base.

Treatment of **1e,f** with excess KOH indeed gave the thiophene 1-oxide intermediates **2e,f** identified by their ^{1}H NMR spectra, followed by the appearance of a pair of isomeric formyls **4f**. In the case of the cymene complex, the rate of isomerization to **4e**$_{therm}$ was 1.6×10^{-6} s^{-1}. Parallel with this isomerization **4e**$_{kin}$ decomposes to give free cymene and an insoluble black solid, this process is slightly slower at 7.0×10^{-7} s^{-1}. Distinctive ^{1}H NMR signals for the C*H*O group in these two isomers were seen as doublets in the range 9–11 ppm. Because of the competing decomposition pathway for **4e**$_{kin}$ we could not ascertain K_{eq}. In the case of **4f** the spectra were further assigned via a series of ^{1}H–^{1}H decoupling experiments. The rate of isomerization of the hexamethylbenzene complex was ~10× faster than that for **4e**. The equilibrium ratio of the isomers **4f**$_{kin}$:**4f**$_{therm}$ was 1:2.85.

Protonation of the Acyl Thiolate Complexes. In previous work we found that acetyl thiolates of the type (C_5R_5)Rh(SC_3Me_3COMe) react with acid (e.g. HOTf) to give back thiophene complexes [(C_5R_5)Rh(C_4Me_4S)]$^{2+}$.[2] The acyls **4a** derived from tetramethylthiophene were found to behave similarly, reverting to the dication **1a**. Furthermore we confirmed the formation of the intermediate [(cymene)Ru(C_4Me_4S-2-OH)]BF_4 (**3a**), arising from treatment of **4a** with NH_4BF_4. The ammonium ion is a sufficiently weak acid that it only monoprotonates the acyl thiolate. The ^{1}H NMR spectrum of **3a** features five methyl singlets. This species was also observed as the eventual product from the reaction of **1a** with 1 equiv of base (see below). pH titrations of aqueous solutions of **4a** revealed a pK_{a2} at 9.73. This value is consistent with the aforementioned observation that **4a** undergoes mono- but not *di*protonation by NH_4^+ (pK_a = 9.25).

Solutions of **4d**$_{kin}$ cleanly revert to **1d** upon treatment with >2 equiv of HOTf. With HCl we observed initial formation of **1d** followed by [(cymene)$RuCl_2]_2$ and free dimethylthiophene. Control experiments showed that **1d** reacts with HCl to give the same products.

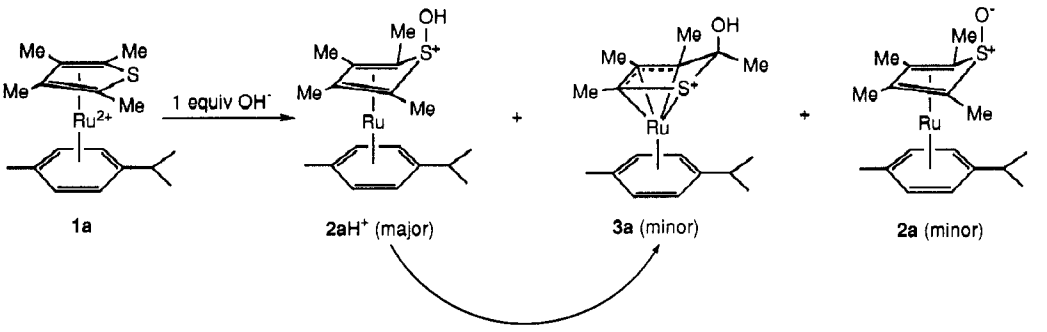
We were intrigued to find that the protonation of **4d**$_{therm}$ proceeds differently from **4d**$_{kin}$ in that only monoprotonation occurs.[10] A bright yellow precipitate [**5dH**]$_2^{2+}$ forms upon addition of HOTf to a CH_2Cl_2 solution of **4d**$_{therm}$. The CH_2Cl_2 solvent is important since it promotes rapid precipitation of the product. The IR spectrum of [**5dH**]$_2^{2+}$ shows bands assigned to the uncoordinated OTf^- and a sharp absorption at 1713 cm^{-1} for the carbonyl. The latter is consistent with an unperturbed ketone, in contrast to related derivatives such as **4d**$_{therm}$ which absorbs at 1654 cm^{-1}. The ^{1}H NMR spectrum of a CD_3CN solution of [**5dH**]$_2^{2+}$ indicates that protonation occurs at the carbon γ to sulfur. The coupling pattern of the multiplets at 4.09 and 3.73 ppm was simulated as an ABX spin system. The signs and magnitudes of the coupling constants (J_{AB} = −19.76, J_{AX} = 6.33, and J_{BX} = 6.61 Hz) are consistent with the fragment CH_AH_B–CH_X. The ^{13}C NMR signal assigned to C3 shifts from 59.3 (C_6D_6) in **4d**$_{therm}$ to 46.2 ppm (CD_3-CN) in [**5dH**]$_2^{2+}$. The $C_6H_4Me(i\text{-}Pr)$ portion of the ^{1}H

(8) Luo, S.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1992**, *114*, 8515.

(9) Sauer, N. N.; Angelici, R. J. *Organometallics* **1987**, *6*, 1146. Spies, G. H.; Angelici, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 5569.

(10) Representative studies on ruthenium allyl complexes: Cole-Hamilton, D. J.; Wilkinson, G. *Nouv. J. Chem.* **1977**, *1*, 141. Hsu, L.-H.; Nordman, C. E.; Gibson, D. H.; Hsu, W.-L. *Organometallics* **1989**, *8*, 241. Powell, J.; Shaw, B. L. *J. Chem. Soc. A* **1968**, 160. Cooke, M.; Goodfellow, R. J.; Green, M.; Parker, G. *J. Chem. Soc. A* **1971**, 16.

Scheme II

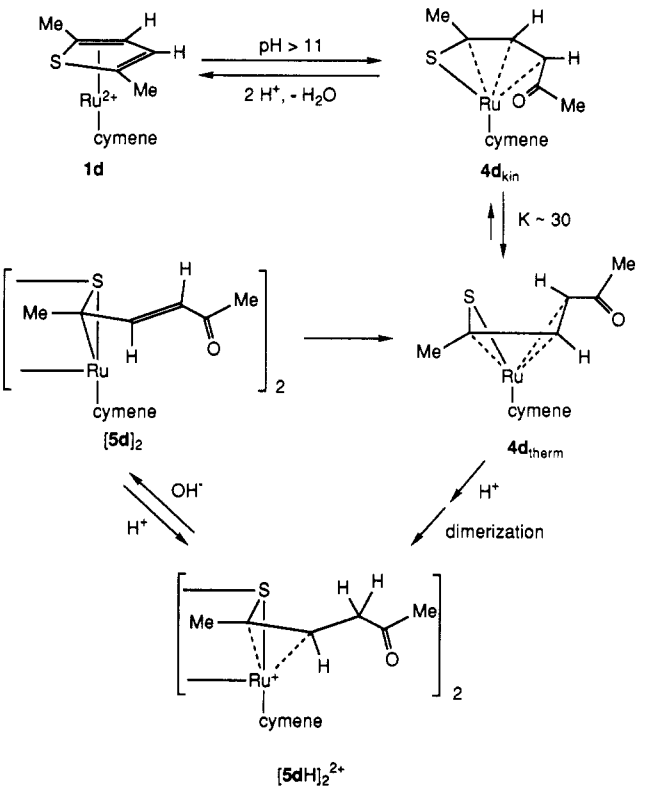


NMR spectrum consists of four well-resolved multiplets indicating that the Ru center is chiral. Collectively, the NMR data show that the Ru is coordinated to the arene and a vinyl mercaptide.[11] As this would result in a 16e configuration at Ru, the salt is proposed to be a dimer with bridging mercaptide. Aside from mass spectral data and reactivity (see below) the dimer formulation for $[\mathbf{5dH}]_2^{2+}$ is consistent with its solubility in acetonitrile but poor solubility in CH_2Cl_2 (all other monocations in this work are CH_2Cl_2 soluble).

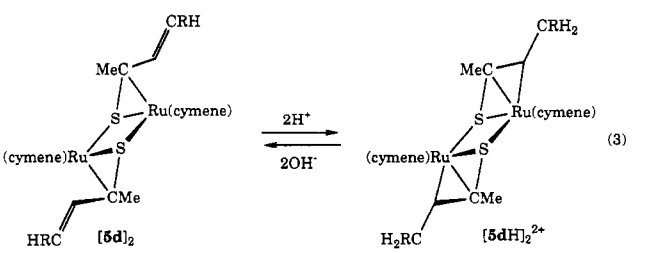
The fast atom bombardment mass spectrum of $[\mathbf{5dH}]_2(OTf)_2$ shows an intense ion current for $[\mathbf{5dH}]_x^{x+}$ (x = 1, 2) as well as a peak envelope for $[\mathbf{5dH}]_2OTf^+$. Field desorption mass spectra for the same salt showed two major peak envelopes, one centered at m/z = 364, corresponding to **4d**, and one at m/z = 598. The m/z 598 envelope corresponds to the formula $[(cymene)_2Ru_2(SC_3MeH_2COMe)]^+$ which could arise by intramolecular proton transfer releasing HSC_3MeH_2COMe.

Basification of a sample of $[\mathbf{5dH}]_2(OTf)_2$ partitioned between CH_2Cl_2 and water resulted in an immediate color change to dark orange which transferred completely to the nonaqueous layer. ^1H NMR analysis showed that the resulting solution consisted mainly of $\mathbf{4d}_{therm}$. These observations suggest that $[\mathbf{5dH}]_2^{2+}$ undergoes deprotonation followed by cleavage of the mercaptide bridge. The implied dimetallic intermediate could be isolated when the basification was conducted on an aqueous suspension of $[\mathbf{5dH}]_2^{2+}$. The FAB-MS of the red-orange solid showed a molecular ion envelope corresponding to a dimer of **4d** as well as a weaker signal for the monomer. The ^1H NMR spectrum indicates that this compound has either a center of symmetry or a C_2 axis since four $C_6H_4Me(i\text{-}Pr)$ multiplets are observed. A widely spaced ($\Delta\delta$ = 2.1 ppm) AB quartet (J_{AB} = 15 Hz) indicates a polar trans R*H*C=C*H*R group. Thirteen of the sixteen ^{13}C NMR resonances can be assigned to aromatic, alkyl, and the carbonyl centers. The remaining three signals are assigned to the unsymmetrical olefin (160.8, 111.6 ppm) and a bridging, side-bonded (η^2) thiocarbonyl (68.3 ppm).[12] The assignments of the olefin CH resonances are supported by a ^1H–^{13}C correlation spectrum at −20 °C. Furthermore the IR spectrum shows strong bands at 1613 and 1548 cm^{-1}, which we assign to

Scheme III



ν_{CO} and $\nu_{C=C}$, respectively. These bands occur at rather low frequencies compared with conventional α,β-unsaturated carbonyls, which this species is not. The structure proposed for $[\mathbf{5d}]_2$ could form by simple detachment of a carbon upon deprotonation of the methylene group (eq 3). Solutions of $[\mathbf{5d}]_2$ convert to $\mathbf{4d}_{therm}$ via a first order



(3)

pathway ($t_{1/2}$ = 23 min, 25 °C, CD_2Cl_2 solution). This conversion even occurs in solid samples over the course of several days. Scheme III depicts the centrosymmetric *RS* structure for $[\mathbf{5dH}]_2^{2+}$ and $[\mathbf{5d}]_2$ although our data are consistent with a racemic mixture of *RR* and *SS* structures.

Detection of the [(ring)Ru(C_4Me_4S-1-OH)]$^+$ Intermediate. The preceding experiments drew our attention to the initial step in the hydrolysis reactions. pH titrations

(11) Other examples of η^3-vinyl–thiolates: Birnbaum, J.; Haltiwanger, R. C.; Bernatis, P.; Teachout, C.; Parker, K.; Rakowski DuBois, M. *Organometallics* **1991**, *10*, 1779. Rosini, G. P.; Jones, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 10767.

(12) A previous example of a μ-thioaldehyde complex, $Cp_2Mo_2(S_2CH_2)(SCH_3)(\mu\text{-}SCH_2)^+$: Bernatis, P.; Haltiwanger, R. C.; Rakowski DuBois, M. *Organometallics* **1992**, *11*, 2435. See also, $Cp_2Mo_2(CO)_4(SCPh_2)$: Alper, H.; Silavwe, N. D.; Birnbaum, G. I.; Ahmed, F. R. *J. Am. Chem. Soc.* **1979**, *101*, 6582. The ^{13}C NMR assignment for the R_2CS in $Cp_2Mo_2(CO)_4(R_2CS)$ places these signals at rather downfield positions (ca. 100 ppm) whereas the Rakowski DuBois species has shifts more similar to ours (79–63 ppm).

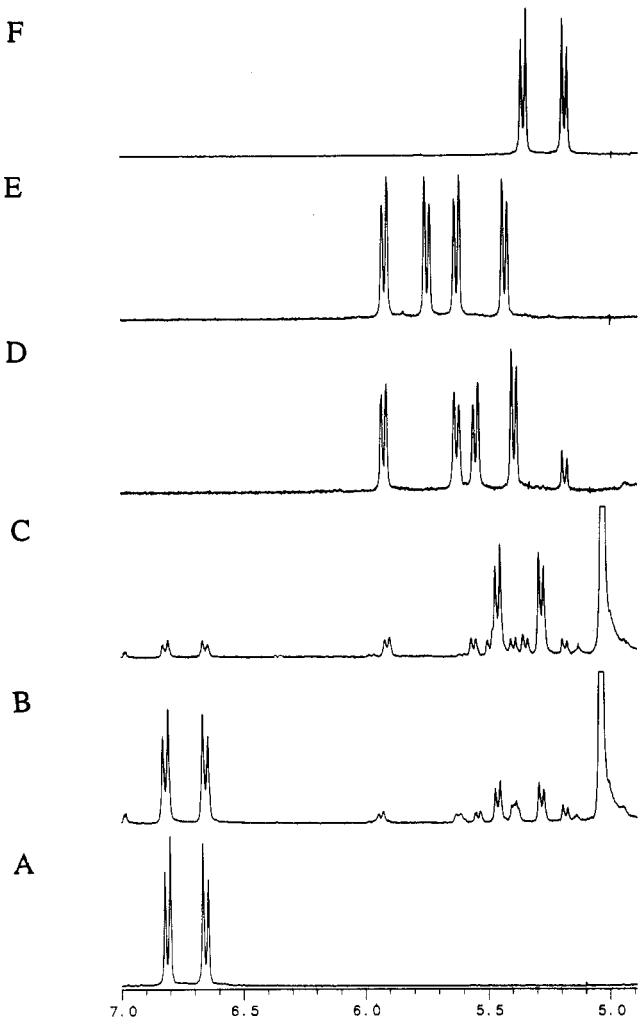


Figure 2. 300-MHz ^{1}H NMR spectra (aromatic region) for the reaction of [(cymene)Ru(C_4Me_4S)]$^{2+}$ (**1a**) with KOH: (A) **1a** in D_2O; (B) **1a** + ~0.5 equiv of KOD in D_2O (3 °C); (C) as for (B) plus an additional 0.5 equiv of KOD; (D) as for (C) after standing for 20 h at ambient temperature; (E) isolated [(cymene)Ru(SC_4Me_4-2-OH)]$^+$ (**3a**); (F) [(cymene)Ru(C_4Me_4S-1-O)] (**2a**) prepared in situ from [(cymene)Ru(C_4Me_4S)]$^{2+}$ (**1a**) and excess KOD. Spectra D–F were obtained at ambient temperatures.

of aqueous solutions of **1a** with KOH showed that the addition of the first equivalent of OH^- is not simple since several minutes are required for the system to reach equilibrium after addition of small aliquots of base. In order to gain some structural information the basification was monitored by ^{1}H NMR spectroscopy (Figure 2). The addition of ~1 equiv of KOD to **1a** gives initially small amounts of the *S*-oxide **2a**, the 2-hydroxythiopheneyl complex **3a** (Scheme II). A major product is a thermally labile species which decomposes to **3a**. The C_6H_4(*i*-Pr)-Me ^{1}H NMR resonances of this unstable intermediate consist of a single AB quartet centered at 5.35 ppm, indicating that it has a plane of symmetry, consistent with the structure expected for [(cymene)Ru(C_4Me_4S-1-OH)]$^+$, **2a**H$^+$.

Methylation of Acyl Thiolate Complexes. We wished to probe the effect of S-methylation on the isomerization of compounds of type **4**. Solutions of **4a** were found to undergo methylation with MeOTf. The resulting ochre salt exhibited a ^{1}H NMR spectrum that indicated a static structure (six methyl singlets, +35 to −60 °C). To pursue this matter further, we subjected the two isomers of **4d** of S-methylation and examined their properties. The ^{1}H NMR spectrum of each of the products shows signals for six methyl groups consistent with the proposed structures. The IR spectra of these salts show ν_{CO} at 1654 and 1682 cm^{-1}, respectively. The isomerism of **4d**$_{kin}$Me$^+$ to **4d**$_{therm}$Me$^+$ is very slow ($t_{1/2}$ > 1 week at 35 °C), in contrast to the rate for **4d**$_{kin}$ to **4d**$_{therm}$.

We found that HOTf catalyzes the isomerization of **4d**$_{kin}$-Me$^+$ to **4d**$_{therm}$Me$^+$. In this way we established that the equilibrium strongly favored **4d**$_{therm}$Me$^+$, with a K_{eq} > 30. We suspect that isomerization proceeds via protonation at the carbon α to the ketone, but on the basis of other evidence the most basic site is probably the carbonyl oxygen. Thus protonation of a CH_3NO_2 solution of **4d**$_{kin}$-Me$^+$ with excess HOTf resulted in the appearance of sets of peaks assignable to two isomers of H**4d**Me^{2+}, one of which quickly ($t_{1/2}$ < 10 min, 40 °C) disappeared, leaving the same spectrum as obtained for addition of HOTf to **4d**$_{therm}$Me$^+$. The attendant structural chemistry is difficult to confidently assign, but the lability of the thiophene-derived ligand (which has been hydrolyzed, methylated, and then protonated) was demonstrated by the reaction ($t_{1/2}$ = hours, 40 °C) of H**4d**$_{therm}$Me^{2+} with 2,5-dimethylthiophene to give **1d** in good yield.

Hydride Reduction of (cymene)Ru(SC_3MeH_2-COMe). The carbonyl in **4d**$_{therm}$ could be reduced with methanolic lithium borohydride to give the alcohol (cymene)Ru{$SC_3MeH_2CH(OH)Me$} which was isolated as an oil. ^{1}H and ^{13}C NMR spectra showed that the reduction is selective for the addition of the hydride to one of the two faces of the carbonyl. Important signals in the ^{1}H NMR spectrum are the mutually coupled doublet, multiplet, and triplet at 4.39, 3.45, and 2.10 ppm, respectively. These are assigned to the three unique protons on the thiolato ligand on the basis of a decoupling experiment that showed that irradiation of the 2.10 ppm signal collapses the doublet to a singlet and the multiplet to a quartet. The selectivity of the reduction may be attributed to the bulkiness of the active agent $BH(OMe)_3^-$ which results from the methanolysis of the tetrahydroborate.[13] The alcohol was further characterized by FD mass spectrometry. Its IR spectrum showed the absence of a carbonyl band and a broad absorption at 3415 cm^{-1} assigned to ν_{OH}. Attempted reduction of **4d**$_{kin}$ was both slow and complicated by the competitive isomerization of the acyl to **4d**$_{therm}$.

Discussion

The base hydrolysis of dicationic ruthenium thiophene complexes has been shown to lead to five products which are sketched in Schemes II and III. As disclosed in our recent paper, the surprising feature of this chemistry is the nucleophilic attack of OH^- at sulfur.[3] The addition of 1 equiv of OH^- to **1a** gives a symmetrical species whose behavior is consistent with its assignment as the *S*-hydroxythiophene complex **2a**H$^+$. This species converts to the alcohol **3a** upon standing. The hydroxysulfonium derivative **2a**H$^+$ is structurally related to other complexes of 1-substituted thiophenes, e.g. Mn(CO)$_3$(η^4-C_4R_4S-1-C_6F_5).[14] We observed that *S*-hydroxy cations are readily deprotonated to give the *S*-oxides **2a**–**f**; this deprotonation

(13) *Organikum*, 15th ed.; VEB Deutscher Verlag des Wissenschaften: Berlin, 1984.

(14) Davidson, J. L.; Sharp, D. W. A. *J. Chem. Soc., Dalton Trans.* **1975**, 2283.

competes with transfer of OH to the α-carbon. The *S*-oxides **2a–f** convert upon standing in solution to the acyls **4a–f**, thereby establishing the relative thermodynamic stabilities of these two forms of (arene)Ru(C_4R_4SO). The high kinetic acidity of the S–OH compounds (vs the 2-hydroxy complexes) is ascribed to the increased localization of the positive charge at sulfur in this nonplanar ligand.

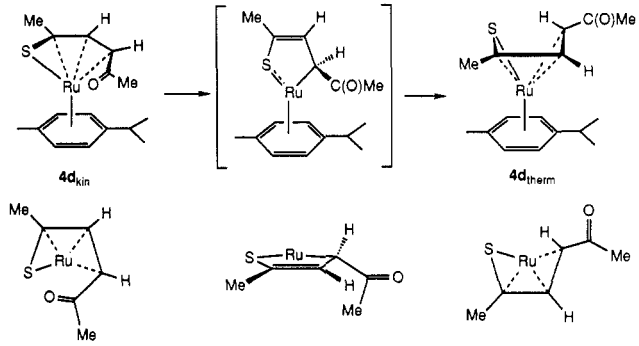
The *S*-oxide intermediates **2** are noticeably less stable than the previously observed (C_5Me_5)Rh(C_4Me_4S-1-O).[3] The conversion of the initial *S*-oxides to the acyls occurs in hours upon standing and isolated samples convert even upon grinding with KBr whereas (C_5Me_5)Rh(C_4Me_4S-1-O) can be freely handled in a variety of solvents and showed no evidence for spontaneous conversion to its acyl isomer. An explanation for the differing reactivities of the Rh and Ru acyls is provided by previous electrochemical measurements showing that (arene)Ru(C_4R_4S)$^{2+}$ are more difficult to reduce than the (C_5Me_5)Rh(C_4R_4S)$^{2+}$ analogues by ~300 mV.[15] This suggests that the Ru(0) complexes are more electron rich, resulting in enhanced basicity of the ruthenium *S*-oxide complexes. This enhanced basicity promotes protonation at oxygen, leading to SOH compounds which we have shown rearrange quickly to 2-hydroxy species which in turn are precursors to acyls.

The ultimate products from base hydrolysis of the thiophene ligand are the so-called acyl thiolates **4a-f**. These species are related to thioacrolein complexes, e.g. CpCo(SC_3H_4), first described by Dittmer and co-workers.[16] The acyls exist in two isomeric forms. In the cases of the dimethylthiophene and thiophene complexes the isomers, **4d** and **4e**, were observed to form sequentially. The formation of the kinetic isomer of the acyl thiolate can be traced to the fact that the C–S cleavage process occurs with retention of stereochemistry at carbon. This isomerism explains why the kinetic isomer is able to reclose to give the thiophene but the thermodynamic isomer is not.

The acyl isomerization, which is unimolecular in the cases of **4d** and **4e**, is proposed to proceed via η^3–η^1 conversion for the allyl group.[17] On the basis of its ^{1}H NMR spectroscopy, **4a** lacks a plane of symmetry even in the fast exchange limit.[18] This is consistent with the fact that chirality at the Ru is fixed upon the attack of the hydroxide at one of the prochiral α-C centers in **1a–f**. The diastereoisomerism arises because of the presence of chirality at the acetylated (formylated) carbon as well as Ru. Thus the isomerization under study in this report does not entail racemization (Scheme IV). The rates of isomerization parallel the degree of substitution of the thiophene ligand, suggesting that it is driven by relief of steric congestion in the kinetic isomers. The isomerism of the acyl thiolates explains complexities observed previously[3] for (C_5Me_5)Rh(SC_3Me_3COMe) which we have also shown to be dynamic.

The unsaturated intermediate proposed for the isomerization of the acyl could be stabilized by a π-donor

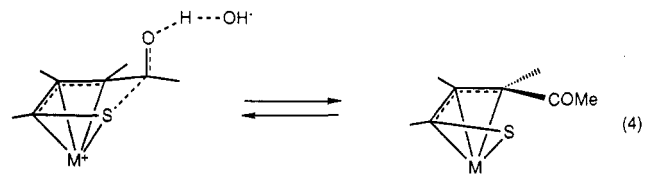
Scheme IV[a]



[a] Side and top views (cymene ligand omitted).

interaction between thiolate and ruthenium. This proposal is supported by the finding that S-methylation of the acyl thiolates impedes the isomerization while keeping the equilibrium constant large (in the case of **4d**). Also supporting this view is the fact that the isomerization of Ru(SC_3H_3CHO)(arene) is faster for the C_6Me_6 (vs the cymene) complex. Due to its superior donor capabilities, C_6Me_6 is more effective in stabilizing the unsaturated intermediate. A model for such an intermediate is (cymene)Ru($SAr)_2$, where SAr is 2,4,6-triisopropylbenzenethiolate.[19]

The isolation of two isomeric forms of **4d** afforded the opportunity to study the reverse of the base hydrolysis in some detail. As expected, protonation of **4d**$_{kin}$ affords **1d**. The first step in the ring closure is envisioned as occurring via the reverse of the process shown in eq 4. Protonation



(4)

of **4d**$_{therm}$ does not afford **1d**; instead, the proton adds to carbon giving a vinyl–thiolate complex. The relative orientation of the carbonyl and the thiolate groups in **4d**$_{kin}$ allows the C–S bond to reform, but this ring closure is not possible for **4d**$_{therm}$. Instead, protonation of **4d**$_{therm}$ proceeds in a manner seen for more conventional allyl ligands.[20] Thus protonation at carbon results in the formation of a vinyl–thiolate which is dinuclear by virtue of a pair of mercaptide bridges.[21] Deprotonation of this dimeric species produces a fourth isomer of [(cymene)-Ru($C_4Me_2H_2SO$)]$_n$.

Experimental Section

Materials and Methods. Hydrated ruthenium trichloride was obtained from Johnson Mathey Inc., 2,5-dimethylthiophene was from Penta, and AgOTF, HOTf, and MeOTf were obtained from Aldrich. Tetramethylthiophene, tetramethylfuran, [(*p*-cymene)$RuCl_2]_2$, [(C_4Me_4S)$RuCl_2]_2$, and [(C_6Me_6)Ru(C_4H_4S)]$^{2+}$ were prepared according to published procedures.[3] Syntheses and workups (excluding column chromatography) were performed

(15) Ogilvy, A. E.; Skaugset, A. E.; Rauchfuss, T. B. *Organometallics* **1989**, *8*, 2739. Luo, S.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1992**, *114*, 8515.

(16) Parker, E. J.; Bodwell, J. R.; Sedergau, T. C.; Dittmer, D. C. *Organometallics* **1982**, *1*, 517 and references therein.

(17) Faller, J. W. *Adv. Organomet. Chem.* **1978**, *16*, 211.

(18) An approximate structural model for this proposed intermediate is Ir(SCHCHC=CH_2)($PEt_3)_3$: Bleeke, J. R.; Ortwerth, M. F.; Chiang, M. Y. *Organometallics* **1992**, *11*, 2740.

(19) Mashima, K.; Mikami, A.; Nakamura, A. *Chem. Lett.* **1992**, 1473. A related precedent is ($C_5Me_5)_2Ru_2(SMe)_2$ as described in: Koelle, U.; Rietmann, Chr.; Englert, U. *J. Organomet. Chem.* **1992**, *423*, C20.

(20) Elschenbroich, Ch.; Salzer, A. *Organometallics*; VCH: Weinheim, 1992.

(21) S-bridged arene–Ru–thiolates of the type (arene)$_2Ru_2(SAr)_3^+$ have been reported: Schacht, H. T.; Haltiwanger, R. C.; Rakowski DuBois, M. *Inorg. Chem.* **1992**, *31*, 1992. Mashima, K.; Mikami, A.; Nakamura, A. *Chem. Lett.* **1992**, 1795.

under an inert atmosphere using purified nitrogen. The reagent grade solvents were distilled from Na/benzophenone (ether, THF, toluene, hexane) or CaH_2 (acetonitrile, methylene chloride).

IR spectra were acquired using a Mattson Galaxy Series FTIR 3000 spectrometer. NMR spectra were collected on General Electric instruments GN500, GN300NB, and QE300 and the Varian spectrometer XL200. Spectra on D_2O solutions were referenced to HDO (assigned as 4.63 ppm). Since the chemical shift for HDO depends on pH and temperature, the reported chemical shifts in D_2O are not highly accurate. The coupling pattern for $[\mathbf{5d}H]_2^{2+}$ was simulated with the program Laocoon 5.[22] Field desorption mass spectra were measured on a VG 70-VSE or a Finnigan MAT-731, and fast atom bombardment spectra on a VG ZAB-SE. Elemental analyses were performed by the University of Illinois Microanalytical Laboratory. Elemental analyses for **1a–f** and **4a–f** have been published elsewhere.[23]

[(ring)Ru(C_4R_4S)](OTf)$_2$ (1a, 1c, 1d, 1e, 1f). Following the procedures described previously,[4] CH_2Cl_2 solutions of [(ring)-$RuCl_2]_2$ (ring = cymene, C_4Me_4S, C_6Me_6) were treated with 4 equiv of AgOTf. After 8 h, the stirred suspensions were filtered and treated with stoichiometric amounts of the thiophene. Complexes **1d** and **1f** precipitated as pale yellow or gray powders which were washed with CH_2Cl_2. Complexes **1a**, **1c**, and **1e** precipitated as oils which converted to yellow or ochre powders upon trituration with ether. Yields ranged from 82 to 92% (when tetramethylfuran was employed in place of tetramethylthiophene, no precipitate formed and ^{1}H NMR analysis of the evaporated reaction solution gave no evidence for C_4Me_4O complexation). ^{1}H NMR data, δ: **1a** (D_2O) 6.60 (d, 2H), 6.46 (d, 2H), 2.76 (sept, 1H), 2.25 (s, 6H), 2.22 (s, 6H), 2.17 (s, 3H), 1.16 (d, 6H); **1b** (D_2O) 2.22 (s, 18H), 2.11 (s, 6H), 1.99 (s, 6H); **1b** (acetone) 2.50 (s, 18H), 2.41 (s, 6H), 2.26 (s, 6H); **1c** (D_2O) 2.23 (s, 6H), 2.03 (s, 6H); **1c** (acetone) 2.59 (s, 6H), 2.39 (s, 6H); **1d** (D_2O) 6.85 (s, 2H), 6.69 (s, 4H), 2.75 (sept, 1H), 2.31 (s, 6H), 2.28 (s, 3H), 1.18 (d, 6H); **1d** (CD_3CN) 6.77 (s, 2H), 6.67 (s, 4H), 2.90 (sept, J = 6.9 Hz, 1H), 2.42 (s, 6H), 2.41 (s, 3H), 1.30 (d, J = 6.9 Hz, 6H); **1e** (acetone) 7.49 (m, 4H), 7.12 (m, 4H), 3.16 (sept, 1H), 2.65 (s, 3H), 1.41 (d, 6H); **1f** (D_2O) 6.50 (s, 2H), 2.35 (s, 6H), 2.32 (s, 6H), 2.19 (s, 6H); **1f** (acetone) 7.30 (m, 2H), 7.24 (m, 2H), 2.70 (s, 18H).

Base Hydrolyses of [(ring)Ru(C_4R_4S)](OTf)$_2$ (1a–f). Isolation of the *S*-Oxide Intermediates. Three equivalents of 0.5 M aqueous KOH were added to a yellowish solution of the complexes **1a–f** in H_2O (30 mL/g complex). Only a slight color change can be observed during the reaction. Extracting the reaction solution immediately with CH_2Cl_2 after addition of KOH, washing of the CH_2Cl_2 phase with water, and removing the solvent in vacuum yielded the yellow sulfoxide complexes **2a–f** as pale yellow oils. NMR tube experiments on D_2O solutions of **1a–f** showed that the *S*-oxide formation proceeded spontaneously. Selected data follow. **2a**: ^{1}H NMR (D_2O) δ 5.17 (d, J = 6.2 Hz, 2H), 5.00 (d, J = 6.2 Hz, 2H), 2.32 (sept, J = 7.0 Hz, 1H), 1.82 (s, 3H), 1.69 (s, 6H), 1.50 (s, 6H), 0.98 (d, J = 7.0 Hz, 6H). **2b**: ^{1}H NMR (C_6D_6) δ 1.564 (s, 18H), 1.558 (s, 6H), 1.40 (s, 6H). **2d**: ^{1}H NMR (D_2O) δ 5.35 (s, 4H), 4.67 (s, 2H), 2.39 (sept, 1H), 2.01 (s, 3H), 1.58 (s, 6H), 1.03 (d, 6H). **2d**: ^{1}H NMR (C_6D_6) δ 4.68 (m, 4H), 4.41 (s, 2H), 2.04 (sept, 1H), 1.76 (s, 6H), 1.73 (s, 3H), 1.03 (d, 6H); ^{13}C NMR (D_2O) δ 110.3, 99.4, 85.2, 83.3, 74.4, 70.9, 31.8, 23.9, 19.5, 14.0; IR (polyethylene film): ν 1011 cm^{-1}. **2e**: ^{1}H NMR (C_6D_6) δ 4.75 (m, 4H), 4.65 (m, 2H), 4.10 (m, 2H), 1.93 (sept, 1H), 1.61 (s, 3H), 0.82 (d, 6H). **2f**: ^{1}H NMR (C_6D_6) δ 4.20 (m, 2H), 3.60 (m, 2H), 1.64 (s, 18H).

Isolation of Acyl Thiolates. The base hydrolysis reactions were allowed to continue for 10 h. The resulting orange solutions were extracted with CH_2Cl_2. Evaporating the solvent in vacuo provided the orange acyl complexes **4a–f** which were further purified by chromatography (SiO_2/THF). Acyl products **4** also formed upon stirring organic solutions of **2** over H_2O for several hours. **4d**, **4e**, and **4f** could be isolated in two different isomeric forms, depending on the reaction times.

In testing the effects of the hydroxide concentration, the hydrolysis of **1d** was conducted by treatment of 80 mL/g complex with 0.05, 0.5, and 2.5 M KOH. Extraction of the reaction solution with CH_2Cl_2 gave **2d** which converted to **4d** upon standing over the course of several hours (for all three stoichiometries). In a typical reaction a solution of 10.6 g (15.7 mmol) of **1a** in 200 mL of H_2O was treated with a solution of 2.5 g (44.6 mmol) of KOH in 100 mL of H_2O. After 12 h the product was extracted with CH_2Cl_2, concentrated, and purified by chromatography on silica gel (20 × 4 cm). An orange band eluted with THF. Evaporation of the solvent gave 5.32 g of crystalline **4a** (87%). Selected NMR, IR, and MS data follow. **4a**: ^{1}H NMR (D_2O) δ 5.67 (d, 1H), 5.30 (d, 1H), 5.26 (d, 1H), 5.12 (d, 1H), 2.53 (sept, 1H), 2.16 (s, 3H), 1.90 (s, 3H), 1.78 (s, 3H), 1.73 (s, 3H), 1.46 (s, 3H), 1.05 (d, 6H). **4a**: ^{1}H NMR (toluene-d_8) δ 4.91 (d, 1H), 4.58 (br, 2H), 4.27 (d, 1H), 2.31 (s, 3H), 2.08 (br sept, 4H), 1.71 (s, 3H), 1.62 (s, 3H), 1.43 (s, 3H), 1.06 (d, br, 6H); ^{13}C NMR (CH_2Cl_2, −60 °C) (minor isomer) δ 210.7, 110.7, 100.8, 96.6, 90.7, 85.7, 84.2, 81.9, 81.5, 68.8, 37.0, 31.5, 25.9, 24.22, 23.8, 23.1, 17.6, 15.5; ^{13}C NMR (CH_2Cl_2, −60 °C) (major isomer) δ 205.5, 108.1, 100.6, 97.4, 92.5, 83.9, 83.4, 83.2, 80.8, 74.1, 31.4, 28.4, 25.2, 23.9, 22.4, 22.3, 17.9, 16.1; IR ν_{CO} 1652 cm^{-1}. **4b**: ^{1}H NMR (C_6D_6) δ 2.15 (br 3H), 2.09 (br, 3H), 1.63 (br, 18H), 1.52 (s, 3H), 1.31 (br, 3H). **4c**: ^{1}H NMR (C_6D_6) δ 2.44 (br, 3H), 2.13 (s, 3H), 1.51 (s, 3H), 1.47 (s, 3H), 1.44 (s, 3H), 1.43 (s, 3H), 1.17 (s, 3H), 1.06 (s, 3H); IR ν_{CO} 1654 cm^{-1}. **4d$_{kin}$**: ^{1}H NMR (C_6D_6) δ 4.83 (m, 2H), 4.65 (psd, 1H), 4.50 (psd, 1H), 4.49 (d, 1H, 5.6 Hz), 3.29 (d, 1H, 5.6 Hz), 2.26 (s, 3H), 2.21 (sept, 1H), 2.07 (s, 3H), 1.55 (s, 3H), 0.96 (dd, 6H); ^{13}C NMR (C_6D_6) δ 203.5, 108.7, 107.4, 95.7, 84.4, 84.0, 83.0, 81.6, 78.7, 59.5, 32.0, 31.9, 28.6, 23.2, 22.8, 18.9; IR ν_{CO} = 1661 cm^{-1}; FD MS: m/z 364 (~5% dimer peak observed). **4d$_{therm}$**: ^{1}H NMR (C_6D_6) δ 5.58 (d, J = 6.5 Hz, 1H), 4.88 (psd, 1H), 4.72 (psd, 1H), 4.50 (psd, 1H), 4.39 (psd, 1H), 2.39 (d, J = 6.5 Hz, 1H), 2.32 (s, 3H), 2.30 (sept, 1H), 1.98 (s, 3H), 1.66 (s, 3H), 1.01 (d, 6H); ^{13}C NMR (C_6D_6) δ 204.2, 108.7, 104.5, 96.1, 84.1, 83.8, 83.3, 82.2, 59.3, 31.7, 30.5, 28.0, 24.0, 23.3, 18.7; IR (Nujol) ν_{CO} 1654 cm^{-1}; FD-MS m/z 364 (no dimer peak observed). **4e$_{kin}$**: ^{1}H NMR (C_6D_6) δ 10.14 (d, J = 7.1 Hz, 1H), 6.16 (m, 1H), 4.83 (m, 1H), 4.81 (m, 1H), 4.72 (m, 2H), 4.41 (m, 1H), 3.3 (m, 1H), 2.06 (sept, 1H), 1.59 (s, 3H), 0.83 (dd, 6H); ^{13}C NMR (C_6D_6) δ 198.3, 109.5, 98.6, 91.5, 85.5, 84.8, 84.5, 84.1, 83.2, 61.3, 32.5, 23.4, 23.1, 18.8; IR (Nujol) ν_{CO} 1628 cm^{-1}; FD-MS m/z 336. **4e$_{therm}$**: ^{1}H NMR (C_6D_6) δ 9.44 (d, J = 4.4 Hz, 1H), 5.93 (m, 1H), 5.35 (m, 1H), 4.86 (m, 1H), 4.74 (m, 1H), 4.61 (m, 1H), 4.46 (m, 1H), 2.57 (m, 1H), 2.12 (sept, 1H), 1.61 (s, 3H), 0.87 (dd, 6H). **4f$_{kin}$**: (C_6D_6) δ 9.90 (d, $J_{4,3}$ = 7.3 Hz, 1H), 5.82 (dd, $J_{3,2}$ = 6.5 Hz, 1H), 4.35 (dd, $J_{2,1}$ = 4.3 Hz, 1H), 3.01 (ddd, 1H), 1.72 (s, 18H). **4f$_{therm}$**: (C_6D_6) δ 9.35 (d, $J_{4,3}$ = 4.9 Hz, 1H), 5.49 (dd, $J_{3,2}$ = 7.2 Hz, 1H), 5.09 (dd, $J_{2,1}$ = 3.8 Hz, 1H), 2.72 (ddd, 1H), 1.66 (s, 18H); IR ν_{CO} 1662 cm^{-1} (mixture of two isomers).

Titrations of 1a with KOH. A solution of 0.5 mmol of **1a** in 100 mL of H_2O was titrated with 0.02 M KOH while monitoring the pH of the reaction. The initial pH was 4.0.

Isolation and Isomerization of 4d$_{kin}$. After the hydrolysis had proceeded for 2 h, the reaction solution was extracted with CH_2Cl_2. This extract was concentrated and chromatographed on silica gel, eluting with THF. ^{1}H NMR analysis showed that the orange crystals consisted of almost pure (>95%) **4d$_{kin}$**. The isomerization of a C_6D_6 solution of this species was monitored by ^{1}H NMR spectroscopy (sealed sample). The sample was maintained at 35 °C and integrated spectra were recorded after 0.5 h followed by 1-h intervals. Anal. Calcd for $C_{16}H_{22}ORuS$: C, 52.87; H, 6.10; Ru, 27.80; S, 8.82. Found: C, 53.09; H, 6.15; Ru, 28.67; S, 9.10. FD-MS: m/z 363, 726. IR: ν_{CO} 1661 cm^{-1}.

Isolation and Isomerization of 4e$_{kin}$. After the hydrolysis had proceeded for 1 h, the reaction solution was extracted with CH_2Cl_2. This extract was concentrated and chromatographed on silica gel, eluting with THF. ^{1}H NMR analysis showed that the orange-red oil consisted of almost pure **4e$_{kin}$**. The isomerization of this species was monitored by ^{1}H NMR spectroscopy on a sample in a sealed tube in C_6D_6 solution. The sample was

(22) Laocoon 5: Cassidei, L.; Sciaconelli, O.; Bothner-By, A. A.; Castellano, S. M., Carnegie-Mellon University, Pittsburgh, PA.

(23) Skaugset, A. E.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **1990**, *9*, 2875.

maintained at 35 °C and integrated spectra were recorded after 4, 12, and finally, 24 h intervals.

Protonation of 4a. Addition of 18 μL (0.21 mmol) of HOTf to a solution of 37 mg (0.095 mmol) of **4a** in 15 mL of CH_2Cl_2 precipitated an orange oil. After 1 h the precipitation was completed by the addition of several volumes of hexane. The product was identified as **1a** by its ^1H NMR spectrum (D_2O solution).

Protonation of $4d_{kin}$. In an analogous experiment with 15 mg (0.041 mmol) of the kinetic isomer of **4d** and 7.5 μL (0.085 mmol) of HOTf in 10 mL of CH_2Cl_2, the solution initially became green-gray and cloudy and after a few seconds the color disappeared again. A yellow oil of **1d** precipitated which was characterized by ^1H NMR spectroscopy.

Protonation of 1d, 2d, and $4d_{kin}$ with HCl. A solution of **1d** in a NMR tube was treated with solid KOH, resulting in a coloration of the $CDCl_3$ layer to orange. The ^1H NMR spectrum showed pure $4d_{kin}$. Addition of three drops of 10 M HCl (excess) decolorized the organic layer (whose NMR spectrum was featureless) and gave a pale yellow aqueous phase. After 1 day the organic phase was orange and the ^1H NMR spectrum consisted of a 2:1 molar ratio of 2,5-$C_4Me_2H_2S$ and the dimer $[(cymene)RuCl_2]_2$. An independent experiment showed that a CH_2Cl_2 solution of **1d** reacts with 10 M HCl to give 2,5-$C_4Me_2H_2S$ and $[(cymene)RuCl_2]_2$. In a third experiment 40 μL of 10 M (aqueous) HCl (0.4 mmol) was added to a bright yellow solution of 10 mg (0.028 mmol) of **2d** in 5 mL of THF. An almost colorless precipitate formed which redissolved after a few minutes, giving an orange solution. The solvent was removed in vacuum, and the residue was analyzed by ^1H NMR spectroscopy which showed that it was $[(cymene)RuCl_2]_2$.

$[(cymene)Ru(SC_3MeH_3COMe)]_2(OTf)_2$ ($[5dH]_2(OTf)_2$) via Protonation of $4d_{therm}$. Addition of 7.0 μL of HOTf (0.080 mmol) to a solution of 13.5 mg of $4d_{therm}$ (0.037 mmol) and 10 mL of CH_2Cl_2 gave a bright yellow precipitate. The product is soluble in MeCN and only slightly soluble in H_2O, acetone, and CH_2Cl_2. ^1H NMR analysis showed that the crude product contained ~5% **1d**. ^1H NMR of the major product (MeCN-d_3): δ 6.32 (m, 1H), 5.97 (m, 1H), 5.84 (m, 1H), 5.33 (m, 1H), 4.09 (m, 1H, X of ABX), 3.73 (m, 2H, AB of ABX), 2.65 (sept, J = 6.9 Hz, 1H), 2.36 (s, 3H), 2.29 (s, 3H), 2.15 (s, 3H), 1.20 (2d, J = 6.9 Hz, 6H). ^{13}C NMR (CD_3CN): δ 204.8, 113.0, 110.3, 94.7, 93.6, 92.5, 91.6, 89.0, 85.9, 46.2, 31.4, 29.8, 22.8, 22.3, 22.1, 18.5. IR: ν_{CO} 1713 cm^{-1}. Anal. Calcd for $C_{17}H_{23}F_3O_4RuS_2$: C, 39.76; H, 4.51; F, 11.10; Ru, 19.68; S, 12.48. Found: C, 39.02; H, 4.69; F, 12.01; Ru, 19.78; S, 11.89. FD-MS: m/z 364 and 598. FAB-MS: m/z 730 (M^+) and 878 (M^+ + OTf). In a separate ^1H NMR experiment, addition of 6 μL (0.067 mmol) of HOTf to a solution of 10 mg (0.027 mmol) of $4d_{therm}$ in 0.6 mL of CD_3NO_2 gave the following spectrum: δ 6.11 (m, 2H), 5.73 (psd, 1H), 5.57 (psd, 1H), 5.34 (psd, 1H), 3.49 (dd, J = 21, 8 Hz, 1H), 3.03 (sept, 1H), 2.68 (d, J = 21 Hz, 1H), 2.47 (s, 3H), 2.31 (s, 3H), 2.13 (s, 3H), 1.43 (d, 3H), 1.4 (d, 3H). Over the course of 12 h this intermediate species converted to $5dH_2^{2+}$ and then **1d**.

$[(cymene)Ru(SC_3MeH_3COMe)]_2$ ($[5d]_2$) via Deprotonation of $[5dH]_2(OTf)_2$. A suspension of 50 mg (0.068 mmol) of $[5dH]_2(OTf)_2$ in 5 mL of H_2O was treated with excess aqueous KOH. The color of the suspension changed from yellow to orange immediately. After 10 min the solid was collected. This solid decomposed after a few days to $4d_{therm}$. ^1H NMR (CD_2Cl_2): δ 8.10 (J = 15 Hz, 2H), 5.93 (d, J = 15 Hz, 2H), 5.45 (psd, 2H, 5.20 (psd, 2H), 4.80 (psd, 2H), 4.20 (psd, 2H), 2.57 (sept, 2H), 2.2 (s, J = 6H), 2.11 (s, 6H), 1.85 (6H), 1.14 (d, 6H). ^{13}C NMR (−20 °C, CD_2Cl_2 with ^1H correlations in parentheses): δ 196.6, 160.8 (8.1), 111.6 (5.93), 103.5, 85.9 (4.8), 84.9 (5.45), 84.1 (4.8), 82.4 (4.19), 68.3, 31.1 (2.54), 28.4 (1.83), 27.7 (2.08), 24.3 (1.12), 21.9 (1.12), 19.0 (2.19). IR (KBr): ν 1613 (s), 1548 (s). FAB-MS: m/z 729. Anal. Calcd for $C_{32}H_{44}Ru_2S_2O_2$: C, 52.79; H, 6.10. Found: C, 52.29; H, 6.22.

The isomerization of $[5d]_2$ to $4d_{therm}$ was monitored by ^1H NMR spectroscopy on a CD_2Cl_2 solution at 25 °C to 80% completion. On the basis of 14 data points, $k = 5 \times 10^{-4}$ s^{-1} with a correlation coefficient of 0.992.

[(cymene)Ru(C_4Me_4S-2-HO)](OTf) (3a) by Monoprotonation of 4a. A solution of 36 mg (0.092 mmol) of **4a** in 15 mL of CH_2Cl_2 was treated with 100 mg (0.95 mmol) of NH_4BF_4. After 4 h the yellow solution was filtered and, evaporated in vacuo, and the yellow oil was washed with hexane. ^1H NMR (CD_2Cl_2): δ 5.63 (d, 1H), 5.46 (d, 1H), 5.33 (d, 1H), 5.15 (d, 1H), 2.66 (sept, J = 6.9 Hz, 1H), 2.37 (s, 3H), 2.23 (s, 3H), 1.95 (s, 3H), 1.86 (s, 3H), 1.59 (s, 3H), 1.25 (d, J = 6.9 Hz, 6H). ^1H NMR (CD_3CN): ν 5.88 (d, J = 5.6 Hz, 1H), 5.72 (d, J = 5.6 Hz, 1H), 5.59 (d, J = 5.9 Hz, 1H), 5.40 (d, J = 5.9 Hz, 1H), 2.68 (sept, J = 5.9 Hz, 1H), 2.34 (s, 3H), 2.10 (s, 3H), 1.97 (s, 3H), 1.70 (s, 3H), 1.60 (s, 3H), 1.22 (2d, J = 6.9 Hz, 6H).

H/D Exchange Studies of 1f. A solution of 10 mg of **1f** in D_2O was monitored by 200-MHz ^1H NMR spectroscopy. Two processes were observed. Due to H/D exchange the intensity (I) of the signal for the 2,5 protons decreased: $I_{3,4}/I_{2,5}$ = 1.17 (20 min); 1.36 (18 h); 1.52 (52 h). Over this time period ~50% of the thiophene dissociated from the starting **1f**.

Methylation of 4a. A solution of 70 mg (0.18 mmol) of **4a** in 10 mL of CH_2Cl_2 was treated with 22 μL (0.20 mmol) of MeOTf, resulting in a color change from orange to yellow. After 30 min the solvent was removed in vacuum, leaving a brown oil which was dissolved in 2 mL of CH_2Cl_2 and slowly added to 20 mL of toluene to give an ochre powder of $[(cymene)Ru(MeSC_3Me_3C(O)Me)](OTf)$. Yield: 72 mg (72%). ^1H NMR (CD_2Cl_2): δ 6.15 (m, 1H), 6.04 (m, 1H), 5.72 (m, 1H), 5.32 (m, 1H), 2.83 (sept, J = 6.8 Hz, 1H), 2.53 (s, 3H), 2.37 (m, 3H), 2.20 (s, 3H), 2.10 (s, 3H), 1.96 (s, 6H), 1.35 (2d, J = 6.8 Hz, 6H). FAB^+-MS: m/z 407 (100%). IR: ν_{CO} 1657 cm^{-1}.

Methylation of $4d_{kin}$. A solution of 70 mg (0.19 mmol) of $4d_{kin}$ in 10 mL of CH_2Cl_2 was treated with 24 μL of (0.21 mmol) MeOTf, resulting in a color change from orange to yellow. After 10 min the solvent was evaporated, leaving a yellow oil which was washed with hexane and dried in vacuo. Anal. Calcd for $C_{18}H_{25}F_3O_4RuS_2$: C, 40.98; H, 4.78; F, 10.80; Ru, 19.16; S, 12.15. Found: C, 41.01; H, 4.93; F, 10.86; Ru, 19.18; S, 12.09. ^1H NMR (CD_2Cl_2): δ 6.32 (psd, 1H), 6.18 (psd, 1H), 5.82 (psd, 1H), 5.53 (psd, 1H), 4.86 (d, 1H), 4.62 (d, 1H), 2.79 (sept, 1H), 2.53 (s, 3H), 2.26 (s, 3H), 2.11 (s, 3H), 1.32 (d, 6H). ^{13}C NMR ($CDCl_3$): δ 198, 113.4, 101.7, 94.2, 90.1, 88.1, 87.0, 85.2, 80.8, 55.5, 31.8, 28.8, 25.1, 23.7, 23.3, 18.8, 18.2. FD-MS: m/z 379 (M^+). IR: ν_{CO} 1654 cm^{-1}.

Methylation of $4d_{therm}$. A solution of 70 mg (0.19 mmol) of $4d_{therm}$ in 10 mL of CH_2Cl_2 was treated with 24 μL of (0.21 mmol) MeOTf, resulting in a color change from red to brown. After 10 min the solvent was evaporated, leaving a brown oil, which was washed with hexane. Anal. Calcd for $C_{18}H_{25}F_3O_4RuS_2$: C, 40.98; H, 4.78; F, 10.80; Ru, 19.16; S, 12.15. Found: C, 40.61; H, 4.89; F, 10.86; Ru, 18.88, S, 11.94. ^1H NMR (CD_2Cl_2): δ 6.0 (psd, 1H), 5.82 (1H), 5.67 (psd, 1H), 5.41 (d, 1H), 5.08 (psd, 1H), 2.74 (sept, 1H), 2.49 (s, 3H), 2.45 (s, 3H), 2.25 (s, 3H), 2.24 (s, 3H), 1.82 (d, 1H), 1.32 (d, 6H). ^{13}C NMR (CD_2Cl_2): δ 203.9, 113.9, 101.6, 89.5, 89.0, 88.4, 87.3, 86.2, 82.1, 54.1, 31.9, 30.4, 23.9, 23.5, 22.7, 19.1, 17.6. FD-MS: m/z 379 (M^+). IR: ν_{CO} 1682 cm^{-1}.

Protonation of [4dMe](OTf). Starting with kin Isomer, CD_3NO_2 Solution. A solution of 20 mg (0.037 mmol) of $[4d_{kin}Me]OTf$ in 0.6 mL of CD_3NO_2 was treated with an excess of HOTf at 0 °C. The ^1H NMR spectrum showed the new compound $[H4d_{kin}Me](OTf)_2$. ^1H NMR (CD_3NO_2): δ 6.51 (psd, 1H), 6.35 (psd, 1H), 6.25 (psd, 1H), 6.13 (psd, 1H), 6.02 (d, J = 5.0 Hz, 1H), 5.09 (d, J = 5.0 Hz, 1H), 2.99 (sept, 1H), 2.89 (s, 3H), 2.56 (s, 3H), 2.55 (s, 3H), 2.42 (s, 3H), 1.40 (d, 3H), 1.38 (d, 3H). ^1H NMR measurements show that $[H4d_{kin}Me](OTf)_2$ isomerized to $[H4d_{therm}Me](OTf)_2$ with $t_{1/2}$ ~ 20 min at ambient temperature.

Starting with therm Isomer, CD_3NO_2 Solution. A solution of 20 mg (0.037 mmol) of $[4d_{therm}Me]OTf$ in 0.6 mL of CD_3NO_2 in an NMR tube was treated with an excess of HOTf. The ^1H NMR spectrum shows that the reaction occurred immediately to give the compound $[H4d_{therm}Me](OTf)_2$, which shows the same ^1H NMR spectrum as obtained from the isomerization of $[H4d_{kin}Me](OTf)_2$. ^1H NMR (CD_3NO_2): δ 6.47 (m, 1H), 6.19 (m, 2H),

5.91 (psd, 1H), 5.69 (m, 1H), 2.98 (sept, 1H), 2.74 (s, 3H), 2.73 (s, 3H), 2.61 (s, 3H), 2.37 (s, 3H), 2.23 (d, J = 4.8 Hz, 1H), 1.43 (d, 6H).

Reaction with 2,5-Dimethylthiophene. 2,5-$Me_2C_4H_2S$ (2 equiv) was added to the solution of [H**4d**$_{therm}$Me](OTf)$_2$ in CD_3NO_2. After 5 h the ^{1}H NMR spectrum showed <1% conversion to **1d**. After 3 days at 50 °C, the conversion of [H**4d**$_{therm}$Me](OTf)$_2$ to **1d** was complete.

Reduction of 4d$_{therm}$ with $NaBH_4$. A solution of 20 mg (0.055 mmol) of **4d**$_{therm}$ in 2 mL of MeOH was added to a solution of 0.5 g (13 mmol) of $NaBH_4$ and a catalytic amount of LiCl in 8 mL of MeOH. After 10 h the reaction mixture was diluted with 5 mL of H_2O and the yellow-brown solution was extracted with toluene. The nonaqueous extracts were washed with H_2O and evaporated in vacuum to yield a brown oil. ^{1}H-NMR (C_6D_6): δ 5.44 (d, J = 5.7 Hz, 1H), 4.83 (m, 2H), 4.67 (d, J = 5.7 Hz, 1H), 4.39 (d, J = 7.3 Hz, 1H), 3.45 (d quar, br, 1H), 2.47 (s, 3H), 2.40 (sept, J = 6.9 Hz, 1H), 2.10 (t, 7.6 Hz, 1H), 1.76 (s, br, 1H), 1.70 (s, 3H), 1.40 (d, J = 6.0 Hz, 3H), 1.07 (2d, J = 6.9 Hz). ^{13}C NMR (C_6D_6): δ 108.3 (w), 101.2 (w), 93.8 (w), 85.5 (s), 83.5 (s), 83.4 (s), 81.8 (s), 81.4 (s), 71.5 (s), 71.0 (s), 32.4 (s), 28.6 (s), 26.8 (s), 24.3 (s), 23.7 (vs), 19.8 (m). An analogous reaction with **4d**$_{kin}$ gave a 1:3:3 mixture of unreacted **4d**$_{kin}$, **4d**$_{therm}$, and a new species characterized by the following incomplete ^{1}H NMR data (C_6D_6): δ 4.93, 4.88, 4.70, 4.53, 4.43, 2.75 (t, 1H), 2.43 (s, 3H), 1.59 (s, 3H), 1.48 (d, 3H), ~1.0 (6H).

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