Base Hydrolysis of Coordinated Thiophene in $(C_5R_5)Rh(C_4Me_4S)^{2+}$: Nucleophilic Attack at Divalent Sulfur and the Reversible Cleavage of C–S Bonds

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Abstract: This report describes studies on the base hydrolysis of $[(C_5Me_5)Rh(C_4Me_4S)]^{2+}$ (**1**) which gives an acyl thiolate $(C_5Me_5)Rh(\eta^4\text{-}SC_3Me_3C(O)Me)$ (**2**) concomitant with cleavage of one C–S bond (C_4Me_4S = 2,3,4,5-tetramethylthiophene). The C–S cleavage event involves deprotonation of $[(C_5Me_5)Rh(C_4Me_4S\text{-}2\text{-}OH)]^+$ (**3**). This cation was prepared by protonation of **2** using HOTf or NH_4PF_6. The conversion of **2** to **3** is proposed to involve protonation of the carbonyl oxygen followed by intramolecular alkylation of the thiolate ligand. This alkylation was modeled by the addition of MeOTf to **2** to give $[(C_5Me_5)Rh(MeSC_3Me_3C(O)Me)]OTf$ (**4**). Single-crystal X-ray diffraction studies show that both **3** and **4** can be described as η^4-thioether allyl complexes of Rh^{III}. Earlier steps in the base hydrolysis reaction were uncovered following the discovery that addition of excess OH^- to the tetramethylcyclopentadienyl complex $[(C_5Me_4H)Rh(C_4Me_4S)]^{2+}$ gave the S-oxide $(C_5Me_4H)Rh(C_4Me_4S\text{-}1\text{-}O)$, not the acyl thiolate. This S-oxide species reacts with NH_4PF_6 to give $[(C_5Me_4H)Rh(C_4Me_4S\text{-}2\text{-}OH)]OTf$, an analog of **3**, which in turn deprotonates to give the acyl thiolate $(C_5Me_4H)Rh(SC_3Me_3C(O)Me)$, an analog of **2**. This conversion establishes that the S-oxide is a kinetic product, less stable thermodynamically than the acyl thiolate isomer. Thus the S-oxide $(C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S\text{-}1\text{-}O)$ reacts with NH_4PF_6 to give **2** and high $[OH^-]$ favors the conversion of **1** to $(C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S\text{-}1\text{-}O)$.

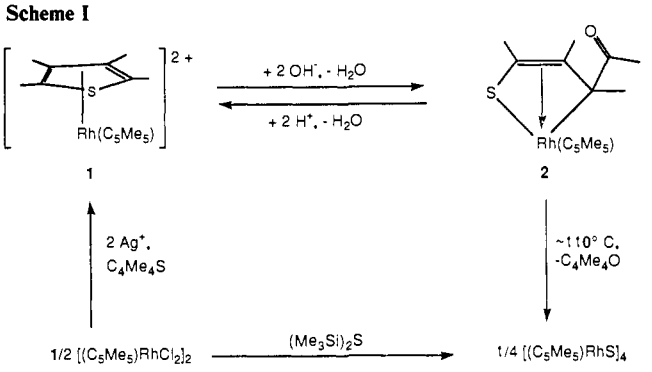
Introduction

Organic ligands attached to cationic metal centers show enhanced susceptibility to nucleophilic addition.[1] This reactivity has been extensively explored for the hydrolysis of esters, amides, nitriles, and many other substrates.[2] Such hydrolyses can be rendered catalytic and form the basis of many important biological and industrial processes. The finding that cationic thiophene complexes are highly susceptible to nucleophilic attack[3] prompted us to investigate the metal ion promoted hydrolysis of thiophenes.

In a preliminary study we indeed found that the tetramethylthiophene complex $[(C_5Me_5)Rh(C_4Me_4S)]^{2+}$ reacts very efficiently with aqueous KOH to give thiolates of the formula $(C_5Me_5)Rh(SC_3Me_3C(O)Me)$.[4] This hydrolysis involves the cleavage of one C–S bond. Furthermore it was found that the resulting thiolate undergoes thermal fragmentation to give tetramethylfuran (C_4Me_4O) and a rhodium sulfido cluster (Scheme I). The hydrolysis reaction has some generality as it has since been found to occur with metals other than rhodium and with thiophenes other than C_4Me_4S. This paper however focuses on the isolation of an intermediate in the base hydrolysis of $[(C_5Me_5)Rh(C_4Me_4S)]^{2+}$ and the relationship of this intermediate to the two isomers of $(C_5Me_5)Rh(C_4Me_4SO)$.

The hydrolysis of $[(C_5R_5)Rh(C_4Me_4S)]^{2+}$ differs from previous examples of nucleophilic additions to coordinated thiophene in two ways; first, it involves the use of OH^- as the nucleophile and, second, the thiophene accepts up to 2 equiv of the hydroxide resulting in the net addition of O^{2-} to the heterocycle.[5,6] The question then naturally arises as to the intermediates in this hydrolysis process when only 1 equiv of OH^- is added. We have successfully searched for such intermediates via the mono-

Scheme I



protonation of the acyl $(C_5R_5)Rh(SC_3Me_3C(O)Me)$. Our studies have yielded unexpected mechanistic insights that open broader questions on the thiophene reactivity of coordinated thiophene ligands. In particular evidence is presented that nucleophilic attack at thiophene can occur at sulfur and that apparent nucleophile additions to carbon can occur via initial attack at sulfur.

The commercially important hydrodesulfurization (HDS) process is aimed at the hydrogenolysis of the organosulfur compounds in fossil fuels, a large fraction of which are thiophenes (eq 1). Given that typical HDS catalysts are oxides,[7] it is con-

$$C_4R_4S + 4H_2 \xrightarrow[\text{catalyst}]{} C_4R_4H_6 + H_2S \qquad (1)$$

ceivable that oxygenated and hydrated thiophenes could arise via the interaction of the heterocycles with the catalysts. The present work describes three such $C_4R_4H_xSO$ species.

Results

Base Hydrolysis of $[(C_5Me_5)Rh(C_4Me_4S)]^{2+}$. The addition of 3 equiv of aqueous KOH to an aqueous solution of $[(C_5Me_5)Rh(C_4Me_4S)]^{2+}$ (**1**) results in the rapid precipitation of the dark red acyl thiolato complex $(C_5Me_5)Rh(SC_3Me_3C(O)Me)$ (**2**). Samples of **2** are soluble in organic solvents and appear stable to air. Its infrared spectrum shows an intense band at 1667 cm^{-1}, assigned to ν_{CO}. The ^1H NMR spectrum for **2** is also consistent with its solid-state structure as all the methyl groups of the $SC_3Me_3C(O)Me$ are nonequivalent. Variable-temperature ^1H

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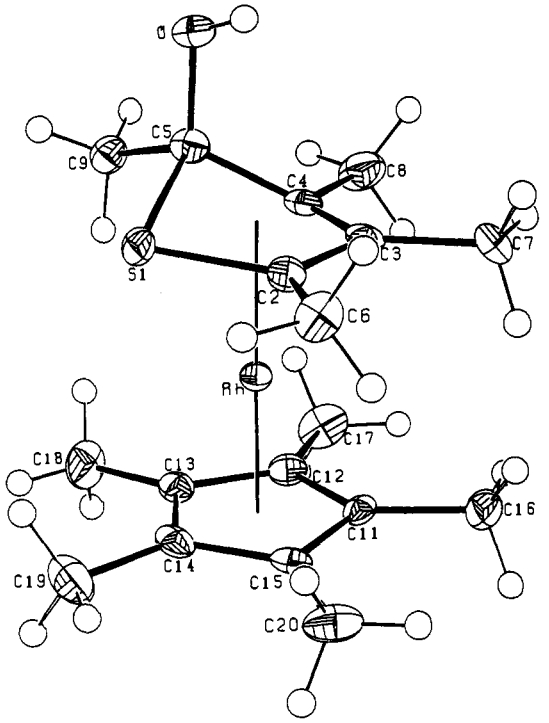

Figure 1. Structure of the non-hydrogen atoms in the cation of $[(C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}OH)]OTf$ with thermal ellipsoids drawn at the 35% probability level.

NMR measurements show that **2** is fluxional in solution. Related fluxional structures are apparent for other acyl thiolates derived from cationic ruthenium thiophene compounds and will be discussed in a separate report.[8]

Acidification of $(C_5Me_5)Rh(SC_3Me_3C(O)Me)$. Treatment of a CH_2Cl_2 solution of **2** with two or more equivalents of HOTf gives **1** in high yield. When a solution of **2** was treated with only 1 equiv of HOTf the monoprotonated complex, $[(C_5Me_5)Rh(C_4Me_4S\text{-}2\text{-}OH)]OTf$, was isolated. In this way we obtained sufficient amounts of this monocation to grow the specimen for the crystallographic investigation discussed below. Samples of the monoprotonated salts prepared by protonation with HOTf were invariably contaminated with small amounts of **1** and purification was hampered by the similar solubilities of these salts. Pure samples of $[(C_5Me_5)Rh(C_4Me_4S\text{-}2\text{-}OH)]PF_6$ (**3**) could be more easily prepared by the reaction of a CH_2Cl_2 solution of **2** with an excess of NH_4PF_6 (**3** refers to the PF_6^- salt, although the counteranion did not noticeably influence the reactivity of these salts). The ammonium ion is sufficiently acidic to protonate **2**, but not acidic enough to convert **3** to **1**.

The ^1H NMR spectrum of **3** consists of a sharp singlet for the C_5Me_5 group and four signals for the nonequivalent methyl groups. One of the Me signals is a doublet with a 1.2 Hz splitting, which we attribute to $J(^{103}Rh,^1H)$. Although such long-distance $^{103}Rh,^1H$ coupling is rare, $J(^{103}Rh,^1H)$ = 1.5 Hz has been observed for the 2-methyl protons in $[Rh_2Cl_2(2\text{-methylallyl})_4]$) and related complexes.[9] A broad hydroxyl proton signal at 4.53 ppm was detected for a solution of **3** in dry deuterated methylene chloride. The IR spectrum of a KBr pellet of the protonated complex shows a strong sharp ν_{OH} band at 3515 cm^{-1}.

The chemistry of **3** is consistent with its being an intermediate in the base hydrolysis of **1**. Solutions of **3** react further with 1 equiv of HOTf in CH_2Cl_2 to give **1** and with 1 equiv of aqueous KOH to give **2**, both in good yield.

Structure of $[(C_5Me_5)Rh(C_4Me_4S\text{-}2\text{-}OH)]OTf$. The molecule contains cyclo-C_4Me_4S-2-OH bound in an η^4 fashion to $(C_5Me_5)Rh$ (Figure 1). The molecule is chiral and both enantiomers occur in the same lattice. The structure shows that

Table I. Selected Distances (Å) and Angles (deg) for $[(C_5Me_5)Rh(C_4Me_4S\text{-}2\text{-}OH)]OTf$

Rh–S1	2.360 (1)	C2–C3	1.403 (7)	C2–C6	1.504 (7)
Rh–C2	2.125 (5)	C3–C4	1.437 (7)	C3–C7	1.493 (7)
Rh–C3	2.168 (5)	C4–C5	1.514 (7)	C4–C8	1.480 (8)
Rh–C4	2.180 (5)	S1–C5	1.906 (5)	C5–O	1.387 (6)
S1–C2	1.771 (5)				

S1–C2–C3	110.8 (4)	C5–O–H	110 (6)
C2–C3–C4	111.1 (4)	S1–C5–O	113.4 (3)
C3–C4–C5	113.3 (4)	C9–C5–O	106.0 (4)
S1–C5–C4	97.0 (3)		

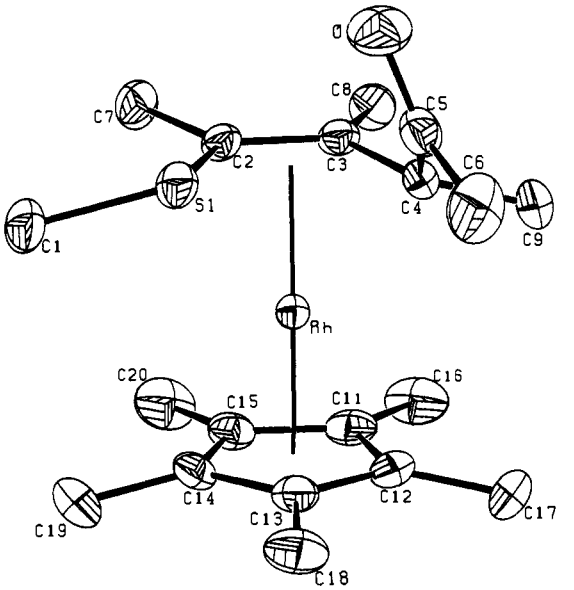

Figure 2. Structure of the non-hydrogen atoms in the cation of $[(C_5Me_5)Rh(\eta^4\text{-}MeSC_3Me_3C(O)Me)]OTf$ (**4**) with thermal ellipsoids drawn at the 35% probability level.

protonation of **2** reforms a second C–S bond. The S–C distances are very different at 1.771 (5) and 1.906 (5) Å (Table I). The latter is very long in comparison with other C–S bonds. Typical C–S distances are 1.82 and 1.72 Å for coordinated thioethers and thiophenes, respectively.[10,11] Even in the related $(CO)_3Mn(C_4H_4S\text{-}2\text{-}CN)$, this C–S bond is somewhat long at 1.831 (6) Å. The Rh–C distances fall in the range 2.125 (3)–2.180 (5) Å, which agree well for other Rh allyls where average values are 2.191 (48) Å for Rh–C1 and 2.148 (41) Å for Rh–C2.[12] The C5–C4 distance is 1.514 (3) Å which is consistent with a single bond, while multiple bonding is indicated for C4–C3 and C2–C3, 1.437 (7) and 1.403 (7) Å, respectively. Collectively the C–C distances suggest allylic character for the C4–C3–C2 fragment.[9] The Rh–S distance is 2.360 (1) Å which is consistent with a single bond and is comparable to that in **2**. The hydroxyl group is axial and ^1H NMR studies show the presence of only one stereoisomer.

Methylation of $(C_5Me_5)Rh(SC_3Me_3C(O)Me)$. The observation of C–S bond formation upon protonation of the acyl compound **3** raises questions about the possible sites of protonation. To investigate this issue we examined the reactivity of **2** towards MeOTf. In this way we obtained orange microcrystals of $[(C_5Me_5)Rh(MeSC_3Me_3C(O)Me)]OTf$ (**4**) whose formula was confirmed by microanalysis and mass spectrometry. The 300 MHz ^1H NMR spectrum of **4** features the pattern 1:1:1:6:1, consistent with a single diastereoisomer wherein the resonances for the C_5Me_5 and one methyl group are coincident. As for **3**, one methyl resonance in **4** exhibits a small but measurable coupling to ^{103}Rh.

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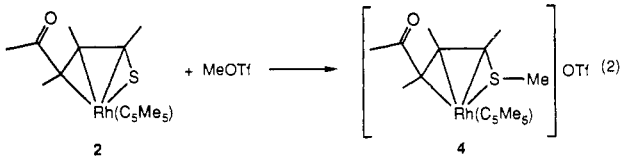
Table II. Selected Distances (Å) and Angles (deg) for $[(C_5Me_5)Rh(MeSC_3Me_3C(O)Me)]OTf$

Rh–S1	2.373 (1)	S1–C1	1.808 (5)	C5–C6	1.500 (8)
Rh–C2	2.180 (4)	S1–C2	1.785 (4)	C2–C7	1.491 (7)
Rh–C3	2.205 (4)	C2–C3	1.415 (6)	C3–C8	1.502 (6)
Rh–C4	2.178 (4)	C3–C4	1.462 (6)	C4–C9	1.515 (6)
		C4–C5	1.497 (6)	O–C5	1.222 (6)

S1–C2–C3	116.9 (3)	O–C5–C4	120.8 (4)
C2–C3–C4	118.4 (4)	O–C5–C6	120.4 (5)
C3–C4–C5	119.9 (4)	C1–S1–C2	103.6 (2)

The IR spectrum of **4** shows a strong ν_{CO} band at 1664 cm^{-1}, close to the value found for **2**. These data are consistent with the results of a single-crystal X-ray diffraction study (eq 2). The ^1H NMR data indicate that only one stereoisomer of **4** is formed.



(2)

2 4

Structure of $[(C_5Me_5)Rh(MeSC_3Me_3C(O)Me)]OTf$. The compound features $(C_5Me_5)Rh$ bound to η^4-$MeSC_3Me_3C(O)Me$ (Figure 2). The methyl electrophile has added to the sulfur atom and the connectivity of the organosulfur ligand resembles that in **2** and **3**. Allylic character is indicated for the C3–C4–C5 fragment similar to that observed for **3**.

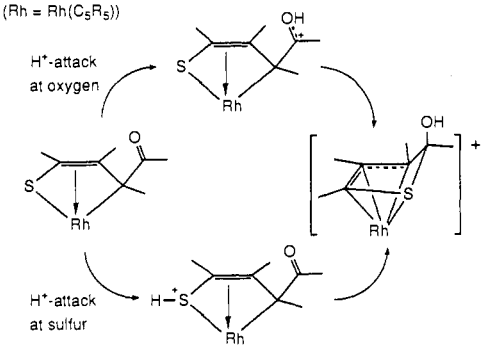
Hydrolysis of $[(C_5Me_4R)Rh(C_4Me_4S)]^{2+}$ (R = H, Et). The base hydrolysis of $[(C_5Me_4Et)Rh(C_4Me_4S)](OTf)_2$ was carried out following the procedure developed for **1**. The spectroscopic characteristics of the product were similar to those for **2**. Of particular interest is the observation of eight methyl singlets in the ^1H NMR spectrum, consistent with a chiral structure. The base hydrolysis of $[(C_5Me_4H)Rh(C_4Me_4S)]^{2+}$, also using the procedure developed for the conversion of **1** to **2**, did not proceed as expected. Instead we obtained $(C_5Me_4H)Rh(C_4Me_4S\text{-}1\text{-}O)$ in good yield. The stoichiometry was confirmed by field desorption mass spectrometry while ^1H NMR and IR spectroscopic analysis showed that this species is properly formulated as a complex of tetramethylthiophene 1-oxide. Particularly telling is the high symmetry indicated by the ^1H NMR spectrum where the CH_3 resonances are found in the intensity ratio 6:6:6:6 relative to the signal for the unique proton. Furthermore, the IR spectrum shows a strong absorption at 1012 cm^{-1} which we assign to ν_{SO}; there were no bands in the $\nu_{C=O}$ region. The data match well that for $(C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S\text{-}1\text{-}O)$, previously prepared by the oxygenation of $(C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S)$.[13]

Experiments were undertaken to understand the relationship of $(C_5Me_4H)Rh(C_4Me_4S\text{-}1\text{-}O)$ to the C_5Me_5-containing hydrolysis products **2** and **3**. $(C_5Me_4H)Rh(C_4Me_4S\text{-}1\text{-}O)$ indeed reacts with an excess of NH_4PF_6 to give bright yellow $[(C_5Me_4H)Rh(C_4Me_4S\text{-}2\text{-}OH)]PF_6$, which proved to be an analogue of **3**. The IR spectrum of this salt is virtually identical with that of **3** and the ^1H NMR spectrum indicates eight nonequivalent methyl groups. Treatment of solutions of $[(C_5Me_4H)Rh(C_4Me_4S\text{-}2\text{-}OH)]^+$ with aqueous KOH afforded the acyl $(C_5Me_4H)Rh(SC_3Me_3C(O)Me)$. Again ^1H NMR and IR spectroscopy clearly indicate that this species is an analogue of **2**. Consistent with this behavior we found that treatment of $(C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S\text{-}1\text{-}O)$ with NH_4PF_6 gave **2**. In returning to our study of the base hydrolysis of $[(C_5Me_5)Rh(C_4Me_4S)]^{2+}$ it was found that high [KOH] indeed favors the formation of $(C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S\text{-}1\text{-}O)$.

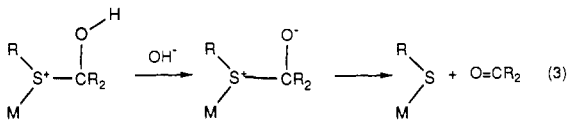
Discussion

The specific focus of this work is the pathway for metal ion promoted hydrolyses of thiophenes. A more general theme concerns the regiochemistry of nucleophilic additions to thiophene ligands where we demonstrate both S- and C-centered reactivity.

Scheme II



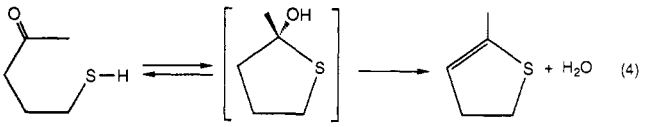
The hydrolytic cleavage of the C–S bond in $[(C_5Me_5)Rh(C_4Me_4S)]^{2+}$ has been shown to proceed via a 2-hydroxythiophenyl complex. The C–S cleavage event occurs upon the deprotonation of this intermediate. One can view 2-hydroxythiophenyl complexes as α-hydroxysulfonium ions ($R_2S^+C(OH)R'_2$) wherein one substituent (R) on sulfur is $Rh(C_5Me_5)$ instead of an alkyl group (eq 3). Sulfonium ions are susceptible to nucleophilic attack at carbon



(3)

with displacement of a thioether.[14] In the case of compounds like **3**, the "thioether" leaving group is a rhodium mercaptide ($(C_5Me_5)Rh$–S–R) and the nucleophile is generated intramolecularly by deprotonation of the hydroxyl group. The long C–S bond in the 2-hydroxythiophenyl complex suggests that this bond is weakened. A similarly long C–S bond of 1.91 Å is observed in the compound $[(C_6Me_6)Ru(\eta^4\text{-}2,5\text{-}Me_2C_4H_2S\text{-}2\text{-}H)]^+$ where again the modified thiophene is attached through three carbon atoms and the thioether.[15]

An alternative perspective on the chemistry of these rhodium thiophene complexes comes from the studies on the protonation of the acyl thiolate. A key finding was that the weakly acidic NH_4^+ allows one to selectively add only one proton to the acyl thiolate. Monoprotonation indeed results in C–S bond formation. With regards to mechanism, this transformation could be triggered by protonation either at oxygen (carbocation mechanism) or at sulfur (hemithioketal mechanism) (Scheme II). Protonation of the carbonyl oxygen would lead to a carbocation which could then attack the thiolate sulfur. Alternatively, C–S formation could proceed via initial protonation at sulfur followed by addition of the coordinated thiol to the carbonyl oxygen. Spontaneous cyclization of mercapto ketones has been observed to give unsaturated heterocycles. The presumed intermediate hemithioacetal is formed by attack of the thiol group on the carbonyl oxygen. This hypothetical intermediate, which spontaneously dehydrates to give the unsaturated heterocyclic ring, has not been isolated (eq 4).[16]



(4)

Both the carbocation and hemithioketal mechanisms invoke the nucleophilicity of the sulfur center in these acyl thiolates. Indeed

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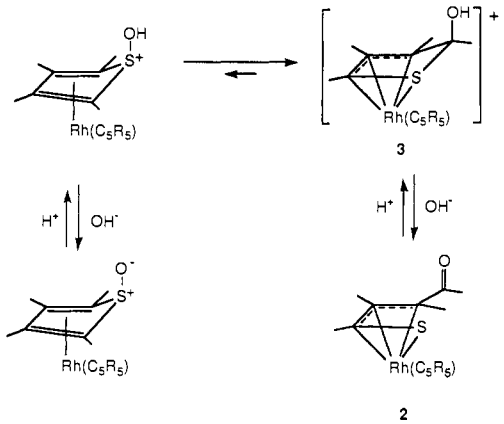
Scheme III

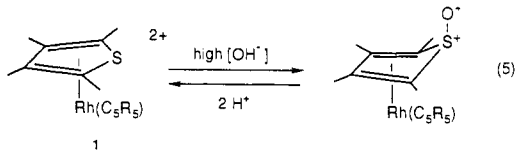


recent work demonstrates that terminal thiolate ligands are highly nucleophilic in charge-neutral 18e complexes, especially those lacking strong π-acceptor coligands.[17] The easy methylation of acyl thiolate **2** to give **4** highlights the nucleophilicity of the thiolate but does not distinguish between the mechanistic possibilities in Scheme II. The nucleophilicity of the sulfur atom in the related ene thiolate $(C_5H_5)Co(SC_3R_4)$ complexes has been demonstrated.[18]

Having elucidated the structural chemistry associated with the C–S cleavage event, our attention turned to the pathway for the addition of OH^- to the coordinated thiophene. Under the conditions employed for the conversion of **1** to **2**, $[(C_5Me_4H)Rh(C_4Me_4S)]^{2+}$ reacts with OH^- to give the sulfoxide $(C_5Me_4H)Rh(C_4Me_4S\text{-}1\text{-}O)$. Previously we could only prepare $(C_5Me_5)Rh(C_4Me_4S\text{-}1\text{-}O)$, in good yield at least,[19] by oxygenation of $(C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S)$.[13] Monopotonation of $(C_5R_5)Rh(C_4Me_4S\text{-}1\text{-}O)$ gave $[(C_5R_5)Rh(C_4Me_4S\text{-}2\text{-}OH)]^+$ for both $C_5R_5 = C_5Me_5$ and C_5Me_4H. These 2-hydroxy derivatives deprotonate with strong base to give acyl thiolates such as **2**. The facile proton-induced conversion of $(C_5R_5)Rh(C_4Me_4S\text{-}1\text{-}O)$ to $[(C_5R_5)Rh(C_4Me_4S\text{-}2\text{-}OH)]^+$ shows that the movement of OH^- from sulfur to carbon is fast. In fact, it is *the diminished mobility of the oxo group that allowed us to isolate the kinetic product of the base hydrolysis*, i.e. $(C_5R_5)Rh(\eta^4\text{-}C_4Me_4S\text{-}1\text{-}O)$. The complex $(CO)_3Mn\{\eta^4\text{-}C_4(CF_3)_4S\text{-}1\text{-}C_6F_5\}$ provides a structurally characterized precedent for the proposed intermediate $[(C_5H_5)Rh(\eta^4\text{-}C_4Me_4S\text{-}1\text{-}OH)]^+$.[20]

It is not established by this work if the relocation of the hydroxyl group from sulfur to carbon is intramolecular, i.e. a true migration, or if this change occurs via a detachment/reattachment sequence. The finding that the hydroxyl substituent in **3** is axial is consistent with a suprafacial migration as the oxo group in $(C_5R_5)Rh(C_4Me_4S\text{-}1\text{-}O)$ is also axially oriented.

Under virtually identical reaction conditions, the course of base hydrolysis of $[(C_5R_5)Rh(C_4Me_4S)]^{2+}$ showed some dependence on the degree of methylation of the cyclopentadienyl groups. Thus the major product for $C_5R_5 = C_5Me_4H$ was the $C_4Me_4S\text{-}1\text{-}O$ complex while the C_5Me_5 and C_5Me_4Et analogues gave primarily $(C_5R_5)Rh(SC_3Me_3COMe)$. Actually more detailed analysis of the reaction products for the case of the permethyl derivative showed that both acyl and S-oxide products are formed in these reactions. It was found that *high* $[OH^-]$ favors the conversion of $[(C_5Me_5)Rh(\eta^5\text{-}C_4Me_4S)]^{2+}$ to the S-oxide isomer (eq 5).[21] As



shown in Scheme III, the factors that determine the formation of the kinetic (sulfoxide) or thermodynamic (acyl) isomers can be ascribed to competition between the rates of deprotonation and isomerization of the initially-formed $[(C_5R_5)M(C_4Me_4S\text{-}1\text{-}OH)]^+$. We suggest that the relatively greater proportion of S-oxide in the case of the C_5Me_4H complex reflects in part the enhanced kinetic acidity of the incipient product $[(C_5Me_4H)Rh(\eta^4\text{-}C_4Me_4S\text{-}1\text{-}OH)]^+$. Complementary studies on the reactivity of cationic thiophene complexes toward $[OH^-]$ are underway in a related ruthenium system.[8]

This work leads to the following intriguing question: In other cases whereby nucleophiles add to the 2-carbon position of thiophenes,[22] do these reactions also proceed via initial nucleophilic attack at sulfur? Molecular orbital calculations suggests that the sulfur atom is the most electropositive site in thiophene.[23] Coordination of such a quasication to a dicationic metal center could only enhance the electrophilicity of the sulfur atom.[24] In fact one could say that the sulfur center in cationic π-thiophene complexes is a "super-sulfonium ion", as it is particularly electrophilic.

Experimental Section

Reactions were performed under nitrogen using Schlenkline methods unless otherwise noted. Solvents were reagent grade. Dichloromethane and acetone were stored over 4 Å molecular sieves for at least 24 h and degassed by purging with nitrogen. Toluene was distilled from Na under nitrogen. $[(C_5Me_5)Rh(C_4Me_4S)](OTf)_2$, $[(C_5Me_4Et)Rh(C_4Me_4S)](OTf)_2$,[25] and $C_5Me_4H_2$[26] were prepared using published procedures.

Infrared spectra were collected on KBr pellets using a Mattson Galaxy 3000 Fourier transform spectrophotometer. ^1H and ^{13}C NMR spectra were collected on a GE QE-300 spectrometer at 300 and 75.48 MHz, respectively.

$(C_5Me_5)Rh(\eta^4\text{-}SC_3Me_3C(O)Me)$ (2) by Base Hydrolysis of $[(C_5Me_5)Rh(\eta^5\text{-}C_4Me_4S)]^{2+}$. To 1.00 g of $[(C_5Me_5)Rh(C_4Me_4S)](OTf)_2$ (1.48 mmol) was added 150 mL of 0.030 M aqueous KOH (4.5 mmol). The initially pale yellow solution immediately became dark orange and upon stirring overnight produced a precipitate. The dark red solid was filtered and washed in air with 2 × 10 mL portions of water. Adding the KOH solution to solid $[(C_5Me_5)Rh(C_4Me_4S)](OTf)_2$ represents a simplification of the previous syntheses,[4] in which the base solution was added to an aqueous solution of $[(C_5Me_5)Rh(C_4Me_4S)](OTf)_2$. Yield: 0.466 g (80%). Anal. Calcd (found) for $C_{18}H_{27}ORhS$: C, 54.82 (54.69); H, 6.90 (7.03); S, 8.13 (8.23); Rh, 26.09 (25.90). ^1H NMR (C_6D_6): δ 2.28 (br s, 3 H), 2.091 (s, 3 H), 1.493 (s, 3 H), 1.450 (s, 15 H), 1.295 (s, 3H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 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: $\nu_{C=O}$ = 1667 cm^{-1}. FDMS: m/z 394 (M^+).

$(C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S\text{-}1\text{-}O)$ by Base Hydrolysis of $[(C_5Me_5)Rh(\eta^5\text{-}C_4Me_4S)]^{2+}$. To 1.00 g of $[(C_5Me_5)Rh(C_4Me_4S)](OTf)_2$ (1.48 mmol) was added 52 mL of 0.085 M aqueous KOH solution (4.4 mmol). A dark red oily solid precipitated within minutes. All solvent was removed under vacuum, and the residue was dissolved in a minimum amount of

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toluene. The dark red solution was filtered, and the filtrate was evaporated under vacuum. The ^1H NMR spectrum of the C_6D_6 solution of the residue showed that this product consisted of a ~1:1 mixture of $(C_5Me_5)Rh(\eta^4\text{-}SC_3Me_3C(O)Me)$ and $(C_5Me_5)Rh(C_4Me_4S\text{-}1\text{-}O)$. Note that the ^1H NMR spectrum of the S-oxide is strongly solvent dependent and that this compound forms a hydrate.

$(C_5Me_4Et)Rh(SC_3Me_3C(O)Me)$. This synthesis was carried out analogously to that for **2** from 218 mg of $[(C_5Me_4Et)Rh(C_4Me_4S)](OTf)_2$ (0.315 mmol) and 34 mL of 0.028 M aqueous KOH (0.94 mmol). ^1H NMR (C_6D_6): δ 2.28 (br s, 3 H), 2.096 (s, 3 H), 1.92 (q, 2 H), 1.500 (s, 3 H), 1.486 (s, 3 H), 1.461 (s, 3 H), 1.447 (s, 3 H), 1.403 (s, 3 H), 1.299 (s, 3 H), 0.82 (t, 3 H). IR: ν_{CO} = 1667 cm^{-1}. FDMS: m/z 408 (M^+).

Conversion of 2 to 1. Addition of 13.5 μL of HOTf (0.15 mmol) to a stirred solution of 30 mg of **2** (0.076 mmol) in 5 mL of CH_2Cl_2 resulted in an immediate color change from dark red to light brown. After 5 min, the solvent was removed under vacuum. The residue was extracted into ~1 mL of acetone (in air) and filtered through Celite. The filtrate was diluted with ~4 mL of $CHCl_3$ and the solution volume was reduced to ~4 mL. The ^1H NMR spectrum of the yellow microcrystalline precipitate matched closely that for **1** prepared by the literature method. Yield: 40.6 mg (79%). ^1H NMR (d_6-acetone): δ 2.66 (s, 6 H), 2.44 (s, 6 H), 2.25 (s, 15 H).

$[(C_5Me_5)Rh(C_4Me_4S\text{-}2\text{-}OH)]PF_6$ (3). A solution of 135 mg of **2** (0.342 mmol) in 20 mL of CH_2Cl_2 was added to a stirred slurry of 61.4 mg of NH_4PF_6 (0.377 mmol) in 20 mL of CH_2Cl_2. The dark red solution gradually assumed an orange color. After being stirred for ~12 h, the solution was concentrated to 10 mL and filtered. Dilution of the filtrate with 30 mL of Et_2O produced bright yellow microcrystals which were washed with Et_2O. Yield: 110 mg (63%). Anal. Calcd (found) for $C_{18}H_{28}F_6OPRhS$: C, 40.01 (40.23); H, 5.22 (5.18); S, 5.93 (5.76); P, 5.73 (5.27). ^1H NMR (d_6-acetone): δ 6.98 (br s, 1 H), 2.38 (s, 3 H), 2.01 (d, 3 H, J = 1.2 Hz), 1.95 (s, 15 H), 1.85 (s, 3 H); 1.66 (s, 3 H). ^1H NMR (CD_2Cl_2): δ 4.53 (br s, 1 H), 2.32 (s, 3 H), 1.95 (d, 3 H, J = 1.2 Hz), 1.85 (s, 15 H), 1.82 (s, 3 H), 1.57 (s 3 H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 108.09 (d, J = 3.55 Hz); 100.27 (d, C_5Me_5, J = 6.87 Hz), 99.67 (d, J = 5.89 Hz), 90.73 (d, J = 9.28 Hz), 82.93 (d, J = 9.96 Hz), 23.93 (s), 14.38 (s), 11.15 (d, J = 0.75 Hz), 9.90 (s), 9.60 (s, C_5Me_5). FAB-MS m/z 395 (M^+). IR: ν_{O-H} = 3515 cm^{-1}.

$[(C_5Me_5)Rh(C_4Me_4S\text{-}2\text{-}OH)]OTf$. To a solution of 148 mg of **2** (0.376 mmol) in 50 mL of CH_2Cl_2 was added 33.3 μL of HOTf (56.4 mg, 0.373 mmol). The solution was stirred for 100 min, during which the initial red color became dark brown. The solution was concentrated to 20 mL under vacuum, and 20 mL of diethyl ether was added, giving a flocculant orange precipitate. The light orange solid was collected and recrystallized from CH_2Cl_2/Et_2O. Yield: 97 mg, 47%. This compound is identical to **3** based on ^1H NMR spectroscopy but was found to contain small amounts of **1**.

$[(C_5Me_5)Rh(\eta^4\text{-}MeSC_3Me_3C(O)Me)]OTf$ (4). A solution of 93 mg of **2** (0.24 mmol) in 20 mL of CH_2Cl_2 was treated with 20.9 μL of MeOTf (0.185 mmol). After 90 min, 30 mL of toluene was added and the solution concentrated to ~30 mL to give a dark orange powder which was washed with toluene. Yield: 71 mg (69%). Anal. Calcd (found) for $C_{20}H_{30}O_4F_6RhS$: C, 43.01 (42.90); H, 5.41 (5.37). ^1H NMR (CD_2Cl_2): δ 2.42 (d, 3 H, J = 0.9 Hz), 2.26 (s, 3 H), 2.11 (s, 3 H), 1.87 (s, 18 H), 1.76 (s, 3 H). $^{13}C\{^1H\}$ NMR (d_6-acetone): δ 198.30 (br s), 102.27 (C_5Me_5, d, J = 10.94 Hz), 99.00 (d, J = 7.92 Hz), 95.78 (d, J = 12.20 Hz), 77.59 (d, J = 23.14 Hz), 27.21 (s), 21.54 (s), 20.25 (s), 15.01 (s), 14.59 (s), 9.36 (C_5Me_5, s). FAB-MS: m/e 409 (M^+). IR: ν_{CO} = 1664 cm^{-1}.

$[(C_5Me_4H)RhCl_2]_2$. To a solution of 3.0 g of $RhCl_3\cdot(H_2O)_x$ (13.2 mmol based on 45% Rh) in 50 mL of degassed MeOH was added 4.22 g of tetramethylcyclopentadiene. The solution was heated at reflux for 18 h. After the solution was cooled to room temperature, all volatiles were removed under vacuum. The residue was rinsed with hexane to remove organics and extracted with 3 × 20 mL of $CHCl_3$. The $CHCl_3$ extract was concentrated and diluted with toluene to give dark red-brown microcrystals. Yield: 1.63 g (42%). ^1H NMR ($CDCl_3$): δ 5.01 (s, 1 H), 1.70 (s, 6 H), 1.64 (s, 6 H).

$[(C_5Me_4H)Rh(C_4Me_4S)](BF_4)_2$. This synthesis was adapted from the method of Maitlis.[15] A solution of 1.25 g of $AgBF_4$ (6.42 mmol) in 20 mL of acetone was added to a slurry of 900 mg of $[(C_5Me_4H)RhCl_2]_2$ (1.53 mmol) in 60 mL of acetone resulting in an instant color change from dark orange to bright yellow and a precipitation of AgCl. After the solution was stirred for 210 min, 715 μL of C_4Me_4S (690 mg, 4.90 mmol) was added, resulting in a lightening of the color of the mixture. After 30 min the slurry was filtered through Celite (in air) and the yellow salt was recrystallized from acetone by dilution with $CHCl_3$. Yield: 1.13 g (69%). Anal. Calcd (found) for $C_{17}H_{25}B_2F_8RhS$: C, 37.96 (37.79); H, 4.68 (4.85); B, 4.02 (3.88); Rh, 19.13 (18.89); S, 5.96 (5.72). ^1H NMR (d_6-acetone): δ 3.77 (s, H), 2.68 (s, 6 H), 2.49 (s, 6 H), 2.27 (s, 6 H), 2.23 (s, 6 H).

$(C_5Me_4H)Rh(C_4Me_4S\text{-}1\text{-}O)$. To a solution of 150 mg of $[(C_5Me_4H)Rh(C_4Me_4S)](BF_4)_2$ (0.28 mmol) in 5 mL of H_2O was added 28 mL of 0.03 M aqueous KOH (0.84 mmol). The solution was stirred for 3 h and then evaporated to dryness. The residue was dissolved in 5 mL of acetone (in air) and diluted with 20 mL of toluene. The solution was concentrated to 10 mL and filtered and evaporated to yield the product. Yield: 83 mg (78%). ^1H NMR (C_6D_6): δ 4.37 (s, 1 H), 1.59 (s, 6 H), 1.44 (s, 6 H), 1.41 (s, 6 H), 1.32 (s, 6 H). IR: ν_{SO} = 1012 cm^{-1}. FDMS: m/z 380 (M^+).

$[(C_5Me_4H)Rh(C_4Me_4S\text{-}2\text{-}OH)]PF_6$. This compound was prepared analogously to **3**. A solution of 80 mg of $(C_5Me_4H)Rh(C_4Me_4S\text{-}1\text{-}O)$ (0.21 mmol) in 15 mL of CH_2Cl_2 was added to a stirred slurry of 41 mg of NH_4PF_6 (0.25 mmol) in 10 mL of CH_2Cl_2. After 18 h, the solution was filtered and diluted with 40 mL of Et_2O to produce bright yellow microcrystals. Yield: 46 mg (42%). Anal. Calcd (found) for $C_{17}H_{26}F_6OPRhS$: C, 38.80 (38.93); H, 4.98 (5.18); P, 5.89 (5.48); Rh, 19.55 (18.41); S, 6.09 (6.52). ^1H NMR (CD_2Cl_2): δ 5.20 (s, 1 H), 4.37 (s, 1 H), 2.38 (s, 3 H), 2.00 (unresolved d, 3 H), 1.89 (s, 3 H), 1.87 (s, 3 H), 1.81 (s, 3 H), 1.77 (s, 3 H), 1.63 (s, 3 H), 1.55 (s, 3 H). IR: ν_{OH} = 3515 cm^{-1}. FAB-MS: m/z 381 (M^+).

$(C_5Me_4H)Rh(SC_3Me_3C(O)Me)$. To a slurry of 33 mg of $[(C_5Me_4H)Rh(C_4Me_4S\text{-}2\text{-}OH)]PF_6$ (0.063 mmol) in 1 mL of H_2O was added 2.3 mL of 0.03 M KOH (0.069 mmol) in air. An instant color change and precipitation of a red solid occurred. After 100 min no further color change was evident and all solvent was removed under vacuum. The residue was dissolved in ~2 mL of acetone. This solution was diluted with ~5 mL of toluene and the volume was reduced to ~5 mL and filtered. The dark red filtrate was evaporated to give a yield of 18 mg (75%). ^1H NMR (C_6D_6): δ 4.39 (br s, 1 H), 2.32 (br s, 3 H), 2.12 (s, 3 H), 1.57 (s, 3 H), 1.54 (s, 3 H), 1.42 (s, 3 H), 1.40 (s, 3 H), 1.35 (s, 3 H), 1.27 (s, 3 H). IR: ν_{CO} = 1665 cm^{-1}.

$[(C_5Me_5)Rh(C_4Me_4S\text{-}2\text{-}OH)]PF_6$ from $(C_5Me_5)Rh(C_4Me_4S\text{-}1\text{-}O)$. This reaction was conducted analogously to the reaction of $(C_5Me_4H)Rh(C_4Me_4S\text{-}1\text{-}O)$ and NH_4PF_6 using 205 mg of $(C_5Me_5)Rh(C_4Me_4S\text{-}1\text{-}O)$ (0.52 mmol) and 102 mg of NH_4PF_6 (0.62 mmol). The yellow microcrystalline product was identified as **3** by ^1H NMR in comparison with an authentic sample. Yield: 82 mg (30%).

$(C_5Me_5)Rh(C_4Me_4S\text{-}1\text{-}O)$ by Oxygenation of $(C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S)$. A solution of 397 mg of $(C_5Me_5)Rh(C_4Me_4S)$ (1.05 mmol) in 50 mL of toluene was stirred under a dry O_2 atmosphere for 12 h. Removal of the solvent gave $(C_5Me_5)Rh(C_4Me_4S\text{-}1\text{-}O)$ in quantitative yield. Anal. Calcd (found) for $C_{18}H_{27}ORhS$: C, 54.82 (54.80); H, 6.90 (6.86). ^1H NMR (C_6D_6): δ 1.55 (s, 6 H), 1.41 (s, 15 H), 1.39 (s, 6 H). ^1H NMR (d_6-acetone): δ 1.81 (s, 6 H), 1.77 (s, 15 H), 1.57 (s, 6 H). $^{13}C\{^1H\}$ NMR (d_6-acetone): δ 95.4 (s, C_5Me_5), 88.71 (d, C_4Me_4, J_{Rh-C} = 6.78 Hz), 75.46 (d, C_4Me_4, J_{Rh-C} = 13.3 Hz), 10.89 (s, C_4Me_4), 10.72 (s, C_4Me_4), 9.44 (s, C_5Me_5). IR: ν_{SO} = 1010 cm^{-1}. FDMS: m/z 394 (M^+).

X-ray Crystallographic Analysis of $[(C_5Me_5)Rh(C_4Me_4S\text{-}2\text{-}OH)]OTf$. The crystal was grown from CH_2Cl_2 by slow diffusion of diethyl ether at −23 °C. The orange-yellow, translucent, prismatic data crystal of **3** had poorly developed faces but uniformly extinguished plane-polarized light. The crystal was mounted with epoxy to a thin glass fiber and then cooled to −40 °C with the (1 −3 5) scattering planes roughly normal to the spindle axis. The crystal was approximately bound by the following forms: {1 0 0}, {0 1 0}, and {0 0 1}. Distances from the crystal center to these facial boundaries were 0.11, 0.13, and 0.22 mm, respectively.

The structure was solved by Patterson methods (SHELXS-86); the correct rhodium position was deduced from a vector map. Subsequent least-squares refinement and difference Fourier syntheses revealed positions for the remaining non-hydrogen atoms. Methyl hydrogen atoms were included as fixed contributors in "idealized" positions; the hydroxyl hydrogen was independently refined. In the final cycle of least-squares refinement, anisotropic thermal coefficients were refined for the non-hydrogen atoms, an isotropic thermal coefficient was refined for the hydroxyl hydrogen, and a common isotropic thermal parameter was varied for the hydrogen atoms. Successful convergence was indicated by the maximum shift/error for the last cycle. The final difference Fourier map had no significant features. A final analysis of variance between observed and calculated structure factors showed no systematic errors.

X-ray Crystallographic Analysis of $[(C_5Me_5)Rh(MeSC_3Me_3C(O)Me)]OTf$. The crystal was grown from CH_2Cl_2 by slow diffusion of diethyl ether at −23 °C. The orange, transparent crystal was cut from a large crystalline mass that had no natural faces. Attempts to shape the data crystal along natural faces were not entirely successful and the boundaries were rough. There were several internal flaws but the crystal uniformly extinguished plane-polarized light. The data crystal was mounted with epoxy to a thin glass fiber and then cooled to −30 °C with the (2 −1 0) scattering planes roughly normal to the spindle axis. The

Table III. Summary of Crystallographic Data

formula	$[C_{18}H_{28}ORhS][CF_3O_3S]$	$[C_{19}H_{30}ORhS][CF_3O_3S]$
crystal system	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a, Å	8.618 (3)	8.986 (2)
b, Å	18.192 (3)	9.343 (2)
c, Å	14.209 (5)	14.745 (4)
α, deg	90	92.920 (7)
β, deg	96.39 (1)	107.510 (7)
γ, deg	90	94.214 (8)
Z	4	2
V, Å^3	2214 (2)	1173.9 (8)
density (calcd), g/cm^{-3}	1.633	1.580
color	orange-yellow	orange
dimensions, mm	0.2 × 0.3 × 0.4	0.2 × 0.2 × 0.4
temp, °C	−40	−30
diffractometer	Syntex $P2_1$	Syntex $P2_1$
radiation	Mo Kα	Mo Kα
μ, cm^{-1}	9.86	9.31
transmission factor range	0.813–0.760	0.874–0.800
2θ limit	$3° < 2\theta < 46°$	$3° < 2\theta < 50°$
no. of reflcns measured	3563	5169
no. of unique reflcns	2891	4037
no. of reflcns with $I > 2.58\sigma(I)$	2542	3791
R	0.034	0.041
R_w	0.049	0.063
$\Delta(\rho)$, e Å^{-3}	$0.53 > \Delta(\rho) > -0.71$	$1.63 > \Delta(\rho) > -0.76$

crystal was approximately bound by the {0 0 1} and {2 0 −1} forms and the (1 4 −4) and (0 −1 1) faces. Distances from the crystal center to these facial boundaries were 0.09, 0.22, 0.09, and 0.10 mm, respectively.

The structure was solved by direct methods (SHELXS-86); the correct rhodium atom position was deduced from the E-map. Subsequent least-squares refinements and difference Fourier syntheses revealed positions for the remaining non-hydrogen atoms. Hydrogen atoms were included as fixed contributors in idealized positions. In the final cycle of least-squares refinement, anisotropic thermal coefficients were refined for non-hydrogen atoms and a common isotropic thermal parameter was varied for hydrogen atoms. Successful convergence was indicated by the maximum shift/error for the last least-squares cycle. The highest peak in the final difference Fourier map was in the vicinity of the anion and the only other peaks above background were in the vicinity of the rhodium atom; the final map had no other significant features. An analysis of variance between observed and calculated structure factors showed a slight dependence on sin (Θ). Refinement in the acentric space group $P\bar{1}$ converged with significant differences between chemically equivalent bond lengths and failed to significantly improve the weighted residual. Average values of the normalized structure factors supported the acentric choice which was ultimately rejected on the basis of refinements. Bond lengths and angles for the $CF_3SO_3^-$ ion reflected excessive thermal motion and possibly disorder. Attempts to describe a disordered model for this ion were not successful.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond angles and distances for $[(C_5Me_5)Rh(C_4Me_4S\text{-}2\text{-}OH)]OTf$ and $[(C_5Me_5)Rh(MeSC_3Me_3COMe)]OTf$ (10 pages); listing of structure factors (43 pages). Ordering information is given on any current masthead page.

General Approaches to Phosphinidenes via Retroadditions

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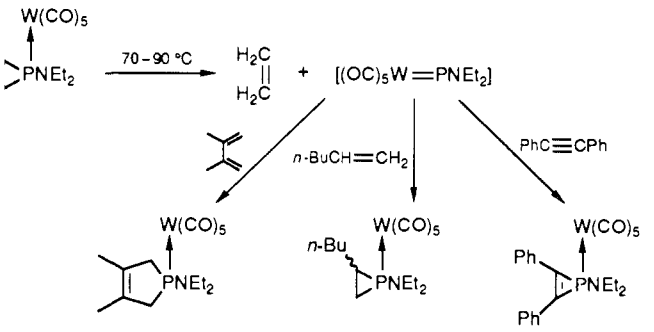
Abstract: The retroaddition strategy for the generation of phosphinidenes involves thermal and photochemical decomposition of 1-arylphosphiranes and photolysis of 1-aryl-3-phospholenes. Evidence that free phosphinidenes are produced as reactive intermediates includes a lack of dependence of the conversion rate on precursor and substrate concentrations and the nature of the reaction products. These are best rationalized by the addition of phosphinidenes to carbon–carbon π-bonds forming three-membered rings and the dimerization of phosphinidenes to diphosphenes.

The novelty and synthetic utility of the reactions of species containing subvalent six-electron neutral atoms have led to a wide interest in the chemistry of carbenes,[1] nitrenes,[2] silylenes,[3] and, more recently, germylenes.[4] Despite considerable effort,[5] little is known about the monovalent phosphorus species, phosphinidenes, largely for want of general routes to them. Indeed, Mathey has voiced skepticism toward the entire enterprise: "...generation of these transient phosphinidenes is deduced from the isolation of products whose formation can be explained by a mechanism involving such intermediates. However, in almost every case, it is possible to conceive alternate mechanisms which do not involve phosphinidenes."[5]

A striking difference between the chemistry of carbenes and that of their silicon and germanium analogs is that virtually every silylene and germylene reaction is *reversible*. Having generated silylenes and germylenes by extrusion from their familiar addition

Scheme I



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