Order Number 9503606

Selenophene transition metal complexes

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Iowa State University, 1994

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Selenophene transition metal complexes

by

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A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Inorganic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1994

Dedication

To my mother, Roberta C. White,

and brothers,

John W. White, Lawrence C. White and Robert L. White.

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ACKNOWLEDGMENTS

I would like to thank my mother, Roberta, and my brothers, John, Lawrence, and Robert, to whom this work is dedicated, for their support and encouragement during all my years of scholarship. Without them I would not be where I am today.

I also would like to thank my extended family: Terese Rakow; Tyler Sunazie Rakite; Alexander Sunazie Rakite; Glenn and Dorothy Rakow; Moira, Douglas and Eoin Forsyth; and last, but not least, Leslie Perkins, for their understanding and encouragement when I needed it most.

Finally, I would like to acknowledge the following people for their professional and occasional personal support and help: Dr. Robert Angelici as my major professor; Dr. James Espenson, Dr. Eric Henderson, Dr. Dennis Johnson, Dr. Robert Mc Carley, Dr. Nenad Kostic, and Dr. Glenn Schrader all of whom have served on my Program of Study Committee; Dr. Moon Gun Choi, Dr. John Sowa, Dr. John Benson, Dr. Mitchell Robertson, Dr. Mary Rottink, Mike Sanger, and Dr. Hyoung Jun, as past colleagues of the Angelici group; Dong Mei Wang, Chip Nataro, Wayde Konze, James Rudd, Alan Ontko and Oltea Siclovan, the current Angelici group; Dr. Karen Ann Smith, Dr. Dave Scott, and Dr. Victor Young of ISU Chemistry Instrument Services; and naturally all the people in the Chemistry Department who have loaned me chemicals, equipment or advice.

This work was performed at Ames Laboratory at Iowa State University, Ames IA under Contract No. W-7405-eng-82 with the U. S. Department of Energy. The United States government has assigned the DOE Report number IS-T1699 to this dissertation.

GENERAL INTRODUCTION

Dissertation Organization

This dissertation contains three papers describing the research I have performed while at Iowa State University. Preceding these papers is a general introduction and an overview of selenophene chemistry relevant to the project. The general introduction contains two subsections, the first regarding the organization of this dissertation, and the second a general description of the goals and significance of this research. Following the general introduction, an overview of the structure, bonding, spectroscopy, synthesis, organic reaction chemistry and transition metal complexes of selenophene known prior to this research is presented to familiarize the reader. After the last paper, a final summary is given of the results of this research.

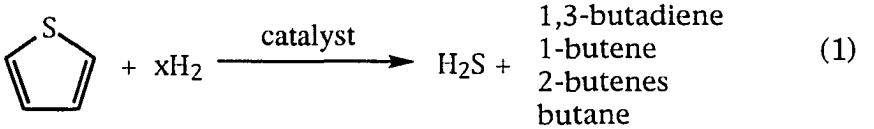
The papers in this dissertation are in the format required for publication in the the journal *Organometallics*. All table, figure, scheme, and equation numbers, literature citations and other footnotes pertain only to the section in which they appear.

Significance of Research and General Goals

Hydrodesulfurization (HDS) is a heterogeneous catalytic process which removes sulfur containing compounds from crude oil and coal liquids.[1-3] The HDS process is one of the largest catalytic reactions conducted in industry; as of January 1, 1993 capacities worldwide were 27.2 million barrels of oil per day worldwide and 9.2 million barrels per day in the USA.[4] This preteatment of

petroleum feedstocks is necessary for a number of reasons. The primary reason for removal of sulfur containing compounds from crude petroleum feedstocks is that these compounds poison the precious metal catalysts used in catalytic reforming. Further, HDS is a required step in the refinement of heavy crude oil residua with a boiling point > 350°C which consists of 5-10% sulfur. Second, during the combustion of petroleum and coal containing sulfur compounds, sulfur oxides are introduced to the air which are a known source of acid rain.[5-9] Lastly, the HDS process removes pungent sulfur compounds from petroleum products and feedstocks used for consumer items.

Although crude petroleum feedstockes contain an incredibly complex mixture of mercaptans, dialkyl and diarylsulfides, and thiophenes, thiophene (Figure 1) is one of the most difficult to desulfurize.[1,10] Thus, it is the coordination chemistry of thiophenes to transition metals that has been of interest to inorganic and organometallic chemists for the past ten years.[11-14] The HDS of thiophene itself (eq 1) gives H_2S and a mixture of C_4



(1)

hydrocarbons.[2] Often 1,3-butadiene in not observed, evidence[15] supports the suggestion that it is the inital desulfurization product. Although significant insight into the HDS procees has come from organometallic model studies, the binding of thiophene to the catalytic surface remains uncertain. This stems from the complicated nature of the catalytic surface.[16,17] Nuclear magnetic resonance (NMR) spectroscopy has been used to study the binding of benzene[18]

and ethylene[19-22] to catalytic surfaces with moderate success. These studies have relied on isotopic ^{13}C enrichment and large chemical shifts in the ^{13}C resonances caused by the binding of the molecule to the surface.[23-25] Unfortunately, analogous studies using ^{13}C enriched thiophene have not been conducted due to the high cost of ^{13}C isotopic enrichment of thiophene and the small chemical shift differences found between unbound thiophene and metal bound thiophene.[14]

Selenophene, the selenium analogue of thiophene, has a strucuture and chemistry similar to that of thiophene (Figure 1).[26-31] Selenium compounds

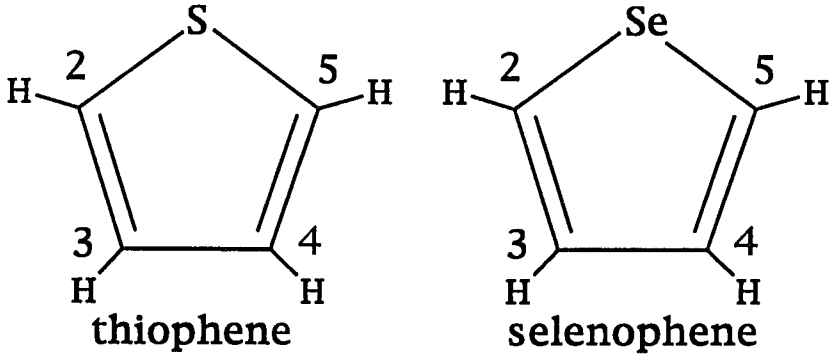


Figure 1. Structure and numbering of thiophene and selenophene.

and selenophene are virtually unknown in fossil fuels[32] and therefore do not represent the problem that sulfur compounds present. The ^{77}Se isotope is a NMR active nucleus with high quality, narrow line width NMR spectra having been known for years.[33,34] With a natural abundance of 7.58%, a relative receptivity three times greater than ^{13}C and a chemical shift range over 3000 ppm,[33] ^{77}Se surface NMR and selenophene have the potential for being an effective probe of the HDS catalytic surface.

Before initiating ^{77}Se NMR surface studies of the HDS catalyst using selenophene, several questions need to be answered. First, what are the effects of changing the heteroatom from sulfur to selenium on the HDS process and the related organometallic model chemistry? If the differences in chemistry are great, than the utility of selenophene as a surface probe is diminished. Secondly, can the differences in the chemistry of metal coordinated thiophene and selenophene be used to gain insight into the possible mechanism of the HDS process? The ^{77}Se NMR chemical shifts associated with the different coordination modes of selenophene are unknown. If these shifts are not large, as is the case for the ^{13}C chemical shifts, than broadening due to surface effects may eliminate any useful information. Therefore, what are the changes in the ^{77}Se NMR upon metal coordination and can the ^{77}Se chemical shift be associated with the different binding modes of selenophene? The general goals of the research reported in this dissertation are to answer these questions and to discover any new chemistry associated with the coordination of selenophene in transition metal complexes.

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OVERVIEW OF SELENOPHENE AND SELENOPHENE TRANSITION METAL CHEMISTRY

Introduction

Selenophene was first described in the literature in 1928;[1] however, references to its derivatives were reported eariler.[2,3] This makes selenophene a relatively new compound when compared to thiophene and furan. One main reason for the slow evolution of selenophene chemistry is that selenophene is a manmade compound and not found in nature. The development of selenophene chemistry was stimulated by questions regarding the effect of selenium on the aromaticity of five membered heterocyclic rings.[1]

Several earlier reviews[4-7] are available which cover the chemistry of selenophene and its related heterocycles in greater depth. This section of the dissertation is not intended to be an in-depth review of all selenophene chemistry. Instead, the focus will be to familiarize the reader with the chemistry of selenophene in relation to thiophene, thiophene coordination and modeling of hydrodesulfurization.

Structure and Bonding in Selenophene

Selenophene (Sel) (Figure 1) has a molecular structure that closely resembles that of its sulfur containing analogue thiophene (T). The numbering of the ring system begins with the heteroatom and proceeds sequentially around the ring as shown in Figure 1. In the older literature C(2) and C(5) are commonly referred to as the α-positions, while C(3) and C(4) are the β-positions. The molecular geometries of selenophene [8-10] and thiophene [11]

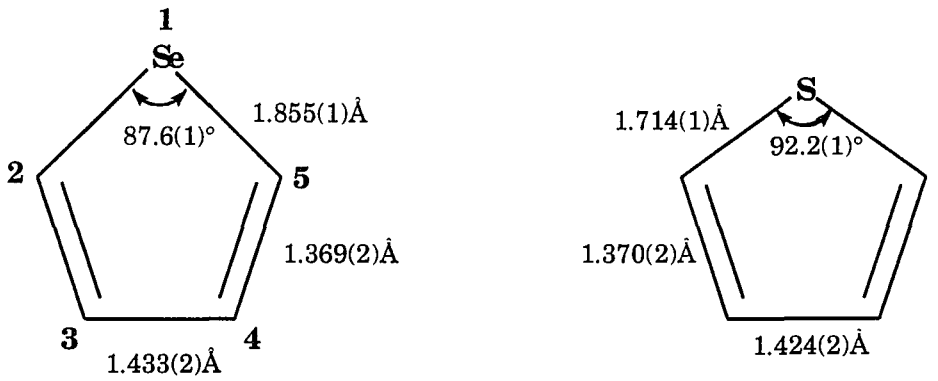


Figure 1. Structural Drawing of Selenophene and Thiophene

Table 1. Molecular Geometries of Thiophene and Selenophene

Bond Length (Å)	Thiophene X=S [a]	Selenophene X=Se [b]
X-C(2)	1.714	1.855
C(2)-C(3)	1.370	1.369
C(3)-C(4)	1.423	1.433
C(2)-H	1.078	1.070
C(3)-H	1.081	1.079

Atoms	Angle (degrees)	Angle (degrees)
C(2)-X-C(5)	92.17	87.76
X-C(2)-C(3)	111.47	111.56
C(2)-C(3)-C(4)	112.45	114.55
X-C(2)-H	119.85	121.73
C(2)-C(3)-H	123.28	122.59

[a] Reference 10 [b] Reference 11

have been established by microwave spectroscopy. A comparison of the bond distances and angles is given in Figure 1 and Table 1. As would be expected, the C-Se bond length in Sel is 0.141Å longer than the C-S bond of the thiophene, principally due to the larger size of the heteroatom. A decrease in the angle C(2)-X-C(5) by 4.41° is also found which is also due to the larger size of the Se heteroatom. Comparison of the C(2)-C(3) and C(3)-C(4) bond lengths for Sel and T show no experimental differences between the two. The remaining bond angles within the ring are slightly different, however this once again can be attributed to the larger size of selenium. Overall, the longer C-Se bond distances and smaller C(2)-Se-C(3) angle of selenophene give selenophene an elongated shape in comparison to thiophene or furan.

The delocalization of electron density by the π-orbital system of the ring is often called the "aromaticity" of the ring. Measurements of the ground state aromaticity of thiophene, benzene and furan have been based on either thermodynamic, structural or magnetic methods. These studies have shown that thiophene is more aromatic than furan, but substantially less aromatic than benzene.[12] The aromaticity of selenophene has been determined to be similar to that of thiophene from studies based on chemical, spectroscopic[4] and magnetic properties.[13] The aromatic resonance energy estimated from heats of combustion or heats of hydrogenation are not considered accurate due to experimental difficulties.[7]

Quantitative comparison of aromaticity under homogeneous conditions in solution have been carried out using spectroscopic, structural and the mesomeric dipole moment techniques (Table 2).[14-17] The first two parameters (Table 2) are derived from the NMR spectra of the heterocycles and are based

Table 2. Aromaticity Criteria for Selenophene and its Congeners

Compound	A[a]	B[a]	ΣΔN[a,b]	J[a]	N[c]	μ_m[a]
furan	7.67	1.72	1.42	0.87	43	1.03
thiophene	11.56	3.85	0.90	0.91	66	1.35
selenophene	10.44	2.94	1.02	0.91	59	1.29
tellurophene	8.50	1.85	1.30	0.88	48	1.17

[a] Reference 42 [b] Sum of bond C-C bond order. [c] Reference 17

on either the dilution shift method (A)[18,19] or the uniformity of the methyl effects on the aromatic proton chemical shifts (B).[20] The next three indices, the sum of the differences in bond orders for the three C-C bonds (ΣΔN), Julg's (J) parameter[21] and the aromaticity index (N)[17] are a combination of bond order calculations and measured bond lengths. These criteria are based on the idea that as the aromaticity of the ring increases, the C-C bonds become more intermediate between single and double bond, with nonequivalent bonds becoming similar in length and bond order. The final index is the mesomeric dipole moment(μ_m), which is related to the π-electron delocalization, and has been proposed as a criterion for measuring aromaticity of delocalized rings.[22] All of these criteria give the same order of aromaticity: thiophene > selenophene > telleurophene > furan.

The order of aromaticity can be rationalized by considering two opposing properties of the heteroatoms: the electronegativity and the amount of p-orbital overlap. In the first case, the increase in electronegativity from Te to O makes the relative size of the available p-orbital smaller and therefore decreases overlap with the adjacent π-orbital of the carbon atoms. In a valence bond description, the resonance structures in which a positive charge is localized on

the heteroatom are less favored as the electronegativity of the heteroatom increases. This then gives a decreasing trend of Te > Se > S > O for the ability of the heteroatom to conjugate with the carbon system. An opposing trend is found when the amount of heteroatom p-orbital overlap with the carbon π-orbitals is considered. As the covalent radius of the heteroatom increases (O < S < Se < Te) the length of the C-X bond and the difference in the size of the p-orbitals of X and C increases. The overlap of orbitals should be greatest for O in furan and smallest for Te in tellurophene. The actual aromaticity, therefore, must be a balance between these two effects which gives the observed trend: benzene >> thiophene > selenophene >> tellurophene > furan.

Spectroscopy of Selenophene

Vibrational Spectroscopy

The full vibrational assignments of the infrared and Raman spectra of selenophene[4] and thiophene[23] have been made through the use of deuterated derivatives (Table 3). The symmetry point group of both thiophene and selenophene is C_{2v} , therefore each has 21 vibrations with the following distribution: $\Gamma = 8A_1 + 3A_2 + 7B_1 + 3B_2$. In the C_{2v} point group, the A_2 vibrations are symmetry forbidden in the infrared and are seen in the Raman spectra. The B_1 and B_2 vibrations are observed in both the infrared and Raman spectra, while the A_1 vibrations are restricted to the infrared. Most of the vibrations are only slightly affected by the heteroatom indicating a degree of structural similarity between the two rings. The lower frequencies in selenophene for the symmetric ν_3 and antisymmetric ν_{17} stretching of the C(2)-X-C(5) and the ring deformation modes ν_8, ν_{18}, and ν_{21} have been attributed to

Table 3. Fundamental Vibrational Frequencies (in cm^{-1}) for Thiophene and Selenophene

Vibration	Approximate description	Point Group: C_{2v}	Thiophene[a] (cm^{-1})	Selenophene[b] (cm^{-1})
ν_1	C-H stretch	A_1	3110	3110
ν_2	C-H stretch		3086	3083
ν_5	ring stretch		1408	1419
ν_4	ring stretch		1360	1341
ν_6	C-H scissoring		1081	1080
ν_7	C-H scissoring		1033	1010
ν_3	ring stretch		833	758
ν_8	ring breathing		606	456
ν_9	C-H waging	A_2	900	905
ν_{10}	C-H waging		686	685
ν_{11}	ring twisting		565	544
ν_{12}	C-H stretch	B_1	3110	3100
ν_{13}	C-H stretch		3073	3054
ν_{14}	ring stretch		1506	1515
ν_{15}	C-H scissoring		1250	1243
ν_{16}	C-H scissoring		1081	1080
ν_{17}	ring deformation		871	820
ν_{18}	ring breathing		750	623
ν_{20}	C-H wagging	B_2	864	870
ν_{19}	C-H wagging		712	700
ν_{21}	ring twisting		453	394

[a] Reference 23 [b] Reference 4

the changes in geometry and mass of the different heteroatoms.

^{1}H NMR Spectroscopy

^{1}H NMR parameters for selenophene and thiophene are given in Table 4. A solvent induced change in the resonances is seen by changing the solvent

Table 4. ^{1}H NMR Parameters for Selenophene and Thiophene [a,b]

Compound	H(2), H(5) (δ)	H(3), H(4) (δ)	$J_{2,3}$ (Hz)	$J_{2,4}$ (Hz)	$J_{2,5}$ (Hz)	$J_{3,4}$ (Hz)
Selenophene	7.88	7.23	5.40	1.46	2.34	3.74
Thiophene	7.18	6.99	4.90	1.04	2.84	3.50

[a] In d_6-acetone. [b] Reference 4

from deuterochloroform to d_6-acetone with a shift of +0.22 ppm and +0.10 ppm for protons in the 2,5- and the 3,4-position respectively. The difference in chemical shifts for the resonances of the H(2),H(5) and H(3), H(4) protons in deuterochloroform is 0.65 ppm for selenophene but only 0.19 ppm in thiophene. The ^{1}H NMR spectrum of selenophene shows spin-spin coupling of ^{77}Se with the protons in the 2, 5-position with the signal having distinct satellite peaks. Spin-spin coupling of ^{77}Se with the protons in the 3,4-position of selenophene are not observed in the ^{1}H NMR spectrum because of the small value of $^3J_{Se-H}$ and the difficulty in resolving the satellite peaks.

Tabulations of the ^{1}H NMR chemical shifts and coupling constants for 2- and 3-substituted selenophenes are available.[24,25] Extrapolation to infinite dilution of the ^{1}H NMR chemical shifts in deuterioacetone for these compounds shows a difference of less than 0.05 ppm from the values for solutions containing 20% compound. A correlation has been drawn between

the ^1H NMR chemical shift of the ring protons and the electron donating ability of the substituent.[25] Derivatives containing strong electron donating substituents, e.g., OCH_3 or CH_3, have chemical shifts upfield of selenophene while strong electron withdrawing groups (NO_2, CN, or $COOCH_3$) cause a downfield shift. The trend is valid for either 2- or 3-substituted selenophenes; however, the change in chemical shift is greater in the 2-position.

^{13}C NMR Spectroscopy

The ^{13}C NMR spectrum for selenophene contains two resonances, one with a value of δ 131.0 (C(2), C(5)) and the other with δ 129.8 (C(3), C(4)) (Table 5). Assignment of the resonaces has been made based on the one bond $^1J_{C-H}$

Table 5. ^{13}C NMR Parameters for Selenophene and Thiophene[a,b]

Compound	C(2), C(5) (δ)	$^1J_{C-H}$ (Hz)	C(3), C(4) (δ)	$^1J_{C-H}$ (Hz)
Selenophene	131.0	189	129.8	166
Thiophene	125.6	185	127.3	168

[a] In d_6-acetone. [b] Reference 24

coupling values. The larger one-bond coupling constant for the carbon adjacent to the heteroatom is found in all of the five-membered heterocycles with one heteroatom.[7] Confirmation of the assignments have been made using 2-D $^1H/^{13}C$ NMR techniques.[26] Comparison of the chemical shift values of selenophene and thiophene shows that the selenophene C(2),C(5) resonaces are +4.4 ppm downfield and the resonances for C(3),C(4) are +2.5 ppm downfield of those in thiophene.

A compilation of ^{13}C NMR chemical shift data for 2- and 3-substituted selenophenes is available.[25,27] As was done with the ^1H NMR chemical shifts,

the ^{13}C NMR chemical shifts of C(5) have been correlated with the electron-donating or withdrawing abilty of the substituent.[25] Substitution of electron donating substituents in the 2-position causes an upfield shift of C(5), while electron-withdrawing groups causes a downfield shift. The same trend is seen for C(2) and C(5) of 3-substituted selenophenes; however, the effect is less pronounced. A correlation with the Swain and Lupton reactivity parameters (*F* and *R*)[28] gives a linear correlation for both 2- and 3-substituted selenophenes.[25]

Heteroatom NMR Spectroscopy

The heteroatom in both selenophene and thiophene contain NMR active isotopes. Several good references to ^{77}Se [29,30]and ^{33}S NMR[31] spectroscopy exist in the literature. A comparison of the NMR properties of ^{77}Se and ^{33}S with the more common nuclei ^{13}C and ^{1}H is given in Table 6.[29] With a nuclear spin of 1/2 and a larger natural abundance, ^{77}Se is a much easier nucleus to observe than ^{33}S. Chemical shifts for ^{77}Se range over 3000 ppm, however, selenophene compounds are usually between δ 500 to 700 (δ Me_2Se = 0.0) with linewidths less

Table 6. Heteroatom NMR Parameters for Selenophene and Thiophene[a]

Nucleus	NMR frequency (MHz)	Nuclear spin	Natural Abundance (%)	Relative receptivity	Chemical Shift Standard (δ = 0.00)
^{1}H	100	1/2	99.98	1	Me_4Si
^{13}C	25.19	1/2	1.11	1.8×10^{-4}	Me_4Si
^{33}S	7.67	3/2	0.74	1.7×10^{-5}	$(NH_4)_2SO_4$
^{77}Se	19.135	1/2	7.58	5.2×10^{-4}	Me_2Se

[a] Reference 29

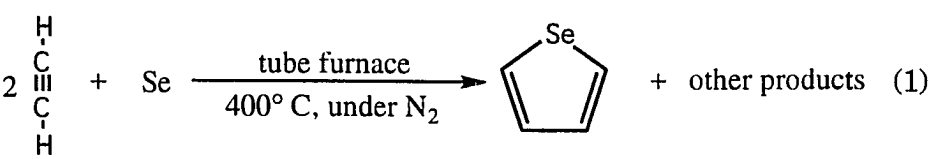
than 4 Hz. In contrast, ^{33}S chemical shifts for thiophene compounds range from δ -111 to -197 ($\delta(NH_4)_2SO_4$) = 0.0) with linewidths of 600-1600 Hz due to the quadrapole of the nucleus.

An extensive study of the ^{77}Se NMR chemical shifts of substituted selenophenes has been reported.[32] A correlation of the Swain and Lupton reactivity parameters (*F* and *R*)[28] for 3-substituted selenophenes with the change in the ^{77}Se chemical shift (ΔSe = δ(Sel) - δ(sample)) gave the equation: $\Delta Se = 8.5 + 17.5F + 170.9R$ with a σ = 13.1 and $r = 0.96$. This equation is similar to that for the correlation of the same reactivity parameters with the ^{13}C chemical shift for the same compounds with the coefficients related to each other by a factor of 6. Application of Swain and Lupton parameters to the 2-substituted selenophenes failed to give a correlation.

Synthesis and Chemical Reactions of Selenophene

Synthesis of Selenophene

Selenophene is made in the reaction of acetylene gas with selenium metal in a tube furnace at 400°C.[33] (eq 1) Addition of sand or deactivated



alumina support increases the surface area for the reaction and gives a three fold increase in the yield of selenophene. Previously used support is preferable to clean, new support because the presence of carbon deposits on the surface

eliminates an induction period before selenophene is produced. The product is gathered as a smelly oily liquid that contains red selenium, selenophene, benzene and other organoselenium compounds. The overall yield of selenophene from the reaction can be as great as 95% (based on Se) if the excess red selenium is recycled. Isolation of pure selenophene from the crude reaction mixture is done by careful distillation under N_2 with selenophene distilling at 109-112°C. Pure selenophene is a colorless clear liquid with only a moderate odor. Contamination of selenophene by organoselenides gives a yellowish appearance to the liquid and a very pungent lingering odor.

The synthesis of substituted selenophene compounds is similar to that of the analogous thiophene compounds.[34] Substitution occurs almost exclusively in the 2,5-positions making the 3,4-substituted selenophenes difficult to prepare.[7] The synthesis of 2-methylselenophene and 2,5-dimethylselenophene is best accomplished using a series of formylation and reduction reactions (Figure 2).[35-37] The yield of 2-methyl selenophene is 70% and is 40% for 2,5-dimethylselenophene utilizing this method. Other methods can be used to make 2-methylselenophene and 2,5-dimethylselenophene that involve the

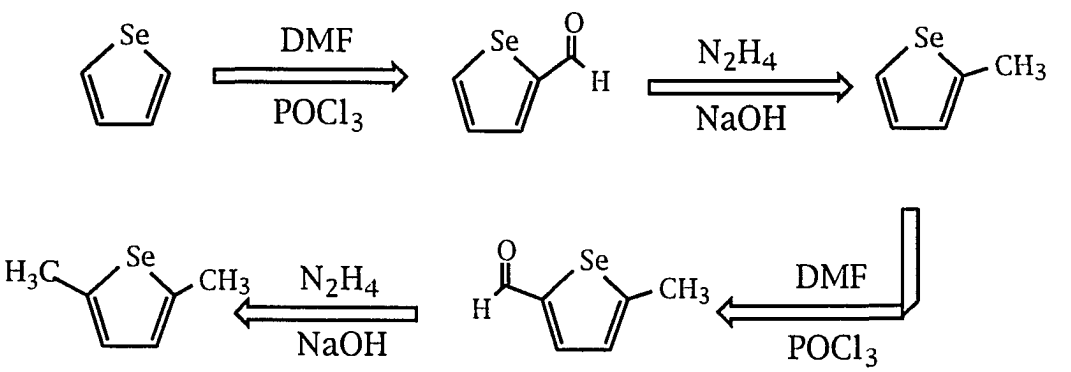


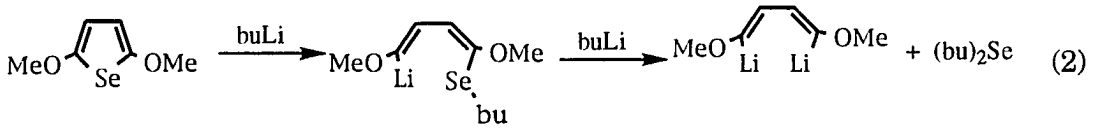
Figure 2. Synthetic scheme for the synthesis of 2-MeSel and 2,5-Me_2Sel

replacement of the oxygen in furan with selenium using H_2Se.[38] This method is impracticable and time-consuming due to the difficult method of generating H_2Se in the lab from the reaction of Al_2Se_3 and water.[39] An alternative means of making 2,5-dimethylselenophene involves the reaction of 2,5-hexadione with phosphorus pentaselenide at high temperature (190°C) in a sealed tube with a yield of 38%.[40]

Chemical Reactions

A large portion of the reaction chemistry of selenophene is identical to that of thiophene. A brief summary of selenophene chemistry that is related to the HDS process follows. More information regarding the chemical reactions of selenophene can be found in several reviews[4-7,41,42] of both selenophene and thiophene chemistry.

Reactions with Nucleophiles Selenophene readily reacts with metal alkoxides, aryls, alkyls and amides resulting in proton removal from C(2),C(5) of the ring. Kinetics of the base-catalyzed deuterium exchange of deuterioselenophene in DMSO using lithium or potassium butoxide have been studied.[4] Exchange of the deuterium in the 2-position of selenophene occurs approximately 50,000 times faster than exchange in the 3-position. Comparison of the relative exchange rates for selenophene and thiophene shows that selenophene reacts 1.5 time faster in the 2-position and 7.5 times faster in the 3-position. Metalation of selenophene by lithium alkyl reagents readily occurs and gives the 2-lithioselenophene exclusively.[25] In an interesting reaction,[43] 2,5-dimethoxyselenophene is attacked by butyllithium (eq 2) at the selenium heteroatom. This is followed by ring opening and



(2)

further reaction with butyllithium giving a mixture of products including dibutylselenide in 55% yield.

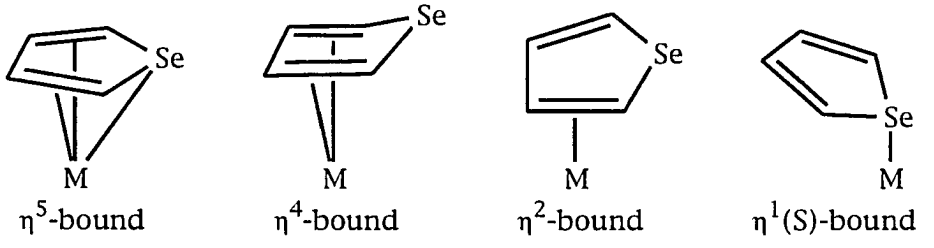
Reactions with Electrophiles Selenophene and thiophene both undergo substitution reactions when reacted with electrophiles. Substitution occurs preferentially in the 2-position due to the heteroatom. The relative reactivities of selenophene and thiophene have been measured for a range of electrophiles.[44] The largest difference (47.5) in reactivity occurs for bromination in acetic acid, while the smallest difference (1.9) is observed for acetylation with acetic anhydride and a tin(IV)chloride catalyst. A general relationship has been found between the electrophilic substitution rates for furan, thiophene, selenophene and tellurophene and the resonance energy of the ring.[42] Thus furan, with the lowest resonance energy, is the most reactive, while thiophene, with the highest resonance energy, is the least reactive. Comparison of the rates of formylation for selenophene and 2-methyl selenophene with those of thiophene and 2-methylthiophene shows selenophene is only slightly more sensitive than thiophene to the directing effects of the methyl group.[45]

Selenophene is reported to decompose in strong organic and mineral acids.[7] Nevertheless, acid-catalyzed isotopic exchange occurs for deuterated selenophene in a mixture of 4:1 acetic : trifluoroacetic acids.[4] The kinetic rate constants for the exchange reaction at 25°C show that exchange reaction occurs six to ten times faster for selenophene than thiophene. Methyl

substitution of the ring in the 2-position increases the rate of exchange in the 5-position by 107 times. Methyl substitution in the 3-position increases the exchange of the 2-position deuterium by a factor of 236 over the non-substituted selenophene.

Transition Metal Complexes of Selenophene

Coordination of thiophene in transition metal complexes has been studied principally as a model system for the hydrodesulfurization (HDS) process.[46,47] Selenophene (Sel) coordination in transition metal complexes, in contrast has been limited to a handful of examples. The potential metal binding modes of selenophene, η^5, η^4, η^2, and η^1(Se), (Figure 3) are similar



η^5-bound η^4-bound η^2-bound η^1(S)-bound

Figure 3. Potential Binding Modes of Selenophene

to those exhibited in thiophene.[48,49]

Reported in 1966 by Karl Öfele[50], the η^5-selenophene complex, (η^5-Sel)$Cr(CO)_3$, was the first known compound to be prepared in which selenophene is coordinated to a transition metal. The compound was synthesized in 40-50% yield using the reaction of selenophene with $Cr(CO)_3(NC_5H_5)_3$ and BF_3 (eq 4). Recently an alternative route for

$$Cr(CO)_3(NC_5H_5)_3 + 3\ BF_3 + Sel \xrightarrow[25°C]{ether} (\eta^5\text{-Sel})Cr(CO)_3 + 3\ BF_3\ NC_5H_5 \quad (4)$$

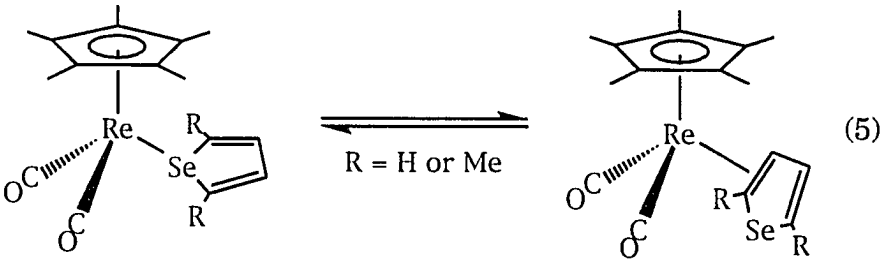
the synthesis of $(\eta^5\text{-Sel})Cr(CO)_3$ using the direct reaction of selenophene with $Cr(CO)_6$ has been reported by our research group.[26] The complex $(\eta^5\text{-Sel})Cr(CO)_3$ has been characterized by IR, UV, ^1H and ^{13}C NMR(Table 7).[26,50,51] Comparison of the IR and UV spectroscopic data for the selenophene complex with that of the analogous thiophene complex $(\eta^5\text{-T})Cr(CO)_3$ shows the selenophene ligand to be slightly more electron donating than thiophene. In the ^1H NMR spectrum of $(\eta^5\text{-Sel})Cr(CO)_3$, resonances for the ring protons are upfield by approximately 2 ppm from those of the unbound ligand. This upfield of shift is typical of π-coordinated arene complexs of chromium tricarbonyl.[52] The ^{13}C NMR resonances for the ring carbons are upfield by ~38 ppm for both C(2),C(5) and C(4),C(4) of those for the free ligand indicating η^5-coordination of the selenophene ring.[53,54]

Both η^1(Se)- or η^2-coordination selenophene (Figure 3) have been observed in the complexes $CpRe(CO)_2(\eta^1(Se)\text{-Sel})$ and $Cp^*Re(CO)_2(\eta^1(Se)\text{-Sel})$.[55-57] Selenophene is η^2-coordinated through one of the C=C double bonds in the electron rich complex $Cp^*Re(CO)_2(Sel)$ ($Cp^* = \eta^5\text{-}C_5H_5$). In the analogous 2,5-dimethylselenophene (2,5-Me_2Sel) complex $Cp^*(CO)_2Re(2,5\text{-}Me_2Sel)$ the ligand is coordinated through the Se atom. The intermediate methyl substituted ligand, 2-methylselenophene (2-MeSel) exhibits an equilibrium of the η^1(Se) and η^2 isomers. (eq 5) The equilibrium amount of the η^1(Se) isomer increases when the Cp* ligand is replaced by the less electron-donating ligand $Cp(\eta^5\text{-}C_5H_5)$ as in $CpRe(CO)_2(Sel)$. In the analogous

Table 7. Spectroscopic Data for (η^5-Sel)Cr(CO)3 and (η^5-T)Cr(CO)3

Compound	UV (cm^{-1})[a,b]	log ε	IR νCO (cm^{-1})[a,b]	^{1}H NMR δ [c,d]	^{13}C NMR δ [c,d]
(η^5-Sel)Cr(CO)3	18,800	2.90	1897	5.95 (m, H(2), H(5))	91.63 (C(2),C(5))
	23,800	3.74	1917	5.79 (m, H(3),H(4))	91.91 (C(3),C(4))
	26,670	3.86	1985		
	38,600	4.10			
	44,640	4.44			
(η^5-T)Cr(CO)3	19,200	3.00	1897	5.37 (m, H(2),H(5))	85.87 (C(2),C(5))
	24,450	3.83	1914	5.59 (m, H(3), H(4))	91.24 (C(3),C(4))
	31,250	3.82	1985		
	38,500	4.13			
	44,450	4.49			

[a] Reference 50 and 51 [b] Cyclohexane [c] Reference 26 [d] $CDCl_3$



(5)

thiophene (Th) complexes, $Cp'Re(CO)_2(Th)$ (Cp' = Cp or Cp*), only the $\eta^1(S)$ isomer is observed regardless of the electron richness of the metal or the methyl substitution of thiophene.[58,59]

Summary

The structure and chemistry of selenophene closely resembles that of its more studied congener, thiophene. The differences result from the greater size of the Se heteroatom and the 'localization' of the C=C bonds of the diene making selenophene less aromatic than thiophene. The lower aromatic character of selenophene leads to greater reactivity than thiophene towards both electrophiles and nucleophiles. Finnally, selenophene is a better electron donating ligand and therefore will form more stable transition metal complexes than thiophene.

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SYNTHESIS, REACTIONS AND ^{77}Se NMR STUDIES OF η^5-SELENOPHENE COMPLEXES OF CHROMIUM, MANGANESE, RUTHENIUM AND IRIDIUM

A paper submitted to *Organometallics*

Carter J. White, Moon-Gun Choi and Robert J. Angelici

Abstract

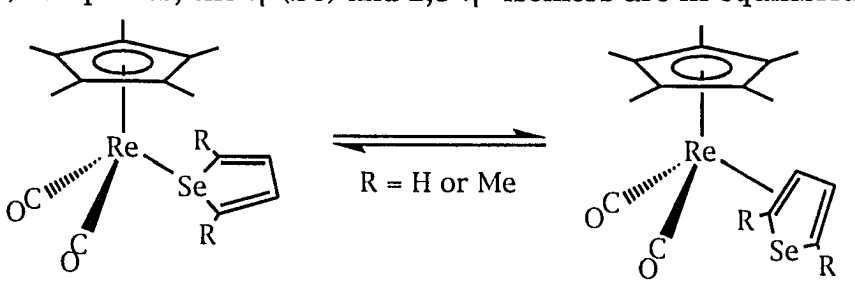
The series of η^5-selenophene transition metal complexes (η^5-Seln)$Cr(CO)_3$ (**1-3**), [(η^5-Seln)$Mn(CO)_3$]SO_3CF_3 (**4-6**), [(η^5-Seln)RuCp*]SO_3CF_3 (**7-9**), and [(η^5-Seln)IrCp*]$(BF_4)_2$ (**10-12**), where Seln = selenophene(Sel), 2-methylselenophene (2-MeSel), or 2,5-dimethylselenophene(2,5-Me_2Sel), were synthesized and characterized by ^{1}H, ^{13}C, and ^{77}Se NMR and IR spectroscopy. The molecular structure of (η^5-2,5-Me_2Sel)$Cr(CO)_3$ (**3**) was determined. Reactions of [(η^5-Sel)$Mn(CO)_3$]SO_3CF_3 (**4**) with nucleophiles (Nuc = H^-, CN^-) give the neutral addition products [(Sel•Nuc)$Mn(CO)_3$] (Nuc = H^- (**4a**), Nuc = CN^- (**4b**)) in which three carbon atoms and the Se are bonded to the Mn. The reaction of [(η^5-Sel)RuCp*]SO_3CF_3 (**7**) with H^-, however, results in cleavage of the C-Se bond to form a butadiene selenide complex ((η^5-SeCH=CH-CH=CH_2)RuCp*) (**7a**). Still another type of product results from the reaction of [(η^5-2,5-Me_2Sel)IrCp*]$(BF_4)_2$ (**12**) with two equivalents of H^-; in this case, the H^- acts as a reducing agent to give the ring-opened complex (C, Se-2,5-Me_2Sel)IrCp* (**12a**). All of these reactions are similar to those of the analogous η^5-thiophene complexes. The ^{77}Se NMR chemical shift values for the η^5-Seln ligands in complexes **1-12** fall within a range of 225 ppm; they are influenced

by the metal and its ligands, the charge on the complex and the number of methyl groups in the selenophene.

Introduction

In studies of the mechanism(s) of thiophene (T) hydrodesulfurization (HDS), we and others have sought to understand how thiophene is bound to metal sites on the heterogeneous catalyst.[1-3] In HDS model organometallic complexes, thiophene is commonly known to coordinate either through the entire π-system (η^5) or through the sulfur atom (η^1(S)) only. Reactions of the η^5 thiophene complexes have been linked to possible HDS mechanisms.[4] Thiophene has also been reported to coordinate to metals through a single C=C bond $(\eta^2)^5$ or through both C=C bonds (η^4).[6,7]

Selenophene is a five-membered heterocyclic compound with a structure and chemistry similar to that of thiophene(Figure 1).[8-11] Our group has previously reported on the coordination of selenophenes (Seln) in the complexes $Cp'Re(CO)_2(Seln)$.[12,13] In the electron-rich complex $Cp^*Re(CO)_2(Seln)$ ($Cp^* = \eta^5$-C_5Me_5), the selenophene (Sel) ligand is 2,3-η^2-coordinated through two of the carbons of Sel, while in the analogous 2,5-dimethylselenophene (2,5-Me_2Sel) complex $Cp^*(CO)_2Re$(2,5-Me_2Sel) the ligand is coordinated through the Se atom. For the analogous 2-methylselenophene (2-MeSel) complexes, the η^1(Se) and 2,3-η^2 isomers are in equilibrium(eq 1).



(1)

Not only does the selenophene binding mode depend on the number of methyl groups in the Seln, but the equilibrium amount of the η^1(Se) isomer increases when the Cp* ligand is replaced by the less electron-donating Cp (η^5-C_5H_5) in $CpRe(CO)_2$(Seln). Lowering the electron density on Re favors the η^1(Se) isomer, in which the Se acts as a two electron donor to the Re. The 2,3-η^2 isomer becomes less favored in this case because the lower electron density on Re makes it less capable of π-back-bonding to the olefin. In the analogous thiophene (Th) complexes, $Cp'Re(CO)_2$(Th), only the η^1(S) isomer is observed regardless of the electron richness at the metal center or the methyl substitution in the thiophene.[14,15] The distinctly different ^{77}Se chemical shifts of the η^1(Se) and 2,3-η^2 isomers of the $CpRe(CO)_2$(Seln) complexes suggest that ^{77}Se NMR studies could be used to investigate the modes of selenophene binding on heterogeneous catalysts.

The only other known selenophene complexes are (η^5-Seln)$Cr(CO)_3$ (Seln = selenophene, 2,5-dimethylselenophene), first reported by Öfele in 1966.[16] Recent ^{13}C NMR studies of these complexes[17] show that the rotational barrier of the selenophene is higher than that of thiophene in the analogous complexes. The results suggest that selenophenes donate slightly more electron density to chromium than thiophenes do.

Although attempts to establish the mode of thiophene binding on HDS catalysts have not been successful, the existence of the NMR active isotope ^{77}Se (7.58% natural abundance) may make it possible to study selenophene binding to catalyst surfaces. Therefore, it is of interest to determine whether ^{77}Se NMR spectroscopy is capable of distinguishing η^5 coordination from η^1(Se) coordination based on the chemical shift. In the investigations reported

herein, we determine the ^{77}Se NMR chemical shifts in the following series of complexes, (η^5-Seln)$Cr(CO)_3$, [(η^5-Seln)$Mn(CO)_3$]$^+$, [(η^5-Seln)$RuCp^*$]$^+$, and [(η^5-Seln)$IrCp^*$]$^{2+}$ (where Seln = Sel, 2-MeSel, 2,5-Me_2Sel) in which the metal, the charge on the complex and the surrounding ligands are varied. The synthesis, characterization and reaction chemistry of the new complexes are reported and compared to the previously studied thiophene analogs. In addition, the molecular structure of (η^5-2,5-Me_2Sel)$Cr(CO)_3$ determined by x-ray crystallography is compared with the recently published structure of the analogous η^5-thiophene complex (η^5-2,5-Me_2T)$Cr(CO)_3$.[17]

Experimental Section

General Procedures. All reactions and manipulations were carried out under an atmosphere of N_2 using standard Schlenk techniques unless otherwise stated.[18,19] Solvents were reagent grade and dried under N_2 by the following methods. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from Na/benzophenone. Hexanes, CH_2Cl_2, and MeCN were distilled from CaH_2. Acetone was dried with potassium carbonate (K_2CO_3) and distilled. Nitromethane ($MeNO_2$) was dried over $CaCl_2$ and distilled. The solvents were used immediately after distillation or were stored over 4 Å molecular sieves under N_2. The neutral alumina (Brockman, Activity I, ~150 mesh) used for chromatography was deoxygenated at room temperature in high vacuum for 16 hours, then deactivated with 5% w/w N_2-saturated water, and stored under N_2.

The ^1H and ^{13}C NMR spectra were recorded on either a Nicolet NT-300 MHz or a Varian VXR-300 MHz spectrometer with deuteriated solvents as the

internal locks and referenced to tetramethylsilane (TMS). The ^{77}Se NMR spectra were recorded on the Varian VXR-300 spectrometer at room temperature and referenced to selenophene (δ=605.0 ppm).[20-22] Electron-ionization mass spectra (EIMS) were performed on a Finnigan 4000 mass spectrometer. Fast atom bombardment (FAB) mass spectra were obtained using a Kratos MS-50 mass spectrometer. Infrared spectra were obtained on a Nicolet 710 FTIR spectrophotometer. Elemental analyses were performed by either Galbraith Laboratories, Inc., Knoxville TN or Desert Analytics, Tucson, AZ.

The following compounds were prepared by literature methods: $Cr(MeCN)_3(CO)_3$,[23] $Mn(CO)_5(OTf)$ ($OTf = SO_3CF_3$),[24] $[Cp^*Ru(MeCN)_3]OTf$,[25] $[Cp^*IrCl_2]_2$,[26] Sel,[27,28] 2-MeSel,[29] 2,5-Me_2Sel.[30] All other compounds were purchased from commercial sources and used as received.

(η^5-Sel)$Cr(CO)_3$ (1). To prepare $Cr(MeCN)_3(CO)_3$, a solution of $Cr(CO)_6$ (1.10 g, 5.00 mmol) in freshly distilled MeCN (10 mL) was refluxed for 24 h under Ar. After the solution was cooled to room temperature, the solvent was removed under vacuum giving a very air-sensitive yellow solid which was redissolved in 5 mL of THF. Following the addition of selenophene (2.6 g, 20 mmol), the solution was refluxed for 10 min. The solution changed to a deep red color. After cooling to room temperature and removing the solvent under vacuum, the residue was dissolved in CH_2Cl_2/hexanes (1:9) and chromatographed on a neutral alumina column (2.2 x 30 cm). An initial yellow band was eluted with ether/hexanes (1:10). Then a red band was eluted with Et_2O; it was collected and the solvent was evaporated in vacuo to give the red crystalline solid

product **1** (0.81 g, 61% based on $Cr(CO)_6$). ^1H NMR δ ($CDCl_3$): 5.95 (m, $J_{H\text{-}Se}$ = 18.8 Hz, H(2),H(5)), 5.79 (m, H(3),H(4)). ^{13}C NMR δ ($CDCl_3$): 91.82 (s, C(3), C(4)), 91.53 (s, C(2), C(5)), 233.03 (s, CO). ^{77}Se NMR δ ($CDCl_3$): 152.3 (s). IR ν(CO) cm^{-1} (hexanes): 1984 (s), 1918 (s), 1897 (s). Anal. Calcd for $C_7H_4O_3CrSe$: C, 31.48; H, 1.51. Found: C, 30.87; H, 1.27.

(η^5-2-MeSel)Cr(CO)$_3$ (2). This compound was prepared in the same manner as for **1** from $Cr(CO)_6$ (1.10 g, 5.00 mmol) and 2-MeSel (2.8 g, 15 mmol). **2** is an orange solid (0.91 g, 65% based on $Cr(CO)_6$). ^1H NMR δ ($CDCl_3$): 5.79 (d, J_{HH} = 4.2 Hz, H(5)), 5.75 (t, J_{HH} = 3.8 Hz, H(4)), 5.46 (d, J_{HH} = 3.3 Hz, H(3)), 2.37 (s, CH_3). ^{13}C NMR δ ($CDCl_3$): 113.77 (s, C(2)), 92.64 (s,C(4)), 92.59 (s, C(3)), 90.96 (s, C(5)), 18.09 (s, CH_3), 233.2 (s, CO). ^{77}Se NMR δ ($CDCl_3$): 186.1 (s). IR ν(CO) cm^{-1} (hexanes): 1978 (s); 1912 (s); 1893 (s). Anal. Calcd for $C_8H_6O_3CrSe$: C, 34.18; H, 2.14. Found: C, 33.99; H, 2.11.

(η^5-2,5-Me$_2$Sel)Cr(CO)$_3$ (3). This compound was prepared in the same manner as for **1** using $Cr(CO)_6$ (1.10 g, 5.00 mmol) and 2,5-Me_2Sel (1.6 g, 10 mmol). **3** (0.77 g, 52% based on $Cr(CO)_6$) was isolated as a red solid. ^1H NMR δ ($CDCl_3$): 5.39 (s, H(3), H(4)), 2.29 (s, CH_3). ^{13}C NMR δ ($CDCl_3$): 113.55 (s, C(2),C(5)), 93.31 (s, C(3),C(4)), 18.11 (s, CH_3), 233.9 (s, CO). ^{77}Se NMR δ ($CDCl_3$): 222.2 (s). IR ν(CO) cm^{-1} (hexanes): 1972 (s), 1905 (s), 1887 (s). Anal. Calcd for $C_9H_8O_3CrSe$: C, 36.63; H, 2.73. Found: C, 36.58; H, 2.74.

[(η^5-Sel)Mn(CO)$_3$](OTf) (4). To a solution of $Mn(CO)_5(OTf)$ (0.0880 g, 0.250 mmol) in Et_2O (50 mL) was added selenophene (0.16 g, 1.2 mmol); the solution was

refluxed under N_2 in the dark for 48 h. The solution turned brown/red and a yellow precipitate formed. After filtration, the yellow precipitate was washed with Et_2O (5 mL) once and hexanes (10 mL) twice and vacuum dried. The product **4** (0.0726 g, 68%) is a yellow crystalline powder. ^1H NMR δ (CD_3NO_2): 7.32 (m, $J_{H\text{-}Se}$ = 18.3 Hz, H(2),H(5)), 6.98 (m, H(3),H(4)). ^{13}C NMR δ (CD_3NO_2): 108.10 (s, C(3),C(4)), 101.55 ppm (s, C(2),C(5)), 231.17 (s, CO). ^{77}Se NMR δ (CD_3NO_2): 255.9 (s). IR ν(CO) cm^{-1} (CH_3NO_2): 2075 (s), 2016 (s) , 2014 (sh). Anal. Calcd for $C_8H_4O_6MnSeSF_3$: C, 20.57; H, 0.86. Found: C, 21.28; H, 1.13.

[(η^5-2-MeSel)Mn(CO)$_3$](OTf) (5). This synthesis was performed in the same manner as that for **4**; $Mn(CO)_5(OTf)$ (0.0880 g, 0.255 mmol) and 2-MeSel (0.16 g, 1.1 mmol) were used. Pale yellow crystals of **5** (0.0783 g, 71%) were obtained. ^1H NMR δ (CD_3NO_2): 6.91 (d, H(5)), 6.87 (t, H(4)), 6.68 (d, H(3)), 2.58 (s, CH_3). ^{13}C NMR δ (CD_3NO_2): 115.4 (s, C(2)), 106.1 (s, C(4)), 101.3 (s, C(3)), 100.6 (s, C(5)), 14.5(s, CH_3), 232.1 (s, CO). ^{77}Se NMR δ (CD_3NO_2): 274.7 (s). IR ν(CO) cm^{-1} (CH_3NO_2): 2071 (s), 2009 (s).

[(η^5-2,5-Me$_2$Sel)Mn(CO)$_3$](OTf) (6). This complex was prepared in the same manner as that for **4** from $Mn(CO)_5(OTf)$ (0.0880 g, 0.255 mmol) and 2,5-Me_2Sel (0.16 g, 1.0 mmol). Pale yellow microcrystals of **6** (0.0871g, 76%) were isolated after drying under vacuum. ^1H NMR δ (CD_3NO_2): 6.45 (s, H(3), H(4)), 2.41 (s, CH_3). ^{13}C NMR δ (CD_3NO_2): 128.9 (s, C(2), C(5)), 100.1 (s, C(3), C(4)), 18.0 (s, CH_3), 230.2 (s, CO). ^{77}Se NMR δ (CD_3NO_2): 295.1 (s). IR ν(CO) cm^{-1} (CH_3NO_2): 2068 (s), 2003 (s) . Anal. Calcd for $C_{10}H_8O_6MnSeSF_3$: C, 24.25; H, 1.63. Found: C, 24.63; H, 1.69.

[Cp*Ru(η5-Sel)](OTf) (7). To a solution of [Cp*Ru(MeCN)3](OTf) (0.100 g, 0.200 mmol) in CH_2Cl_2 (10 mL) was added selenophene (0.16 g, 1.2 mmol); the solution was stirred at room temperature for 1 h. After filtration through Celite, the solution was concentrated to about 3 mL in vacuo. The product **7** was precipitated by slow addition of Et_2O (20 mL) yielding a yellow crystalline powder (0.056g, 55%). ^1H NMR δ (d_6-acetone): 6.39 (m, $J_{H\text{-}Se}$ = 17.8 Hz, H(2),H(5)), 5.94 (m, H(3),H(4)), 2.02 (s, CH_3-Cp*). ^{13}C NMR δ (d_6-acetone): 89.82 (s, C(3),C(4)), 87.31 (s, C(2), C(5)), 96.76 (s, C-Cp*), 11.05 (s, CH_3-Cp*). ^{77}Se NMR δ (CD_3NO_2): 211.9 (s). FAB/MS (CH_2Cl_2/3-nitrobenzyl alcohol matrix): m/e 369 (M^+). The product was sometimes tan colored, but was purified by adding a CH_2Cl_2 solution of **7** onto a short column of neutral Al_2O_3 (1.0 x 5.0 cm). Elution with acetone gave a clean yellow product band that was collected. Removal of the solvent, under vacuum and recrystallization of the residue from CH_2Cl_2 layered with hexanes at -20 °C overnight gave yellow crystals of **7**.

[Cp*Ru(η5-2-MeSel)](OTf) (8). This synthesis was the same as that for **7** but using [Cp*Ru(MeCN)3](OTf) (0.16 g, 0.31 mmol) and 2-MeSel (0.16 g, 1.1 mmol). Pale yellow crystals of **8** (0.097 g, 58%) were obtained. ^1H NMR δ ($CDCl_3$): 6.51 (d, H(5)), 5.89 (t, H(4)), 5.71 (d, H(3)), 2.28 (s, CH_3), 1.99 (s, CH_3-Cp*). ^{13}C NMR δ ($CDCl_3$): 103.9 (s, C(2)), 89.8 (s, C(4)), 88.6 (s, C(3)), 86.9 (s, C(5)), 15.9 (s, CH_3), 95.6 (s, C-Cp*), 10.9 (CH_3-Cp*). ^{77}Se NMR δ (CD_3NO_2): 218.2 (s). FAB/MS (CH_2Cl_2/3-nitrobenzyl alcohol matrix): m/e 383 (M^+). Anal. Calcd for $C_{16}H_{21}RuSeSO_3F_3$: C, 36.23; H, 3.99. Found: C, 36.25; H, 3.97.

[Cp*Ru(η5-2,5-Me2Sel)](OTf) (9). This complex was prepared in the same manner as for **7** from [Cp*Ru(MeCN)3](OTf) (0.15 g, 0.29 mmol) and 2,5-Me_2Sel (0.16 g, 1.0 mmol). Pale yellow microcrystals of **9** (0.096 g, 60%) were isolated after drying under vacuum. ^{1}H NMR δ ($CDCl_3$): 5.69 (s, H(3),H(4)), 2.26 (s, CH_3), 1.96 (s, CH_3-Cp*). ^{13}C NMR δ ($CDCl_3$): 103.9 (s, C(2), C(5)), 89.4 (s, C(3), C(4)), 15.9 (s, CH_3), 94.3 (s, C-Cp*), 9.89 (s, CH_3-Cp*). ^{77}Se NMR δ (CD_3NO_2): 219.8 (s). FAB/MS (CH_2Cl_2/3-nitrobenzyl alcohol matrix): m/e 397 (M^+). Anal. Calcd for $C_{17}H_{23}RuSeSO_3F_3$: C, 37.50; H, 4.26. Found: C, 37.77; H, 4.32.

[Cp*Ir(η5-Sel)](BF4)2 (10). To a solution of [Cp*$IrCl_2$]2 (0.44 g, 0.55 mmol) in acetone (5.0 mL) was added $AgBF_4$ (0.430 g, 2.21 mmol). The resulting mixture was stirred for 15 minutes and then filtered through Celite; the volume of the filtrate was then reduced to approximately 3 mL under vacuum. Selenophene (1.00 mL, 1.64 g, 12.2 mmol) was added and the solution was gently heated at 50°C for 5 min. After cooling to room temperature, the solution was treated with Et_2O (20 mL) which produced a gray-white solid. The solid was filtered from the solution and then redissolved in $MeNO_2$ (5 mL). The $MeNO_2$ solution was filtered to remove a black insoluble impurity; upon addition of Et_2O (40 mL) the product **10** precipitated as a white solid. The product was separated by filtration and dried in vacuo, yielding 0.25 g (41%) of **10**. ^{1}H NMR δ (CD_3NO_2): 7.99 (dd, $J_{H\text{-}Se}$ = 16.9 Hz, H(2), H(5)), 7.70 (dd, H(3),H(4)), 2.50 (s, CH_3-Cp*). ^{13}C NMR δ (CD_3NO_2): 101.2 (s, C(3), C(4)), 100.3 (s, C(2), C(5)), 107.2 (s, C-Cp*), 10.7 (s, CH_3-Cp*). ^{77}Se NMR δ (CD_3NO_2): 371.2 (s). FAB/MS (3-nitrobenzyl alcohol matrix): m/e 547 (parent dication + BF_4^-).

[$Cp^*Ir(\eta^5$-2-MeSel)]$(BF_4)_2$ (11). This compound was prepared from $[Cp^*IrCl_2]_2$ (0.44 g, 0.55 mmol) and 2-MeSel (1.5 g, 10 mmol) using the same method as described for **10**; it gives **11** as a white solid (0.220 g, 30.8%). ^1H NMR δ (CD_3NO_2): 7.81 (d, H(5)), 7.55 (t, H(4)), 7.45 (d, H(3)), 2.76 (s, CH_3), 2.45 (s, CH_3-Cp*). ^{13}C NMR δ (CD_3NO_2): 120.7 (s, C(2)), 101.6 (s, C(4)), 100.8 (s, C(3)), 99.6 (s, C(5)), 16.2 (s, CH_3), 106.8 (s, C-Cp*), 10.6 (s, CH_3-Cp*). ^{77}Se NMR δ (CD_3NO_2): 374.7 (s). Anal. Calcd for $C_{15}H_{21}B_2F_8IrSe$: C, 27.88; H, 3.28. Found: C, 27.54; H, 3.13.

[$Cp^*Ir(\eta^5$-2,5-Me_2Sel)]$(BF_4)_2$ (12). This compound was prepared in the same manner as **11** using $[Cp^*IrCl_2]_2$ (0.44 g, 0.55 mmol) and 2,5-Me_2Sel (1.40 g, 2.58 mmol). White solid **12** (0.359 g, 49.2%) was obtained. ^1H NMR δ (CD_3NO_2): 7.31 (s, H(3), H(4)), 2.74 (s, CH_3), 2.42 (s, CH_3-Cp*). ^{13}C NMR δ (CD_3NO_2): 119.6 (s, C(3), C(4)), 100.8 (s, C(2), C(5)), 105.9 (C-Cp*), 16.4 (s, CH_3), 10.1 (CH_3-Cp*). ^{77}Se NMR δ (CD_3NO_2): 379.8 (s). Anal. Calcd for $C_{16}H_{23}B_2F_8IrSe$: C, 29.11; H, 3.51. Found: C, 28.83; H, 3.53.

Reaction of [$(\eta^5$-Sel)$Mn(CO)_3$](OTf) (4) with Hydride (H^-) Sources. Method A. Reaction with $NaBH_4$. A solution of [$(\eta^5$-Sel)$Mn(CO)_3$](OTf) **(4)** (0.050 g , 0.12 mmol) in 10 mL of degassed deionized water was added all at once to an aqueous solution of 0.005 g (0.1 mmol) of $NaBH_4$ in 10 mL of degassed, deionized water. Immediately upon mixing, a yellow precipitate formed and gas was evolved. Extraction with hexanes (3 x 10mL) gave a bright yellow hexanes layer which was separated and dried over Na_2SO_4. After filtering the yellow solution was chromatographed on an Al_2O_3/hexanes column (1 x 15

cm). Elution with 5:1 hexanes:ether gave a bright yellow band that was collected, and the solvent was evaporated under vacuum to give bright yellow crystals. Yield (**4a**): 0.023 g (0.80 mmol) 69%. Elemental analyses were not possible because the crystals slowly decompose into a yellow/orange oil within 24 hours. **4a** was characterized by the following spectra: ^{1}H NMR δ ($CDCl_3$): 6.95 (m, $J_{H\text{-}Se}$ = 17.4Hz, H(5)), 6.02 (t, H(4)), 4.00 (dd, $J_{H\text{-}Se}$ = 11.7 Hz, H(2, endo)), 3.41 (m, H(3)), 3.07 (d, H(2, exo)). ^{13}C NMR δ ($CDCl_3$): 92.31 (s, C(4)), 77.24 (s, C(5)), 54.99 (s, C(3)), 50.17 (s, C(2)). ^{77}Se NMR δ ($CDCl_3$): -162.3 (s). IR ν(CO) cm^{-1} (hexanes): 2017 (s), 1940 (s), 1924 (s). EIMS m/z: 272 (M^+), 244 (M^+-CO), 216 (M^+- 2CO), 188 (M^+-3CO), 133 ($HSel^+$)

Method B. Reaction with Red-Al ($Na[(CH_3OC_2H_4O)_2AlH_2]$). A solution of 0.050 g (0.12 mmol) of [(η^5-Sel)$Mn(CO)_3$](OTf) (**4**) in 10 mL of THF was cooled to 0 °C in an ice/water bath. To this stirred yellow solution was added all at once 0.175 mL of a 0.34 M Red-Al/THF (0.059 mmol) solution. After the resulting solution was allowed to warm to room temperature, the volatile components were removed under vacuum to give an orange/yellow oily solid. This was extracted with 2 x 10mL of hexanes to give a bright yellow solution. Evaporation of the solution under vaccum gave a yellow oily solid (**4a**). Yield: 0.028 g (0.10 mmol) 91%. The ^{1}H, ^{13}C, ^{77}Se NMR and IR spectra of this product were identical to those reported in the previous paragraph.

Reaction of [(η^5-Sel)$Mn(CO)_3$](OTf) (4) with NaCN. A solution of [(η^5-Sel)$Mn(CO)_3$](OTf) (**4**) (0.200 g , 0.24 mmol) in 10 mL of degassed deionized water was added all at once to an aqueous solution of 0.059 g (1.2 mmol) of

NaCN in 10 mL of degassed, deionized water. Immediately upon mixing a yellow/orange precipitate formed. Extraction with hexanes (3 x 10mL) gave a bright yellow hexanes layer which was separated and dried over Na_2SO_4; the volatiles were removed from this solution under vacuum. The resulting yellow/orange oil was redissolved in hexanes and put onto a hexanes/Al_2O_3 column (1 cm x 5 cm) which was eluted with ether to give a yellow band. This band was collected and evaporated under vacuum to give a yellow oil (**4b**) (0.021 g, 0.070 mmol, 29%). ^1H NMR δ (d_6-acetone): 7.05 (t, $J_{H\text{-}Se}$=16.4Hz, H(5)), 6.28 (dd, H(4)), 4.86 (d, $J_{H\text{-}Se}$=11.8Hz, H(2, endo)), 3.59 (m, H(3)). ^{13}C NMR δ (d_6-acetone): 92.75 (s, C(4)), 78.44 (s, C(5)), 52.13 (s, C(3)), 43.05 (s, C(2)). ^{77}Se NMR δ (d_6-acetone): 24.3 (s). IR ν(CO) cm^{-1} (hexanes): 2028(s), 1954(vs), 1941(s). EIMS m/z: 297 (M^+), 271 (M^+ - CN), 269 (M^+ - CO).

Reaction of [(η^5-Sel)RuCp*]OTf (7) with Red-Al (Na[$(CH_3OC_2H_4O)_2AlH_2$]). To a suspension of 0.100 g (0.194 mmol) of [(η^5-Sel)RuCp*]OTf (**7**) in 20 mL of THF cooled to 0° C in an ice/water bath was added all at once 0.060 mL (0.20 mmol) of a 3.4 M Red-Al/toluene solution. The solid quickly dissolved to give a yellow/orange solution. Evaporation under vacuum gave an orange oily solid that was extracted with ether (2 x 10 mL). The extracts were chromatographed on an Al_2O_3/hexanes column (1 cm x 5 cm) and eluted with ether to give a yellow band. The yellow band was collected and evaporated under vacuum to give the oily yellow solid **7a** (0.055 g, 0.15 mmol, 77%). Due to its slow decomposition at room temperature, it was not possible to obtain elemental analyses. ^1H NMR δ ($CDCl_3$): 6.38 (d, $J_{H\text{-}Se}$ = 16.5 Hz, H(5)), 5.68 (t, H(4)), 4.37 (m, H(3)), 2.72 (d, H(2, endo)), 2.53 (d, H(2, exo)), 1.86 (s, Cp*). ^{13}C NMR δ

($CDCl_3$): 97.9 (s, C(3)), 92.6 (s, C(4)), 90.4 (s, Cp*), 89.0 (s, C(5)), 45.2 (s, C(2)), 10.6 (s, CH_3-Cp*). ^{77}Se NMR δ ($CDCl_3$): 227.3 (s). EIMS exact mass calculated for $C_{14}H_{20}{}^{80}Se^{102}Ru$: 369.97735. Found for M^+: 369.97737

Reaction of [(η^5-2,5-Me_2Sel)IrCp*](OTf)$_2$ (12) with Red-Al(Na[($CH_3OC_2H_4O)_2AlH_2$]). To a cooled (0° C) suspension of 0.100 g (0.15 mmol) of [(η^5-2,5-Me_2Sel)IrCp*](OTf)$_2$ (**12**) in 10 mL of THF was added dropwise 1.00 mL (0.17 mmol) of a 0.17 M Red-Al (Na[($CH_3OC_2H_4O)_2AlH_2$])/THF solution with stirring; an orange/red solution formed. After stirring for 1 h at 0 °C, the volatile components were evaporated under vacuum giving a red oily solid. Extraction with hexanes (3 x 10 mL) was followed by chromatography on an Al_2O_3/hexanes (1 cm x 10 cm) column using a 10% THF/hexanes eluent; this gave a deep red band that was collected. Solvent evaporation under vacuum gave the product **12a** (0.013 g, 0.026 mmol, 17% yield) which was isolated as a deep red oily solid. ^1H NMR δ ($CDCl_3$): 7.59 (d, H(3)), 7.49 (d, H(4)), 3.26 (s, CH_3), 2.84 (s, CH_3), 1.87 (s, CH_3-Cp*). ^{13}C NMR δ ($CDCl_3$): 134.9 (s), 132.1 (s), 129.8 (s), 123.3(s), 8.5 (s, CH_3), 8.4 (s, CH_3), 90.7 (s, Cp*), 10.4 (s, CH_3-Cp*). ^{77}Se NMR δ ($CDCl_3$): 905.4 (s).

X-ray Structure Determination of (η^5-2,5-Me_2Sel)Cr(CO)$_3$ (3). A single crystal of **3** suitable for X-ray diffraction was obtained by vapor diffusion of hexanes into a saturated Et_2O solution of **3** at -20 °C. The single crystal was mounted on the end of a glass fiber. Cell constants were determined from a list of reflections found by an automated search routine. Pertinent data collection and reduction information are given in Table 1. Lorentz and polarization

corrections were applied. A correction based on decay in the standard reflection of 4.8% was applied to the data. An absorption correction was also made on the basis of a series of Ψ-scans. The positions of the Cr and Se atoms were determined by interpretation of the Patterson map. All remaining non-hydrogen atoms were found in one successive difference Fourier map. All non-hydrogen atoms were refined with anisotropic displacement parameters. After the least-squares converged, all hydrogen atoms were found in a difference Fourier map. These were placed into the model with isotopic temperature factors set equal to 1.3 times the isotropic equivalent of the attached atom. The hydrogen positions were not refined. Systematic trends in the F_o/F_c suggested that an extinction correction be included in the final least-squares. Bond distances and angles are presented in Table 2, and an ORTEP drawing of **3** is given in Figure 2. The final positional and thermal parameters are listed in Table 3.

Results and Discussion

Synthesis and Characterization of the η^5-Seln Complexes. The complexes (η^5-Seln)$Cr(CO)_3$ were prepared previously by reaction of $Cr(CO)_3(py)_3$ with selenophenes.[16] Using this method the yields were low (0-25%) and in our hands highly dependent on the careful manipulation and purification of the very air sensitive $Cr(CO)_3(py)_3$ intermediate complex. The reactions (eq 2) of

$$Cr(CO)_6 \xrightarrow[-\,3\ CO]{3\ MeCN} Cr(CO)_3(MeCN)_3 \xrightarrow[-\,3\ MeCN]{Seln} (\eta^5\text{-Seln})Cr(CO)_3 \qquad (2)$$

1, Seln = Sel
2, Seln = 2-Me_2Sel
3, Seln = 2,5-Me_2Sel

$Cr(CO)_3(MeCN)_3$ with selenophenes are more straight forward and give higher yields of (η^5-Seln)$Cr(CO)_3$. The pure moderately air-stable red (η^5-Seln)$Cr(CO)_3$ complexes **1**, **2**, and **3** are obtained in yields between 50 to 70%. The advantage of using this method over the direct reaction of $Cr(CO)_6$ with the Seln ligand is that smaller amounts of the ligand are required to obtain the desired product in reasonable yield.

The ^1H, ^{13}C and ^{77}Se NMR spectral data for **1** are given in Table 4. The ^1H NMR chemical shift values are similar to those reported previously[16,17]; however the fine structure is resolved better and gives coupling constants between protons on adjacent carbons (J_{H-H} = 2.45 Hz) and protons on carbons across the ring (J_{H-H} =1.95 Hz). Coupling of protons in the 2,5 position to the ^{77}Se (7.58% natural abundance) nucleus is observed in the satellite peaks which give a two bond coupling constant of $^2J_{H-Se}$ = 18.8 Hz; the Se satellite peaks are also used to definitively assign the resonances for protons H(2) and H(5). The ^1H NMR resonances for the analogous thiophene complex (η^5-T)$Cr(CO)_3$ in $CDCl_3$ [δ 5.59 (m, H(3),H(4)), 5.37 (m, H(2),H(5))][20,30] are slightly upfield (0.2 - 0.3 ppm) of those of **1** in $CDCl_3$ [δ 5.95 (m, H(2), H(5)), 5.79 (m, H(3), H(4))].

The compounds [(η^5-Seln)$Mn(CO)_3$]OTf ((**4**), (**5**) and (**6**)) are isostructural and isoelectronic with the chromium complexes **1-3**. Due to the limited availablity of the selenophene ligands, compounds **4-6** were prepared (eq 3)

$$Mn(CO)_5(OTf) + Seln \xrightarrow[\text{ether}]{-2\ CO} [(\eta^5\text{-Seln})Mn(CO)_3](OTf) \qquad (3)$$

reflux 48 h in dark

4, Seln = Sel
5, Seln = 2-Me_2Sel
6, Seln = 2,5-Me_2Sel

using only a 4-fold excess of the Seln ligand, rather than the large excess of thiophenes (Th) used in the synthesis of the thiophene complexes [(η^5-Th)Mn(CO)$_3$]OTf.[24] The product is totally insoluble in the ether solvent and can be isolated directly as the pure compound. The reaction must be protected from direct exposure to light to prevent the formation of unidentified side-products. Yields of compounds **4-6** vary from 20 to 80%. Key factors in obtaining high yields are preventing exposure to light during the long reflux period, moderate reaction temperatures and using high purity starting materials and solvents. In the ^{1}H NMR spectrum (Table 4) the selenophene protons in **4** are slightly downfield (~0.2 ppm) as compared with those in the analogous thiophene complex, [(η^5-T)Mn(CO)$_3^+$] (δ 6.90 (H(2), H(5)), 6.77 (H(3), H(4))).[25]

Syntheses of the compounds [(η^5-Seln)RuCp*]OTf ((**7**), (**8**), and (**9**)) are accomplished by the same method (eq 4) used for the previously reported

$$[(MeCN)_3RuCp^*]OTf + Seln \xrightarrow[-\ 3\ MeCN]{CH_2Cl_2} [(\eta^5\text{-Seln})RuCp^*](OTf) \qquad (4)$$

7, Seln = Sel
8, Seln = 2-MeSel
9, Seln = 2,5-Me$_2$Sel

thiophene complexes [(η^5-Th)RuCp*]OTf.[32,33] As was the case for **1** and **4**, the ^{1}H NMR resonances of the Sel in **7** (Table 4) are slightly deshielded as compared with those in the analogous thiophene compound [(η^5-T)RuCp*]$^+$ in acetone-d$_6$ [δ 6.22 (m, H(3), H(4)), 6.19 (m, H(2), H(5)), 2.07 (s, Cp*)][32].

Selenophene compounds of the type [(η^5-Seln)IrCp*](BF$_4$)$_2$ ((**10**), (**11**), and (**12**)) are prepared by the same method (eq 5) used for the thiophene analogs.[34,35] These complexes are isolated as white air-stable solids in yields of 41 to 49%. The ^{1}H NMR chemical shift values for the Sel ligand in **10** (Table

$$[Cp^*Ir(Cl)_2]_2 + 4\ AgOTf + 2\ SeIn \xrightarrow[-\ 4\ AgCl]{acetone} 2\ [(\eta^5\text{-}SeIn)IrCp^*](OTf)_2 \qquad (5)$$

10, SeIn = Sel
11, SeIn = 2-Me Sel
12, SeIn = 2,5-Me_2Sel

4) are slightly downfield of those of the thiophene analog $[(\eta^5\text{-T})IrCp^*]^{2+}$ in CD_3NO_2 (δ 7.60 (m, H(3),H(4)), 7.55 (m, H(2),H(5)), 2.50 (s, Cp*)).[35]

Comparison of the ^1H, ^{13}C and ^{77}Se NMR Spectra of 1, 4, 7 and 10. In all of these complexes, the H(2) and H(5) protons are assigned to the ^1H NMR peaks that exhibit satellites due to ^1H-^{77}Se coupling. These coupling constants, $J_{H\text{-}Se}$, are in a narrow range, 16.9-18.8 Hz (Table 4). No coupling between ^{77}Se and the protons on C(3) and C(4) is observed in any of the complexes. Peaks in the ^{13}C NMR spectra of the complexes are assigned (Table 4) to the Sel ring carbon atoms based on HETCOR spectra and making use of the proton assignments.

As is evident in Figure 3, ^1H chemical shifts of both the H(2), H(5) and H(3), H(4) protons move upfield as expected with decreasing positive charge on the complex: **10** < **7** < **4** < **1**. Only the +2 complex (**10**), has chemical shifts lower than those of the free Sel. The higher chemical shifts of the Sel in complexes **7**, **4** and **1** is commonly observed when arene and thiophene[17,24,31] ligands are π-bound in complexes with 0 and +1 charges.

Since ^{13}C NMR chemical shifts are more sensitive to factors other than complex charge, it is not suprising that chemical shift values (Figure 3) for both the C(2), C(5) and C(3), C(4) carbon atoms follow a somewhat different trend, **7** < **10** < **1** < **4**, than was observed in the ^1H NMR spectra. Moreover, the

coordinated carbons of Sel in all of the complexes are upfield of those in the free Sel. Such upfield shifts are normally observed in π-arene[36] and π-thiophene[17,24] complexes.

^{77}Se NMR Studies of η^5-Seln. A goal of the studies described in this report is to determine the usefulness of ^{77}Se NMR spectroscopy for establishing the mode of selenophene binding in transition metal complexes and on catalyst surfaces. The ^{77}Se nucleus has a natural abundance of 7.58% and a relative receptivity that is 2.98 times larger than ^{13}C, with a chemical shift range of more than 3000 ppm.[20] The ^{77}Se NMR chemical shift values of the η^5-Sel complexes are given in Table 4 and Figure 4. It is evident that the ^{77}Se NMR signal moves downfield from the neutral complex (**1**), to the +1 charged complexes (**4** and **7**) to the +2 charged complex (**10**). The chemical shift of the free selenophene ligand is further downfield than any of the complexes. Methyl substitution of the heterocyclic ring also affects the ^{77}Se chemical shift of the coordinated selenophene ring; increasing the number of methyl groups in the 2- and 5-positions causes the ^{77}Se chemical shift to move downfield. A similar trend occurs for the free ligands in $CDCl_3$: Sel(δ 605) > 2-MeSel (δ 612) > 2,5-Me_2Sel (δ 621).[20,21]

Molecular Structure of (η^5-2,5-Me_2Sel)$Cr(CO)_3$. The ORTEP drawing of (η^5-2,5-Me_2Sel)$Cr(CO)_3$ (**3**) is given in Figure 2. The 2,5-Me_2Sel complex was choosen for the structural study in order to avoid the disorder previously found in the analogous thiophene complex (η^5-T)$Cr(CO)_3$.[37] The selenophene ring in **3** binds to the chromium tricarbonyl fragment through the selenium and the two

C=C bonds each *trans* to a carbonyl ligand thereby giving pseudo-octahedral coordination around the Cr. This is the same geometry found in both (η^5-T)$Cr(CO)_3$[37] and (η^5-2,5-Me_2T)$Cr(CO)_3$.[17] The selenophene ring is slightly bent with the selenium atom out of the plane of the four carbon atoms (C(2), C(3), C(4) and C(5)) by 0.162(3) Å. The dihedral angle between the plane of the ring carbons (C(2), C(3), C(4) and C(5)) and the C(2)-Se-C(5) plane is 6.7(0.6)°. This angle is larger by 2.2(8)° than the corresponding angle in the sulfur-containing analog (η^5-2,5-Me_2T)$Cr(CO)_3$. Other dihedral angles for thiophene rings are reported for the following complexes: $Ru(Me_4T)_2^{2+}$ (5.0(0.5)° and 3.7(1.5)°), and {[(η^5-Me_4T)RuCl]$_3$S}$^+$ (11.8(1.9)°, 13.4(1.9)°, and 13.7(1.9)°).[38] The C-Se bond distances (1.899(8) and 1.912(7) Å) in the 2,5-Me_2Sel ring in **3** are slightly longer than that (1.855(7) Å) in free selenophene.[10] The C-Se distances in **3** are approximately 0.15 Å longer than the C-S distances in (η^5-2,5-Me_2T)$Cr(CO)_3$ due to the larger size of the selenium heteroatom. The ring C-C bond distances in the coordinated 2,5-Me_2Sel are within experimental error the same as in (η^5-2,5-Me_2T)$Cr(CO)_3$. The Cr-Se bond (2.488(5)Å) in **3** is 0.113(5) Å longer than the Cr-S bond (2.3757(6) Å) in (η^5-2,5-Me_2T)$Cr(CO)_3$, again presumably due to the larger size of Se. The Cr-Se distances in $Cr(CO)_4(CN(Et)_2)(SeC_6H_4F)$[39] (2.562(2) Å) and [CrCp(NO)(μ^2-SeC_6H_5)]$_2$[40] (2.45(1) Å) are longer and shorter, respectively, than that in **3**. The carbonyl Cr-C and C=O bond distances in **3** and (η^5-2,5-Me_2T)$Cr(CO)_3$ are the same within experimental error.

Reactions of η^5-Sel Complexes. Previously, it was reported[1,24] that the η^5-thiophene ligand in (η^5-T)$Mn(CO)_3^+$ is attacked at the 2-position by a hydride donor (BH_4^-, $HFe(CO)_4^-$) to give the product (η^4-T•H)$Mn(CO)_3$ in which three

carbons and the sulfur are coordinated to the Mn. The same reaction of [(η^5-Sel)Mn(CO)$_3$]$^+$ (**4**) with one equivalent of $NaBH_4$ or Red-Al as the hydride source gives the analogous product (η^4-Sel•H)Mn(CO)$_3$ (**4a**) which is isolated in 80-90% (Scheme 1). The ^{1}H NMR spectrum of **4a** in $CDCl_3$ contains signals for the five hydrogens on the ring as follows: δ 6.95 (m, $J_{H\text{-}Se}$ = 17.4 Hz, H(5)), 6.02 (t, H(4)), 4.00 (dd, $J_{H\text{-}Se}$ = 11.7 Hz, H(2, endo)), 3.41 (m, H(3)), 3.07 (d, H(2, exo)). Assignments of these resonances were made by comparison of the data with those previously reported for (η^4-T•H)Mn(CO)$_3$ in d^6-acetone (not in $CDCl_3$ as originally reported[24]): δ 6.42 (s, (H(5)), 5.89 (s, (H(4)), 3.79 (d, H(2, endo)), 3.30 (s, H(3)), 3.29 (d, H(2, exo)). Coupling of ^{77}Se to H(2, endo) ($^2J_{H\text{-}Se}$ = 11.7 Hz) and H(5) ($^2J_{H\text{-}Se}$ = 17.4 Hz) indicates that the ring C-Se bonds remain intact. Coupling is not seen between ^{77}Se and H(2, exo) presumably due to the angle between the atoms. Integration of the ^{2}H NMR spectrum of the product resulting from the reaction of **4** with $NaBD_4$ shows a of 6.4:1.0 ratio of products resulting from exo and endo attack. In the corresponding reaction of [(η^5-T)Mn(CO)$_3$]$^+$ with $NaBD_4$ the ratio of exo to endo attack was 3.6:1.0.[41] It is interesting to note that the ^{77}Se NMR signal for **4a** occurs at δ -162 ppm which is more than 400 ppm upfield from that of complex **4**. This is the highest upfield resonance that we have seen for any of the selenophene complexes; metal organoselenides (NaSeMe δ -332, NaSeEt δ -150)[20,21] have chemical shifts in this range. The electron impact mass spectrum of **4a** shows a parent ion peak (M^+) at m/z = 272.0. The reaction of **4a** with $(Ph)_3C^+$ in CH_2Cl_2 results in the loss of H^- to give back complex **4** in quantitative yield.

Other nucleophiles (CN^-, PR_3 for R = Me, n-Bu) also react (Scheme 1) with **4** giving addition products that have spectral characteristics comparable

to those of the known thiophene analogs.[24] The reaction of **4** with NaCN, carried out in the same manner as described for the analogous reaction of (η^5-T)$Mn(CO)_3^+$ with NaCN, gives a yellow oil (**4b**) after evaporation under vacuum. The ^1H NMR spectrum of **4b** in d_6-acetone [δ 7.05 (t, H(5)), 6.28 (dd, H(4)), 4.86 (d, H(2, endo)), 3.59 (m, H(3))], contains complex second order coupling of the ring protons. The resonances for H(2, endo) and H(5) show ^{77}Se satellites with coupling constants of 11.8 Hz and 16.4 Hz, respectively. The chemical shifts of these peaks are similar to those of the structurally characterized complex (η^4-T•CN)$Mn(CO)_3$ in d_6-acetone [δ 6.67 (s, H(5)), 6.13 (s, H(4)), 4.88 (s, H(2)), 3.56 (s, H(3))]; the peaks in this spectrum were broad, probably because of Mn^{2+} impurities, such that second order coupling was not observed. The ^{13}C NMR spectrum of **4b** in d_6-acetone [δ 92.75 (s, C(4)), 78.44 (s, C(5)), 52.13 (s, C(3)), 43.05 (s, C(2))] also closely resembles that of the thiophene analog (η^4-T•CN)$Mn(CO)_3$ in d_6-acetone (δ 93.08, 69.89, 53.10, 50.77). An upfield shift of 231 ppm for the Sel•CN ligand in **4b** (δ 24.3) is observed in the ^{77}Se NMR spectrum when compared to the chemical shift of the starting material **4** (δ 255.9). Thus, the NMR results suggest that **4b** is (η^4-Sel•CN)$Mn(CO)_3$ in which the CN^- nucleophile has added to the 2-exo-position of Sel (Scheme 1). Comparison of the IR spectrum of **4b** (ν(CO) (hexanes): 2028 (s), 1954 (vs), 1941 (s) cm^{-1}) with that of (η^4-T•CN)$Mn(CO)_3$ (ν(CO) (hexanes): 2029 (s), 1957 (vs), 1945 (vs) cm^{-1}) also supports this assignment. In addition, the electron impact mass spectrum of **4b** contains a parent ion peak ((M^+) m/z = 297).

Reactions of trialkylphosphines (PR_3 for R = Me, n-Bu) with (arene)$Mn(CO)_3^+$ complexes have been previously reported[32,42] to give the

phosphonium ring adducts (arene•PR_3)$Mn(CO)_3^+$ which were not sufficiently stable to be isolated. The analogous reaction of **4** with P(n-Bu)$_3$ gave (η^4-Sel•PBu_3)$Mn(CO)_3^+$ (**4c**) which decomposed upon attempted isolation. The ^1H NMR spectrum of **4c** in d_6-acetone (δ 6.85 (s, H(5)), 6.20 (s, H(4)), 4.91 (s, H(2, endo)), 3.40 (s, H(3)), 1.97 (m), 1.46 (m), 0.965 (m)) and the IR spectrum in MeCN (ν(CO): 2019 (vs), 1938 (s), 1923 (s) cm^{-1}) are very similar to those previously reported for (η^4-T•PBu_3)$Mn(CO)_3^+$.[24] The ^{77}Se NMR spectrum of **4c** shows a doublet at δ -60 (J_{Se-P} = 5 Hz) due to the coupling of ^{77}Se to ^{31}P. Other basic phosphines such as PMe_3 and PEt_3 react like P(n-Bu)$_3$ to give phosphine adducts that could also not be isolated.

In contrast to the simple addition reaction of hydride to the thiophene in [(η^5-T)$Mn(CO)_3$]$^+$, hydride addition at C(2) in [(η^5-T)RuCp]$^+$ results in cleavage of a C-S bond.[32,33,43] The analogous reaction of [(η^5-Sel)RuCp*]$^+$ (**7**) with hydride (Na[$(H_3COC_2H_4O)_2AlH_2$]) also causes C-Se bond cleavage to give the complex (SeCH=CHCH=CH_2)RuCp* (**7a**) in 30% yield (Scheme 1). The ^1H NMR spectrum of **7a** in $CDCl_3$ shows five resonances assignable to the protons of the coordinated selenide/diene ligand (δ 6.38 (d, J_{H-Se} = 17.5 Hz, H(5)), 5.68 (t, H(4)), 4.37 (m, H(3)), 2.72 (d, H(2, endo)), 2.53 (d, H(2, exo)) and 1.85 (s, Me-Cp*)). This spectrum is very similar to that of the thiophene analog (SCH=CHCH=CH_2)RuCp*.[32] Cleavage of the C(2)-Se bond is indicated by the lack of coupling of either the endo or exo proton at C(2) to ^{77}Se. However, coupling is observed between the proton on C(5) and ^{77}Se, with J_{H-Se} (16.5 Hz) approximately the same as that (J_{H-Se} = 17.4 Hz) for the proton on C(5) in **4a**. In the ^{13}C NMR spectrum of **7a** there are four resonances at δ 97.9 (s, C(3)), 92.6 (s, C(4)), 89.0 (s, C(5)) and 45.2 (s, C(2)), assignable to the carbons of the

cleaved ring. The EI mass spectrum of **7a** contains a peak for the parent ion M^+.

The reaction of $[(\eta^5\text{-}2,5\text{-}Me_2T)IrCp^*]^{2+}$ with $Na[(CH_3OC_2H_4O)_2AlH_2]$ or the reducing agent Cp_2Co gives the neutral complex $(\eta^4\text{-}2,5\text{-}Me_2T)IrCp^*$, in which the η^4-2,5-Me_2T ligand is coordinated to the metal only through the four carbon atoms.[6] This η^4-complex rearranges in the presence of base to give the ring-opened product (C,S-2,5-Me_2T)IrCp* in which the Ir is inserted into a C-S bond to give a planar 6-membered ring.[6,34] The analogous reaction of $[(\eta^5\text{-}2,5\text{-}Me_2Sel)IrCp]^{2+}$ (**12**) with two equivalents of $Na[(CH_3OC_2H_4O)_2AlH_2]$ gives the ring-opened complex (C,Se-2,5-Me_2Sel)IrCp*(**12a**) (Scheme 1) as the only isolable product in low yield (17%). The ^1H NMR spectrum of **12a** in $CDCl_3$ contains two deshielded proton resonances at δ 7.59 (d) and 7.49 (d), two methyl resonances at δ 3.26 (s) and 2.84 (s), and a singlet resonance for the Cp* ligand at δ 1.87. This spectrum is almost identical to that of (C,S-2,5-Me_2T)IrCp*, which has a planar 6-membered π-delocalized ring that has been described as an iridathiabenzene.[34] The ^{13}C NMR spectrum of **12a** in $CDCl_3$ exhibits four carbon resonances at δ 134.9, 132.1, 129.8, and 123.3, which are characteristic of aromatic carbon atoms. Complex **12a** has an unusual ^{77}Se NMR chemical shift (δ 905) which is substantially downfield of the resonance of unbound selenophene (δ 605) or the starting material **12** (δ 371). This downfield chemical shift is similar to that (δ 976) of the aromatic six-membered heterocyclic seleninium cation ($\overline{(SeCH\text{-}CH\text{-}CH\text{-}CH\text{-}CH)}^+$).[44] This similarity in ^{77}Se NMR chemical shift further supports the description of the six-membered ring in **12a** as a delocalized π-system making **12a** an iridaselenabenzene compound. The ^1H, ^{13}C and ^{77}Se NMR data therefore suggest that **12a** has a

structure containing a planar 6-membered ring analogous to that established for the sulfur analog (C,S-2,5-Me_2T)IrCp*.

Conclusions

The synthesis of several new η^5-Seln transition metal complexes (**1-12**) has been undertaken so that a comparison of the spectroscopic and chemical properties could be made with the known η^5-Th complexes The ^1H and ^{13}C NMR and IR spectroscopic data for the η^5-Seln complexes (**1-12**) are very similar to those of the analogous η^5-Th complexes. Reactions of the η^5-Sel ligand in **4, 7** and **10** with nucleophiles give the same types of products that are formed in the corresponding reactions of the analogous η^5-T complexes. Differences between the structures of (η^5-2,5-Me_2Sel)$Cr(CO)_3$ and (η^5-2,5-Me_2T)$Cr(CO)_3$ are mostly due to the larger size of the Se as compared to S. The ^{77}Se chemical shifts of these η^5-Seln complexes all fall within the region between δ 375 and 150, the more positive the charge on the complex the more downfield the ^{77}Se signal. The observation that the ^{77}Se NMR chemical shifts fall within a range of only 225 ppm for a series of complexes with different metals, ligands and ionic charges suggests that ^{77}Se NMR spectroscopy may be a useful probe for detecting η^5-selenophene binding on HDS catalytic surfaces.

Acknowledgments. The authors thank Dr Victor G. Young, Jr. of the ISU Molecular Structure Laboratory for solving the molecular structure of **3**. We also thank Johnson-Mathey, Inc. for the generous loan of $RuCl_3$ and $IrCl_3$.

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Table 1. Crystal and Data Collection Parameters for (η^5-2,5-Me_2Sel)$Cr(CO)_3$ (3)

formula	$CrSeC_9H_8O_3$
fw	295.12
space group	$P2_1/c$
a, Å	6.741(1)
b, Å	12.534(3)
c, Å	12.557(3)
α, deg.	90.00
β, deg	102.55(2)
γ, deg	90.00
V, $Å^3$	1035.6(25)
Z	4
D(calc), g/cm^3	1.893
crystal size, mm	0.16 x 0.22 x 0.05
μ(MoK_α), cm^{-1}	45.4
data collection instrument	Enraf-Nonius CAD4
radiation (monochromated in incident beam)	Mo K_α (λ = 0.71073Å)
orientation reflections, number, range (2Θ)	25, 17.8 < 2Θ <35.0
temp, °C	22.0(10)
scan method	θ - 2θ
data col. range, 2θ, deg	4.0-45.0
no data collected	3883
no unique data, total	1988
with $F^2 > 3\sigma(F^2)$	947
no of parameters refined	128
trans. factors, max., min. (Ψ-scans)	0.998, 0.620

R^a	0.024
$R_\omega{}^b$	0.030
quality of fit indicator [c]	0.81
largest shift/esd, final cycle	0.00
largest Peak, e/Å^3	0.36(8)

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$

[b] $R_w = [\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$; $\omega = 1/\sigma^2(|F_o|)$

[c] Quality of fit = $[\Sigma\omega(|F_o| - |F_c|)^2/(N - N_{parameters})]^{1/2}$

Table 2. Bond Distances (Å)[a] and Angles (deg)[a] for (η^5-2,5-Me_2Sel)$Cr(CO)_3$ (3)

Atoms	Distance	Atoms	Distance
Cr-Se	2.488(5)	Se-C(5)	1.912(7)
Cr-C(2)	2.218(6)	C(1)-C(2)	1.500(7)
Cr-C(3)	2.199(4)	C(2)-C(3)	1.364(7)
Cr-C(4)	2.202(6)	C(3)-C(4)	1.409(8)
Cr-C(5)	2.232(4)	C(4)-C(5)	1.386(8)
Cr-C(7)	1.829(6)	C(5)-C(6)	1.507(5)
Cr-C(8)	1.822(6)	C(7)-O(1)	1.151(8)
Cr-C(9)	1.835(6)	C(8)-O(2)	1.145(8)
Se-C(2)	1.899(8)	C(9)-O(3)	1.150(9)

Atoms	Angle	Atoms	Angle
C(2)-Se-C(5)	86.9(3)	C(1)-C(2)-C(3)	128.8(5)
C(2)-C(3)-C(4)	116.2(4)	C(6)-C(5)-C(4)	129.7(4)
C(3)-C(4)-C(5)	116.0(4)	Cr-C(7)-O(1)	178.2(5)
Se-C(2)-C(1)	120.0(4)	Cr-C(8)-O(2)	178.3(6)
Se-C(5)-C(6)	120.1(3)	Cr-C(9)-O(3)	176.7(6)
Se-C(5)-C(4)	109.6(4)	C(7)-Cr-C(9)	92.7(2)
Se-C(2)-C(3)	110.8(4)	C(7)-Cr-C(8)	89.7(2)
		C(8)-Cr-C(9)	86.5(3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 3. Positional and Thermal Parameters for (η^5-2,5-Me_2Sel)$Cr(CO)_3$ (3)

Atom	x	y	z	B[a] (Å2)
Cr	0.50022(1)	0.20323(6)	0.33291(5)	2.83(1)
Se	0.86397(7)	0.19014(4)	0.43137(4)	3.62(1)
C(1)	0.7793(7)	-0.0172(4)	0.3195(4)	4.6(1)
C(2)	0.7586(6)	0.1017(4)	0.3093(4)	3.3(1)
C(3)	0.6932(7)	0.1616(4)	0.2177(4)	3.7(1)
C(4)	0.6987(7)	0.2731(4)	0.2323(4)	4.1(1)
C(5)	0.7707(6)	0.3089(4)	0.3382(4)	3.7(1)
C(6)	0.8083(7)	0.4211(4)	0.3809(5)	5.4(1)
C(7)	0.3967(7)	0.3011(4)	0.4134(4)	3.8(1)
C(8)	0.2733(7)	0.2132(4)	0.2251(4)	3.5(1)
C(9)	0.3770(6)	0.0914(4)	0.3859(4)	3.5(1)
O(1)	0.3321(5)	0.3648(3)	0.4626(3)	5.68(9)
O(2)	0.1280(5)	0.2170(3)	0.1580(3)	5.12(9)
O(3)	0.2934(5)	0.0203(3)	0.4140(3)	5.20(9)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3 * [a^2 * B(1,1) + b^2 * B(2,2) + c^2 * B(3,3) + ab(cos g) * B(1,2) + ac(cos b) * B(1,3) + bc(cos a) * B(2,3)].

Table 4. Spectroscopic Data for η^5-Coordinated Selenophene (Sel) in (η^5-Sel)Cr(CO)3 (1), [(η^5-Sel)Mn(CO)3]+ (4), [(η^5-Sel)RuCp*]+ (7), and [(η^5-Sel)IrCp*]2+(10)

Compound (Solvent)	**^{1}H NMR** (δ in ppm)	**^{13}C NMR** (δ in ppm)	**^{77}Se NMR** (δ in ppm)	**I R** (cm^{-1})
1 ($CDCl_3$)	5.95 (m, H(2), H(5))[a]	91.53 (s, C(2), C(5))	152.3	1984(s)
	5.79 (m, H(3), H(4))	91.82 (s, C(3), C(4))		1918(s)
		233.03 (CO)		1897(s)
4 (CD_3NO_2)	7.32 (s, H(2), H(5))[b]	101.55 (s, C(2), C(5))	255.9	2075(s)
	6.98 (s, H(3), H(4))	108.10 (s, C(3), C(4))		2016(s)
		231.17 (CO)		2014(sh)
7 (d_6-acetone)	6.39 (m, H(2), H(5))[c]	87.31 (s, C(2), C(5))	211.9	n/a
	5.94 (m, H(3), H(4))	89.82 (s, C(3), C(4))		
	2.02 (s, CH_3-Cp*)	96.76 (Cp*), 11.05 (Cp*)		
10 (CD_3NO_2)	7.99(dd, H(2),H(5))[d]	100.3 (s, C(2), C(5))	371.2	n/a
	7.70(dd, H(3), H(4))	101.2 (s, C(3), C(4))		
	2.50(s, CH_3-Cp*)	107.2 (Cp*), 10.7 (Cp*)		
Sel ($CDCl_3$)	7.88(d, H(2),H(5))	129.4 (s, C(2), C(5))	605.0	n/a
	7.23(d, H(3), H(4))	130.4 (s, C(3), C(4))		

[a] $J_{H\text{-}Se}$ = 18.8 Hz. [b] $J_{H\text{-}Se}$ = 18.3 Hz. [c] $J_{H\text{-}Se}$ = 17.8 Hz. [d] $J_{H\text{-}Se}$ = 16.9 Hz.

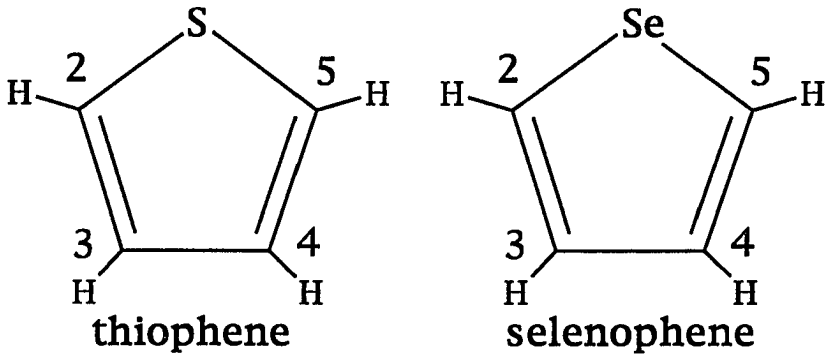


Figure 1. Structures and numbering of thiophene and selenophene.

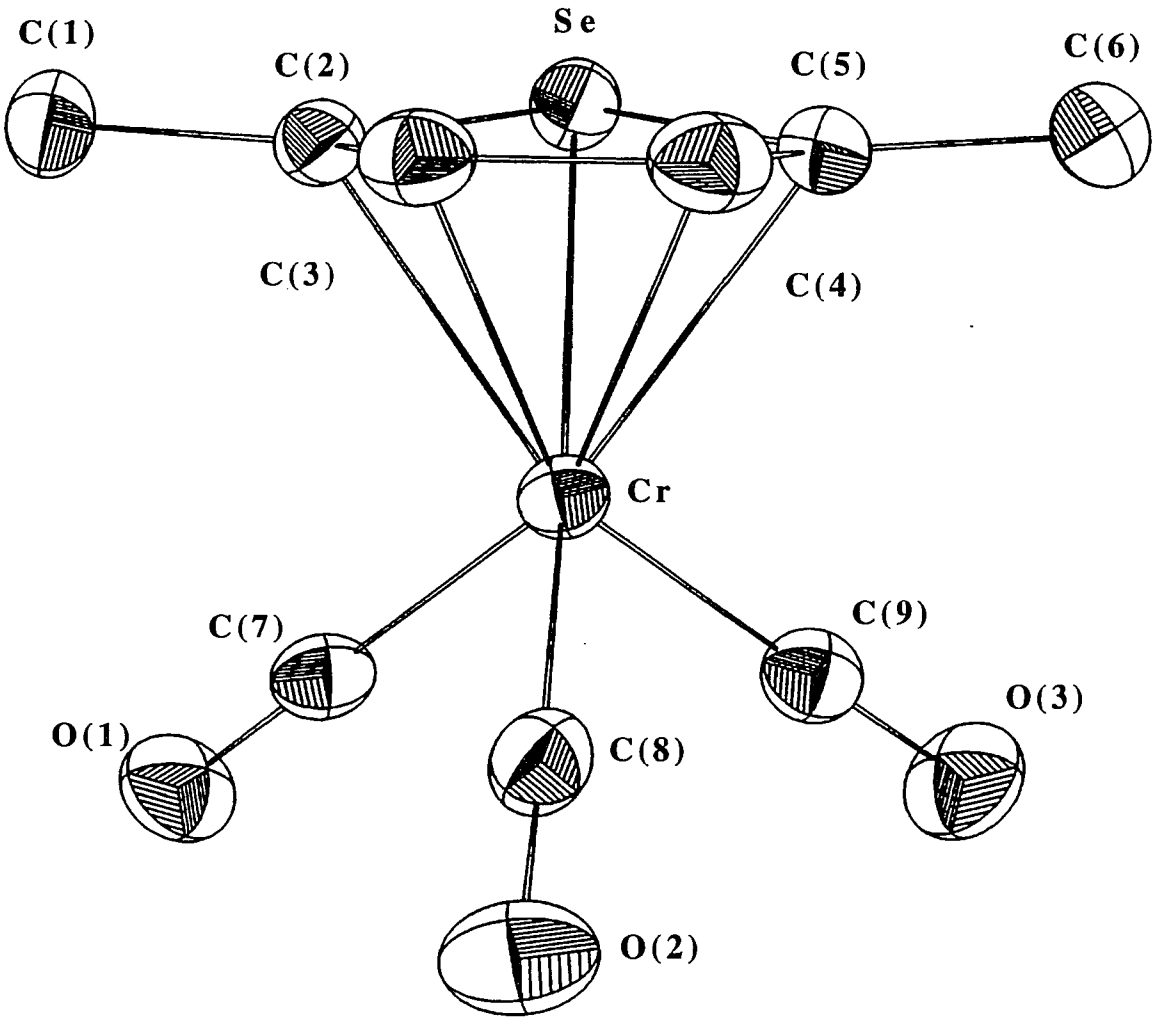


Figure 2. ORTEP Drawing of (η^5-2,5-Me_2Sel)$Cr(CO)_3$ (3)

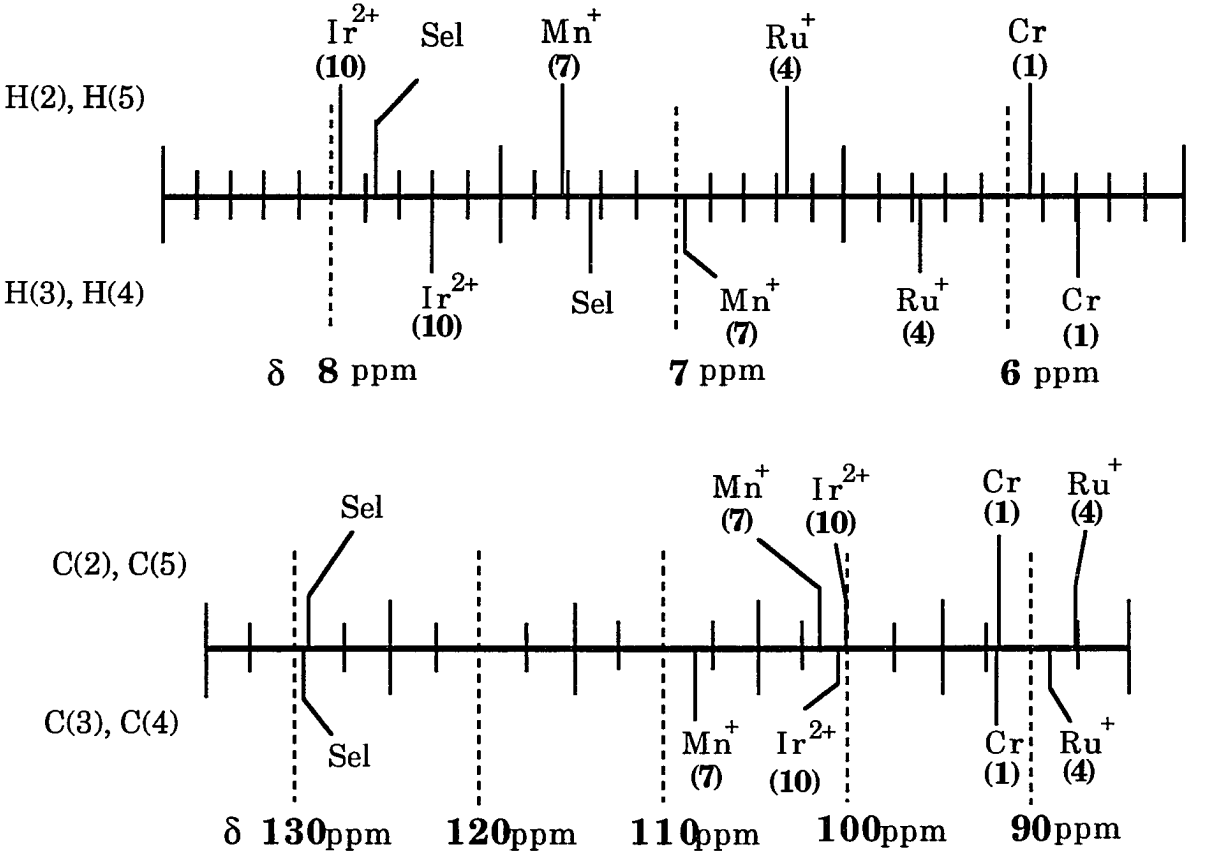
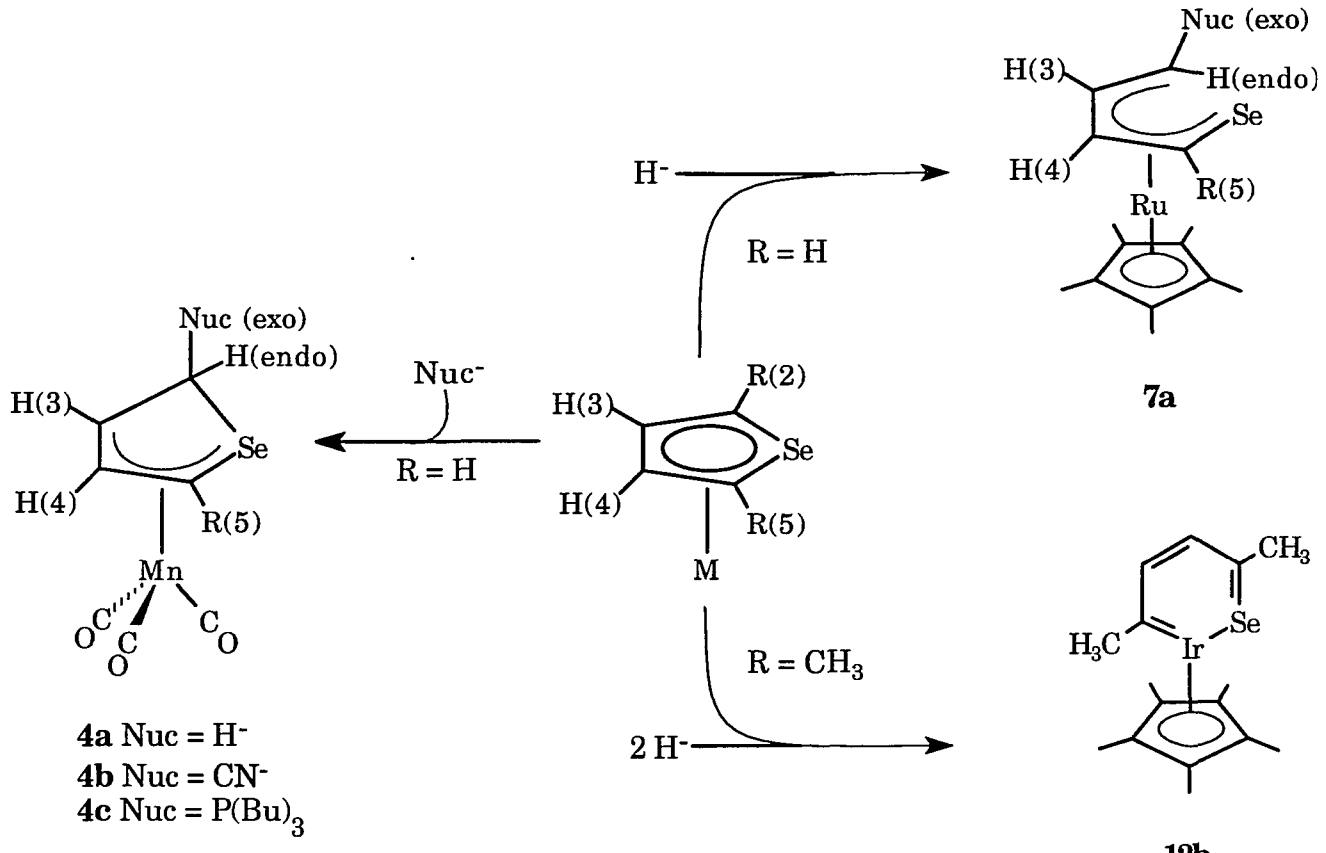


Figure 3. ^{1}H a ıd ^{13}C NMR Chemical shifts of selenophene in complexes (1), (4), (7), and (10).

Figure 4. ^{77}Se NMR Chemical shift data for η^5-Seln complexes (1-12).

Scheme 1



4a Nuc = H^-
4b Nuc = CN^-
4c Nuc = $P(Bu)_3$

SYNTHESIS, EQUILIBRIUM BINDING AND ^{77}Se NMR STUDIES OF η^1-SELENOPHENE (SELN) COMPLEXES: $[CpRu(CO)(PPh_3)(\eta^1(Se)\text{-}Seln)]BF_4$

A paper submitted to *Organometallics*

Carter J. White, Tieli Wang, R. A. Jacobson and Robert J. Angelici

Abstract

Reactions of $Cp(CO)(PPh_3)RuCl$ ($Cp=C_5H_5$) with Ag^+ and selenophenes (Seln) produce the stable selenium-bound (η^1(Se)) selenophene complexes $[Cp(CO)(PPh_3)Ru(\eta^1(Se)\text{-}Seln)]^+$ (Seln = selenophene (Sel), 2-methylselenophene(2-MeSel) and 2,5-dimethylselenophene (2,5-MeSel)). The molecular structure of $Cp(CO)(PPh_3)Ru(\eta^1(Se)\text{-}2\text{-}MeSel)]^+$ was determined and ^1H, ^{13}C NMR and IR data for all of the Seln complexes are compared with those of their thiophene analogs. Equilibrium constants (K') for the replacement of thiophene(T) by selenophenes, thiophenes, benzo[b]thiophene(BT), dibenzothiophene(DBT), 2,8-dimethyldibenzothiophene (2,8-Me_2DBT), and *p*-tolyl sulfide (PTS) increase in the order: T(1.00) < 2,5-Me_2T (2.76) < 2-MeT (4.11) < 3-MeT (6.30) < Sel (23.8) < BT (29.9) < DBT (74.1) < 2-MeSel (100) < 2,5-Me_2Sel (175) < 2,8-Me_2DBT (358) < PTS (7.11×10^3). The selenophenes bind more strongly than the analogous thiophenes. Electron-releasing methyl groups in selenophene and DBT increase the binding constants (K') of the methyl-substituted selenophenes and 2,8-Me_2DBT. A ^{77}Se NMR study of free selenophenes and their complexes establishes ^{77}Se chemical

shift ranges that are characteristic of η^1(Se), η^2, and η^5 modes of selenophene coordination to transition metals.

Introduction

Adsorption of thiophene at an active metal site is a necessary first step in the mechanism of thiophene hydrodesulfurization (HDS) on heterogeneous catalysts.[1] Based on studies of model organometallic complexes, two modes for thiophene (T) binding, η^5 and η^1(S), are most common.[2,3] Equilibrium studies of the adsorption of thiophenes on a $Co/Mo/Al_2O_3$ catalyst have shown that increasing the number of methyl groups in the thiophene increases the adsorption equilibrium constants in the order: T < 2-MeT, 3-MeT < 2,5-Me_2T.[4,5] In the organometallic model complexes $[CpRu(\eta^5\text{-Th})]^+$,[6] where Th is thiophene or its methyl-substituted derivatives, equilibrium constants for η^5 binding of Th increase in the same order, which is consistent with η^5 binding on the $Co/Mo/Al_2O_3$ catalyst. Support for this mode of adsorption can also be found in the results of reactivity studies conducted on η^5-thiophene complexes.[1,3,7-10]

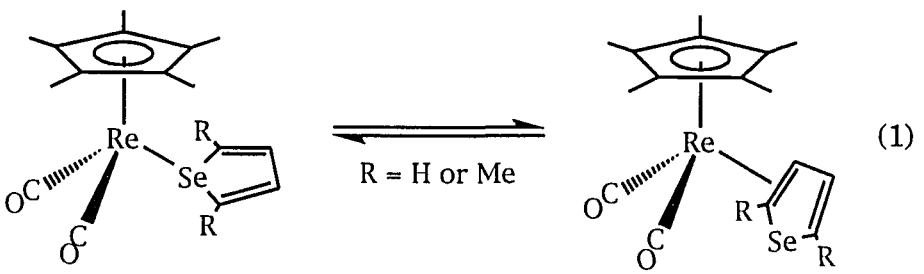
The η^1(S)-thiophene coordination mode occurs in several complexes[2,3] including $[CpRu(CO)(PPh_3)(\eta^1\text{(S)-Th})]^+$,[11] $[CpRu(CO)_2(\eta^1\text{(S)-Th})]^+$,[12] and $CpRe(CO)_2(\eta^1\text{(S)-Th})$.[13] Equilibrium constants (K') for thiophene ligand exchange in $[CpRu(CO)_2(\eta^1\text{(S)-Th})]^+$ show that η^1(S)-thiophene binding increases as the number of methyl groups in the thiophene increases. Thus, K' increases in the order: T < 3-MeT < 2-MeT < 2,5-Me_2T. This is essentially the same order as that for thiophene adsorption on the $Co/Mo/Al_2O_3$ catalyst. Thus, equilibrium constants for the binding of both η^5- and η^1(S)-thiophenes

follow the same trend as that observed on the HDS catalyst. Kinetic studies of η^1(S)-thiophene dissociation from $[CpRu(CO)_2(\eta^1(S)\text{-}Th)]^+$,[12] and $CpRe(CO)_2(\eta^1(S)\text{-}Th)$[13] show that the rate of Th dissociation increases as the number of methyl groups decreases: 2,5-Me_2T < 2-MeT < 3-MeT < T. All of these studies indicate that η^1(S)-thiophene forms a stronger bond to the metal as a result of the increasing number of electron-releasing methyl groups, which makes the sulfur a better σ-donor to the metal.

Selenophene (Sel), the selenium analog of thiophene, (Figure 1) has recently become of interest as a means of determining the mode of selenophene adsorption on HDS catalyst surfaces.[14] Recently we described[15] the synthesis, reactions and ^{77}Se NMR chemical shifts of a series of η^5-selenophene complexes: $(\eta^5\text{-Sel})Cr(CO)_3$,[16,17] $[(\eta^5\text{-Sel})Mn(CO)_3]^+$, $[Cp^*Ru(\eta^5\text{-Sel})]^+$, and $[Cp^*Ir(\eta^5\text{-Sel})]^{2+}$. The η^5-Sel complexes are structurally and chemically very similar to the analogous η^5-thiophene complexes. ^{77}Se NMR chemical shift values for η^5-coordinated Sel fall into the region between δ 370 and δ 150. Within this range the ^{77}Se chemical shift is sensitive to the ionic charge and other ligands in the complex and the number of methyl groups in the selenophene.

Our group has also previously reported on the coordination of selenophenes (Seln) in the complexes $Cp'Re(CO)_2$(Seln) (Cp' = Cp or Cp*).[14,18] In the electron-rich complex $Cp^*Re(CO)_2$(Seln) (Cp* = η^5-C_5Me_5), selenophene (Sel) is η^2-coordinated through a C=C double bond. In the 2,5-dimethylselenophene (2,5-Me_2Sel) complex $Cp^*Re(CO)_2$(2,5-Me_2Sel), the ligand is coordinated through the Se atom in an η^1(Se)-manner. When the selenophene ligand is 2-methylselenophene (2-MeSel), both the η^1(Se) and η^2

isomers are observed and they are in equilibrium with each other (eq 1). Replacement of the Cp* ligand with the less electron donating Cp (η^5-C_5H_5) ligand increases the equilibrium amount of the η^1(Se) isomer and decreases the amount of the η^2 isomer. This shift in isomer distribution is reasonable



(1)

since a decrease in the electron-density on the metal would reduce π backbonding to the olefin in the η^2 isomer but would strengthen selenium to rhenium donation in the η^1(Se) isomer.[19,20]

In this paper, we present the synthesis and characterization of several new η^1(Se)-selenophene complexes [CpRu(CO)(PPh_3)(η^1(Se)-Seln)]BF_4 (Seln = selenophene (Sel), 2-methylselenophene (2-MeSel), or 2,5-dimethylselenophene (2,5-Me_2Sel)). The X-ray-determined structure of [CpRu(CO)(PPh_3)(η^1(Se)-2-MeSel)]BF_4 is described and compared with that of the analogous thiophene complex. Equilibrium constants for the ligand replacement reaction (eq 2)

$$[CpRu(CO)(PPh_3)(L)]^+ + L' \underset{CD_2Cl_2}{\overset{25^\circ C}{\rightleftharpoons}} L + [CpRu(CO)(PPh_3)(L')]^+ \quad (2)$$

are reported and are compared with those of the analogous η^1(S)-thiophene complexes [CpRu(CO)(PPh_3)(η^1(S)-Th)]$^+$.[11] Finally, ^{77}Se NMR chemical shift

values for the new η^1(Se)-SeIn complexes are discussed in relation to those of selenophene in its η^5 and η^2 complexes.

Experimental Section

General Procedures. All reactions and manipulations were carried out under an atmosphere of dry N_2 using standard Schlenk techniques unless otherwise stated.[21,22] All solvents were reagent grade or better and were dried and distilled under N_2 by the following methods. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from Na/benzophenone. Hexanes and dichloromethane (CH_2Cl_2) were distilled from CaH_2. Acetone was dried with potassium carbonate (K_2CO_3) and distilled. The solvents were used immediately after distillation except for acetone which was stored over K_2CO_3 under N_2. The neutral alumina (Brockman, Activity I, ~150 mesh) used for chromatography was deoxygenated at room temperature in high vacuum for 16 hours, then deactivated with 5% w/w N_2-saturated deionized distilled water, and stored under N_2.

The ^1H and ^{13}C NMR spectra were recorded on either a Nicolet NT-300 MHz or a Varian VXR-300 MHz spectrometer with deuteriated solvents as the internal locks and referenced to tetramethylsilane (TMS $\delta = 0.00$) or residual CH_2Cl_2 ($\delta = 5.33$). The ^{77}Se NMR spectra were recorded on the Varian VXR-300 spectrometer at room temperature and referenced to selenophene (δ=605.0 ppm). Fast atom bombardment (FAB) mass spectra were obtained using a Kratos MS-50 mass spectrometer. Infrared spectra were obtained on a Nicolet 710 FTIR spectrophotometer using a solution cell with NaCl salt plates.

Elemental analyses were performed by either Galbraith Laboratories, Inc., Knoxville TN or Desert Analytics, Tucson, AZ.

The following compounds were prepared by literature methods: $CpRu(CO)(PPh_3)Cl$,[23] $[CpRu(CO)(PPh_3)(Th)]BF_4$ (Th = thiophene (T), 2-methylthiophene (2-MeT), 2,5-dimethylthiophene(2,5-Me_2T), benzothiophene (BT), and dibenzothiophene (DBT)),[11] selenophene (Sel),[24,25] 2-methylselenophene (2-MeSel),[26] 2,5-dimethylselenophene (2,5-Me_2Sel),[27] *p*-tolyl sulfide (PTS),[28] 2,8-dimethyldibenzothiophene(2,8-Me_2DBT).[29] All other compounds were used as recieved from commercial sources.

$[Cp(CO)(PPh_3)Ru(\eta^1(Se)\text{-}Sel)](BF_4)$ (1). To a stirred solution of 1.00 mL of Sel and 0.103 g (0.209 mmol) of $Cp(CO)(PPh_3)RuCl$ in 20 mL of CH_2Cl_2 was added 0.056 g (0.288 mmol) of $AgBF_4$. A white AgCl precipitate formed and the solution turned from orange to yellow. After being stirred for 1 h at room temperature, the solution was filtered through Celite and the volatiles were removed under vacuum. The yellow oily residue was taken up into 2-3 mL of CH_2Cl_2; upon addition of 20 mL of Et_2O, product **1** precipitated as a yellow powder. The powder was filtered and washed with 10 mL of Et_2O three times and dried under vacuum. Yield of **1**: 0.167 g , 86%. ^1H NMR δ (CD_2Cl_2) 7.79-7.77(m, H(2)H(5)), 7.31-7.29(m, H(3)H(4)), 4.92 (s, Cp), 7.59-7.35(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 200.74(d, $J_{C\text{-}P}$ = 18.33 Hz, CO), 141.60(d, $J_{C\text{-}P}$= 2.3Hz, C(2) C(5)), 134.24(C(3)C(4)), 133.45(s, Ph), 133.10(d, Ph), 132.05(d, Ph), 129.55(d, Ph), 87.67(d, $J_{P\text{-}C}$ = 1.34Hz, Cp). ^{77}Se NMR δ (CD_2Cl_2): 411.6(d, $J_{Se\text{-}P}$ = 12 Hz). IR cm^{-1} (CH_2Cl_2): 1991. Anal. Calcd for $C_{28}H_{24}OPRuSeBF_4$: C, 49.88; H, 3.59. Found: C, 50.33; H, 3.72. If a more crystalline product was desired, the

powder was recrystallized from a minimum of CH_2Cl_2 layered with a 5-7 fold excess of Et_2O at -20 °C overnight; this yielded bright yellow crystals.

[Cp(CO)(PPh$_3$)Ru(η^1(Se)-2-MeSel)](BF$_4$) (2). Compound **2** was synthesized in the same manner as **1** using 1.00 mL of 2-MeSel, 0.103 g (0.209 mmol) of Cp(CO)(PPh_3)RuCl and 0.056 g (0.29 mmol) of $AgBF_4$. Yellow crystals of **2** were obtained (0.161 g, 81%). ^{1}H NMR δ (CD_2Cl_2): 7.35(H(5)), 7.10(m, H(4)), 6.89(m,H(3)), 2.47(s, CH_3), 4.87(s, Cp), 7.65-7.30(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 200.6(d, J_{C-P} = 17.42 Hz, CO), 157.93(d, J_{C-P} = 4.6Hz, C(2)), 137.35 (s, C(5)), 134.5(s, C(3)), 132.1(s, C(4)),16.48(s, Me) , 132.61(d, Ph), 132.1(d, Ph), 131.4(s, Ph), 129.0(d, Ph), 87.70(Cp). ^{77}Se NMR δ (CD_2Cl_2): 427.4(d, J_{Se-P} = 12 Hz). IR cm^{-1} (CH_2Cl_2): 1988. FAB Mass Spectrum 601.0 (M^+), 456.9 (M^+- 2-MeSel). Anal. Calcd for $C_{29}H_{26}OPRuSeBF_4$: C, 50.44; H, 3.81. Found: C, 49.97; H, 3.78.

[Cp(CO)(PPh$_3$)Ru(η^1(Se)-2,5-Me$_2$Sel)](BF$_4$) (3). Compound **3** was synthesized in the same manner as **1** using 1.00 mL of 2,5 -Me_2Sel, 0.103 g (0.209 mmol) of Cp(CO)(PPh_3)RuCl and 0.056 g (0.288 mmol) of $AgBF_4$. Yellow crystals of **3** were obtained (0.170 g, 84%). ^{1}H NMR δ (CD_2Cl_2): 6.64(s, H(3),H(4)), 2.22 (s, CH_3), 4.88(s, Cp), 7.63-7.35(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 201.4(d, J_{C-P} = 19.23 Hz, CO), 154.2(d, J_{P-C} = 19.2 Hz, C(2),C(5)), 131.13(s, C(3),C(4)), 17.50(CH_3), 133.33(d, Ph), 132.75(s, Ph), 132.03(d, Ph), 129.71(d, Ph), 88.0(Cp). ^{77}Se NMR δ (CD_2Cl_2): 444.0(d, J_{Se-P} = 12 Hz). IR cm^{-1} (CH_2Cl_2): 1987. FAB Mass Spectrum: 616.8 (M^+), 456.9 (M^+ - 2,5-Me_2Sel). Anal. Calcd for $C_{30}H_{28}OPRuSeBF_4$: C, 51.30; H, 4.02. Found: C, 50.82; H, 4.09.

[Cp(CO)(PPh$_3$)Ru(η^1(S)-2,8-Me$_2$DBT)]BF$_4$ (4). Compound **4** was made using the same method previously published[11] for the synthesis of [Cp(CO)(PPh$_3$)Ru(η^1(S)-DBT)]SO$_3$CF$_3$ substituting 2,8-Me$_2$DBT for DBT. The reaction utilized 0.100 g (0.203 mmol) of CpRu(CO)(PPh$_3$)Cl, 0.129 g (0.609 mmol) of 2,8-Me$_2$DBT, and 0.400g (0.205 mmol) of AgBF$_4$. The product **4** was isolated as a yellow solid. Yield: 0.126 g, 76% . ^{1}H NMR (CD$_2$Cl$_2$): 7.87(s, DBT), 2.52(s, CH$_3$), 7.59-7.35(m, PPh$_3$), 4.72(s, Cp). IR cm^{-1} (CH$_2$Cl$_2$): 1992. Anal. Calcd for C$_{38}$H$_{35}$OPRuSBF$_4$ · 0.2 CH$_2$Cl$_2$: C, 60.01; H, 4.16. Found: C, 60.21; H, 4.15.

[Cp(CO)(PPh$_3$)Ru(η^1(S)-(p-H$_3$CC$_6$H$_4$)$_2$S)]SO$_3$CF$_3$ (5). A solution of 0.100 g (0.203 mmol) of CpRu(CO)(PPh$_3$)Cl and 0.053 g (0.21 mmol) AgOTf in 20 mL of CH$_2$Cl$_2$ was stirred in a foil covered flask for 1 h. A white precipitate slowly formed and the dark yellow solution lightened in color. After filtration through Celite, 0.15 g (0.708 mmol) of (p-H$_3$CC$_6$H$_4$)$_2$S) (PTS) was added and the solution stirred for an additional 1 h. The volatiles were removed under vacuum and the resulting yellow solid was washed with hexanes repeatedly (5 x 10 mL) to remove the excess PTS. The yellow solid **5** was dissolved into 5 mL of CH$_2$Cl$_2$; the solution was filtered and 30 mL of hexanes was added to precipitate a bright yellow powder. The product **5** was filtered, dried under a stream of N$_2$ and finally under vacuum. Yield: 0.153 g (92%, based on Ru). ^{1}H NMR δ (CD$_2$Cl$_2$): 7.56-7.52(m), 7.46-7.43(m), 7.21-7.12(m), 7.02-6.99(m), 5.04(s, Cp), 2.37(s, CH$_3$). IR cm^{-1} (CH$_2$Cl$_2$): 1992. Anal. Calcd for C$_{39}$H$_{37}$O$_4$PRuS$_2$F$_3$: C, 57.14; H, 4.18. Found: C, 57.95; H, 4.52.

X-ray Structure Determination of [CpRu(CO)(PPh_3)(η^1(Se)-2-MeSel)]BF_4 (2). A single crystal of **2** suitable for X-ray diffraction study was obtained by vapor diffusion of Et_2O into a saturated CH_2Cl_2 solution of **2** at -20 °C. The single crystal was mounted on the end of a glass fiber. Cell constants were determined from reflections found in a 2θ range of 25 to 30°. Pertinent data collection and reduction information are given in Table 1. The absorption correction was made on the basis of a series of Ψ scans. The positions of the Ru, P, and Se atoms were determined by interpretation of the Patterson map. All remaining non-hydrogen atoms were found from a difference electron density map. All non-hydrogen atoms were refined with anisotropic thermal parameters. After the least-squares converged, all hydrogen atoms were found in a difference map. These were placed into the model with isotopic temperature factors set equal to 1.3 times the isotropic equivalent of the attached atom. The hydrogen positions were not refined.

Selected bond distances and angles are presented in Table 2, and an ORTEP drawing of 2 is given in Figure 2. The final positional and thermal parameters for all non-hydrogen atoms are listed in Table 3.

Exchange Studies. The equilibrium constants (K) for the reaction (eq 2) in which one ligand (L) is displaced by another ligand (L') were determined by integration of ^1H NMR signals of the reactants and products as previously described.[11,12] About 0.020 mmol of a $[Cp(CO)(PPh_3)Ru(L)]^+$ complex was placed in a 5 mm NMR tube, then dissolved in 0.5 mL of CD_2Cl_2 and an equimolar amount of the incoming ligand (L') was added under N_2. The solution was frozen in liquid nitrogen, degassed and the tube was flame-sealed

under vacuum. The solution was thawed, and the tube was kept in a 25.0 °C temperature bath. Spectra of the solution were recorded on a Varian VX-300 NMR spectrometer with the probe pre-cooled and thermostated at 25.0 °C; CD_2Cl_2 was the internal lock and reference (δ 5.32). A 38 sec pulse delay between scans allowed all protons to relax. NMR spectra recorded at various times were followed with time to establish that all of the reactions had reached equilibrium; this occurred usually within 48 h.

The equilibrium constants (K) were calculated using equation 3, where I'_{Cp} and I_{Cp} are the Cp peak integrals of $Cp(CO)(PPh_3)Ru(L')^+$ and

$$K = \frac{\left(\frac{I'_{Cp}}{5}\right)^2}{\left(\frac{I_{Cp}}{5}\right)\left(\frac{I_{Me}}{x}\right)} = \frac{[Cp(CO)(PPh_3)Ru(Th')^+][Th]}{[Cp(CO)(PPh_3)Ru(Th)^+][Th']} \qquad (3)$$

$Cp(CO)(PPh_3)Ru(L)^+$, respectively; I_{Me} is the integral of the Me peak of L' and x is 3 (for L' = 2-MeT, 2-MeSel) or 6 (for L' = 2,5-Me_2T, 2,5-Me_2Sel, 2,8-Me_2DBT, PTS). The K values in Table 5 are averages of at least two independent determinations. The error limits in Table 5 are average deviations from the mean value. The solutions were stable for 6 weeks or longer.

Results and Discussion

Synthesis and Characterization of $[CpRu(CO)(PPh_3)(\eta^1(Se)\text{-Seln})]^+$ Complexes (1-3). The compounds $[CpRu(CO)(PPh_3)(\eta^1(Se)\text{-Seln})]BF_4$ (Seln = Sel (**1**), 2-

MeSel (**2**), or 2,5-Me_2Sel (**3**)) were synthesized from CpRu(CO)(PPh_3)Cl, $AgBF_4$ and the appropriate ligand in CH_2Cl_2 (eq 4). The halide extraction method has

$$CpRu(CO)(PPh_3)Cl + Seln \xrightarrow[CH_2Cl_2]{Ag^+} [CpRu(CO)(PPh_3)(\eta^1(Se)\text{-}Seln)]^+ + AgCl \qquad (4)$$

1 Seln = Sel
2 Seln = 2-MeSel
3 Seln = 2,5-Me_2Sel

been used previously to make a variety of cationic ruthenium complexes $[CpRu(CO)(PPh_3)(L)]^+$ (L = PR_3, CO[24], Th[11,12]). The complexes **1-3** are all bright yellow, air stable solids and are soluble in most polar organic solvents.

The ^1H NMR spectra of **1-3** show selenophene proton resonances that are upfield (~ 0.1 ppm) of those in the free selenophenes. The ^1H chemical shifts of the Sel in **1** are approximately 0.5 ppm downfield of the corresponding protons in the analogous thiophene complex $[CpRu(CO)(PPh_3)(\eta^1(S)\text{-}T)]BF_4$. These differences are approximately the same as those in the two free ligands. Despite the asymmetry at the Ru, the H(2) and H(5) protons in **1** and the methyl groups in **3** occur as single resonances in their room temperature ^1H NMR spectra. At low temperature (198 K) the ^1H NMR spectrum of **3** in CD_2Cl_2 shows two broad resonances at 2.42 ppm and 1.87 ppm for the diastereotopic methyl groups. The free energy of activation for the coalescence of these peaks was calculated to be 44(1) kJ/mol at the coalescence temperature (T_c = 225 K).[30] Coalescence of the methyl groups in the 2,5-dimethylthiophene complex $[CpRu(CO)(PPh_3)(\eta^1(S)\text{-}2,5\text{-}Me_2T)]^+$ occurs at T_c = 213 K with a free energy of activation of 40 kJ/mol.[11] Coalescence in both of these complexes presumably occurs as a result of inversion at the S or Se atom. Such inversion would be

more favorable for S than Se because of the greater π-bonding between the sulfur and the diene segment of the thiophene in the planar intermediate. In other organo-sulfur and selenium complexes[31] such as $ReCl(CO)_3(EMe_2)_2$ and $PtBr(Me)(EMe_2)_2$ the inversion barrier is also lower in the S than the Se analog. A low temperature ^1H NMR spectrum of **1** in CD_2Cl_2 shows only a slight broadening of the proton resonances at the freezing point (178 K) of CD_2Cl_2; this indicates that the T_c for **1** is lower than 178 K. The lower T_c for **1** as compared with that for **3** suggests that steric interactions between the substituents in the 2,5-positions of the selenophene and the bulky triphenylphosphine ligand reduce the rate of inversion at sulfur. The assignment of a resonance to H(5) in **2** was done using the 2D $^1H/^{13}C$ HETCOR NMR spectrum. It was necessary to use this 2D technique because of overlapping ^1H resonances from the PPh_3 and the 2-MeSel ligands.

The ^{13}C NMR spectra of **1-3** were assigned using the 2D $^1H/^{13}C$ HETCOR NMR technique because resonances for both the Seln and the PPh_3 ligands occurred in the same region. The ^{13}C chemical shift values of selenophene in **1-3** are downfield (~ 12 ppm C(2), C(5), and ~4 ppm C(3),C (4)) compared to those of the free selenophene. The ^{13}C resonances of the Seln ring carbons are consistently downfield (~ 4 ppm C(2), C(5) and ~ 2 ppm C(3), C(4)) of those in the corresponding thiophene complex.[11] A similar downfield shift is also seen in the free Seln and thiophene ligands. Resonances for the CO ligands in **1-3** are split into doublets by the phosphine ligand and have virtually the same chemical shifts as those in the analogous thiophene complexes.[11]

The ν (CO) band in the IR spectra of **1-3** is consistently 8-10 cm^{-1} smaller than in the corresponding thiophene complexes,[11] which suggests that

selenophene is a better sigma donor ligand than thiophene.

Molecular Structure of [CpRu(CO)(PPh$_3$)(η^1(Se)-2-MeSel)]BF$_4$ (2). The X-ray determined molecular structure of the cation [CpRu(CO)(PPh$_3$)(η^1(Se)-2-MeSel)]$^+$ is shown in Figure 2. The selenophene ring is essentially planar with a dihedral angle between the least squares planes of C(2)-Se-C(5) and C(2)-C(3)-C(4)-C(5) of only 0.89°. The selenium has pyramidal geometry as indicated by the angle (113.83(7)°) between the Ru-Se bond and the vector between Se and the midpoint between C(2) and C(5); also, the sum (304°) of the three angles around the Se is substantially less than the 360° required if the Se were planar. The Ru-Se bond distance (2.494(2) Å) is 0.102 Å longer than the corresponding Ru-S bond distance (2.392(1) Å) in [CpRu(CO)(PPh$_3$)(η^1(S)-2-MeT)]$^+$ due to the larger size of the selenium atom. The C(2)-Se (1.90(2) Å) and C(5)-Se (1.85(2) Å) bond distances are similar to those in free selenophene (1.855(7) Å)[32] and (η^5-2,5-Me$_2$Sel)Cr(CO)$_3$ (1.910(1)Å),[17] although the error limits are rather large in **2**. The C-Se distances in **2** are approximately 0.15Å longer than the C-S distances in the 2-MeT complex [CpRu(CO)(PPh$_3$)(η^1(S)-2-MeT)]$^+$ due to the larger size of the Se atom. The C(2)-Se-C(5) bond angle in **2** is 4.3° smaller than the corresponding C(2)-S-C(5) angle in [CpRu(CO)(PPh$_3$)(η^1(S)-2-MeT)]$^+$; this difference is probably also due to the larger size of Se. Overall, the combination of the longer Ru-Se and C-Se bonds and the smaller C(2)-Se-C(5) bond angle move the methyl groups in 2-MeSel further from the other ligands in the Ru coordination sphere than occurs with 2-MeT. For this reason, 2-MeSel is a less sterically demanding ligand than 2-MeT.

Equilibrium Studies. Equilibrium constants (K) for the ligand exchange reactions (eq 2) of $[CpRu(CO)(PPh_3)(L)]^+$ with L' were calculated using eq 3 and are shown in Table 4. The consistency of the K values can be verified by calculating them from different data sets. For example, K for reaction 7 can be calculated by dividing the K (7.39) for reaction 4 by the K (4.22) of reaction 3 to give a calculated K of 1.75. The experimentally determined K for reaction 7 is 1.72(4) which is in good agreement (within 5%) with the value calculated from reactions 3 and 7.

Using K values previously determined for Th[11] and the values in Table 5, relative equilibrium constants (K') were calculated (Table 5) for the displacement of thiophene by the other ligands (eq 5). In a previous study[11]

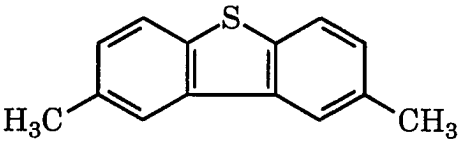
$$CpRu(CO)(PPh_3)(\eta^1(S)\text{-}T)^+ + L' \underset{CD_2Cl_2}{\overset{25°C}{\rightleftharpoons}} CpRu(CO)(PPh_3)(L')^+ + Th \qquad (5)$$

of this equilibrium using substituted thiophenes as L' ligands, it was noted that K' increases (Table 5) in the order: T (1.00) < 2,5-Me_2T (2.76) < 2-MeT (4.11) < 3-MeT (6.30) < Me_4T (57.4) < BT (29.9) < DBT (74.1) << THT (>7.1x10^6). By comparison with tetrahydrothiophene (THT), all the thiophene ligands are weakly coordinating, thiophene (T) being the most weakly binding. The addition of a methyl group as in 2-MeT or 3-MeT increases the coordinating ability of the thiophene; the electron-releasing methyl group presumably makes the sulfur a stronger σ-donor to the Ru. However, two methyl groups in the 2 and 5 positions reduce the coordinating ability of the 2,5-Me_2T, as

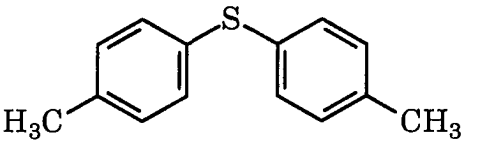
compared with 2-MeT and 3-MeT, due to steric crowding between one of the methyl groups and the bulky PPh_3 ligand. The addition of two more methyl groups in the uncrowded 3 and 4 positions of 2,5-Me_2T makes Me_4T the most strongly ligating thiophene.

In the present study of selenophene ligands, the K' values increase in the order: Sel (23.8) < 2-MeSel (100) < 2,5-Me_2Sel (175). In this series, there is no evidence for steric crowding since the binding ability of the selenophene increases as the number of electron-releasing methyl groups in the selenophene increases. The lack of crowding in 2,5-Me_2Sel presumably results from the larger size of Se, as compared with S, which moves the 2,5-methyl groups away from the bulky PPh_3, as noted in the discussion of the structure of $[CpRu(CO)(PPh_3)(2\text{-MeSel})]^+$. When compared with the analogous thiophene ligands, the selenophenes bind more strongly. Sel and 2-MeSel bind to Ru about 24 times more strongly than T and 2-MeT, respectively. However, 2,5-Me_2Sel binds 63.4 times more strongly than 2,5-Me_2T due to crowding in the 2,5-MeT complex.

For the dibenzothiophene-related ligands, the K' values increase in the order: DBT (74.1) < 2,8-Me_2DBT (358) < PTS (7.11×10^3). The larger K' for 2,8-Me_2DBT as compared with that for DBT undoubtedly results from the electron donating methyl groups which make the sulfur a better σ-donor to Ru. The p-tolylsulfide (PTS) ligand binds about 96 times more strongly than DBT and about 20 times more strongly than 2,8-Me_2DBT. The DBT and 2,8-Me_2DBT ligands are structurally similar except for the C-C bond between the tolyl rings which creates the thiophene ring. Delocalization within the thiophene may be responsible for the lower coordinating ability of 2,8-Me_2DBT as compared with



2,8-Me_2DBT



PTS

PTS. It is also possible that PTS is a less bulky ligand than 2,8-Me_2DBT because of its ability to rotate around the S-tolyl bonds.

^{77}Se NMR Studies of Coordinated Selenophenes. As part of an investigation of ^{77}Se chemical shifts of selenophenes and their complexes, we determined the ^{77}Se chemical shifts of the η^1(Se)-selenophene complexes $[CpRu(CO)(PPh_3)(\eta^1(Se)\text{-Seln})]^+$; these values are reported in the Experimental Section. They are also plotted in Fig. 3 with those of the free selenophenes, and their η^2, η^1(Se) and η5 complexes. In general, the various modes of selenophene coordination define certain ^{77}Se chemical shift regions. The free selenophenes [15,33] are furthest downfield with a chemical shift range from δ621 for 2,5-Me_2Sel to δ605 for Sel. Somewhat upfield are the η^2 complexes in which the Seln is coordinated only through two carbon atoms; at this time only two compounds, $Cp^*Re(CO)_2(\eta^2\text{-Sel})$ (δ 524) and $Cp^*Re(CO)_2(\eta^2\text{-2-MeSel})$ (δ 549),[18] are known with the η^2 structure. Upfield from the η^2 compounds are those with η^1(Se)-Seln ligands, which have chemical shifts in the range δ480-402. Finally, the most upfield selenophenes are those that are η^5-coordinated to transition metals. These chemical shifts[15] cover a broad range and increase in the order: $[(\eta^5\text{-Seln})IrCp^*]^{+2} < [(\eta^5\text{-Seln})Mn(CO)_3]^+ < [(\eta^5\text{-Seln})RuCp^*]^+ < (\eta^5\text{-Seln})Cr(CO)_3$. In general, the ^{77}Se chemical shifts of the η^5-Seln complexes

move to higher field as the positive charge on the complex decreases, but it is evident from the Mn and Ru complexes that the metal and its other ligands also influence the ^{77}Se chemical shift values.

Figure 3 shows that there are rather well defined regions for the different modes of Seln binding. This suggests that ^{77}Se NMR chemical shifts can be used to distinguish Seln binding modes in metal complexes. It also suggests that solid state ^{77}Se NMR studies of selenophene adsorbed on HDS catalysts may be able to establish mode(s) of selenophene binding to the catalyst surface.

Acknowledgments. The authors thank Dr. Karen Ann Smith and Dr. Dave Scott of the Iowa State University Instrument Services for their help with and instructive discussions about ^{77}Se and solid state NMR. We thank Johnson Matthey, Inc. for a loan of $RuCl_3$.

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(5) Ligand abbreviations are as follows: thiophene (T); 2-methylthiophene (2-MeT); 3-methylthiophene (3-MeT); 2,5-dimethylthiophene (2,5-Me_2T); benzo(b)thiophene (BT); dibenzothiophene (DBT); 2,8-dimethyldibenzothiophene (2,8-Me_2DBT); *p*-tolyl sulfide(PTS).

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Table 1. Crystal and Data Collection Parameters for [CpRu(CO)(PPh_3)(η^1(Se)-2-MeSel)]BF_4 (2)

formula	$C_{29}H_{26}OPRuSeBF_4$
fw	688.23
space group	P1 (#2)
a, Å	10.594(2)
b, Å	14.276(2)
c, Å	9.402(2)
α, deg	97.97(2)
β, deg	91.63(2)
γ, deg	87.47(1)
V, Å^3	1406.5(8)
Z	4
d_{calc}, g/cm^3	1.457
crystal size, mm	0.120 x 0.180 x 0.80
μ(Mo Kα), cm^{-1}	36.89
data collection instrument	Rigaku AC6R
radiation (monochromated in incident beam)	MoKα
orientation reflcns: no., range (2Θ)	25 (25.56-30.05°)
temp, °C	23
scan method	ω - 2Θ
data col range, 2Θ, deg	3 - 50°
no data collected	5255
no unique data	4960
no data with $F_e^2 > 4\sigma(F_e^2)$	1702
no of parameters refined	343
transmission factors: max, min (Ψ-scans)	1.00, 0.85
R^a	0.051
$R_w{}^b$	0.054
quality of fit indicator^c	1.46
largest shift / esd. final cycle	0.01
largest peak, e / Å	0.66

[a] $R = \Sigma||F_e| - |F_c|| / \Sigma|F_e|$. [b] $R_w = [\Sigma w(|F_e| - |F_c|)^2 / \Sigma w|F_e|^2]^{1/2}$, $w = 1/\sigma^2(|F_e|)$.
[c] quality-of-fit = $[\Sigma w(|F_e| - |F_c|)^2 / (N_{obs} - N_{param})]^{1/2}$

Table 2. Selected Bond Distances and Angles for [CpRu(CO)(PPh3)(η^1(Se)-2-MeSel)]BF_4 (2)

bond	distance (Å)[a]	bond	distance (Å)[a]
Ru-Se	2.494(2)	Se-C5	1.85(2)
Ru-C	1.87(2)	C1-C2	1.45(2)
O-C	1.13(2)	C2-C3	1.29(2)
Ru-P	2.327(4)	C3-C4	1.43(3)
Se-C2	1.90(2)	C4-C5	1.34(3)

Atoms	Angle (degrees)[a]	Atoms	Angle (degrees)[a]
Se-Ru-P	90.6(1)	C2-Se-C5	88(1)
Se-Ru-C	93.8(6)	Se-C2-C1	120(1)
P-Ru-C	91.9(5)	Se-C2-C3	109(2)
Ru-C-O	173(2)	C1-C2-C3	131(2)
Ru-Se-C2	105.8(5)	C2-C3-C4	118(2)
Ru-Se-C5	109.8(6)		

[a]Estimated standard deviations are given in parentheses.

Table 3. Positional Parameters and B(eq) for [CpRu(CO)(PPh3)(η^1(Se)-2-MeSel)]BF_4 (2)

atom	x [a]	y [a]	z [a]	B(eq) [a]
Ru	0.2277(1)	0.3465(1)	0.2005(1)	2.85(7)
Se	0.3746(2)	0.4353(1)	0.0708(2)	3.8(1
P	0.3453(4)	0.2065(3)	0.1337(4)	3.0(2)
O	0.360(1)	0.386(1)	0.487(1)	7.6(8)
C	0.317(2)	0.370(1)	0.375(2)	5(1)
C(1)	0.375(2)	0.603(1)	0.286(2)	7(1)
C(2)	0.341(2)	0.565(1)	0.138(2)	5(1)
C(3)	0.287(2)	0.606(1)	0.037(3)	6(1)
C(4)	0.266(2)	0.549(2)	-0.098(3)	7(1)
C(5)	0.302(2)	0.457(2)	-0.102(2)	7(1)
C(11)	0.493(1)	0.187(1)	0.230(1)	2.9(7)
C(12)	0.529(1)	0.099(1)	0.263(2)	3.6(8)
C(13)	0.645(2)	0.085(1)	0.328(2)	5(1)
C(14)	0.722(1)	0.159(2)	0.367(2)	5(1)
C(15)	0.687(1)	0.247(1)	0.337(2)	4.2(9)
C(16)	0.573(2)	0.259(1)	0.271(2)	4.0(8)
C(21)	0.392(1)	0.190(1)	-0.054(2)	3.2(8)
C(22)	0.514(2)	0.164(1)	-0.092(2)	3.4(8)
C(23)	0.546(2)	0.154(1)	-0.239(2)	5(1)
C(24)	0.456(2)	0.170(1)	-0.340(2)	5(1)
C(25)	0.336(2)	0.195(1)	-0.302(2)	5(1)
C(26)	0.303(1)	0.206(1)	-0.158(2)	3.8(8)
C(31)	0.254(1)	0.103(1)	0.152(2)	3.7(8)
C(32)	0.232(2)	0.032(1)	0.039(2)	4.4(9)
C(33)	0.160(2)	-0.043(2)	0.062(3)	7(1)
C(34)	0.111(2)	-0.047(2)	0.195(3)	7(2)
C(35)	0.138(2)	0.021(2)	0.306(2)	6(1)
C(36)	0.204(2)	0.095(1)	0.287(2)	5(1)
C(41)	0.056(1)	0.374(2)	0.058(2)	5(1)
C(42)	0.065(2)	0.444(2)	0.182(3)	6(1)
C(43)	0.052(1)	0.403(2)	0.305(2)	5(1)
C(44)	0.047(1)	0.292(1)	0.110(2)	4(1)
C(45)	0.040(1)	0.301(1)	0.260(2)	5(1)
B(1)	0.990(2)	0.288(2)	0.639(2)	6(1)
F(1)	0.955(2)	0.270(1)	0.772(1)	12(1)
F(2)	1.091(1)	0.342(1)	0.664(2)	10.6(9)
F(3)	0.903(1)	0.336(1)	0.573(1)	9.5(8)
F(4)	1.021(1)	0.2052(8)	0.561(1)	8.4(7)

[a] Estimated standard deviations are given in parenthesis.

Table 4. Equilibrium Constants (K)[a] for the Ligand Exchange Reactions (Eq 2) of $[CpRu(CO)(PPh_3)(L)]^+$ with L' in CD_2Cl_2 at 25.0° C

reaction no.	L	L'	K
1	Sel	2-MeT	0.179 (9)
2	Sel	2,5-Me_2T	0.112 (8)
3	Sel	2-MeSel	4.22 (20)
4	Sel	2,5-Me_2Sel	7.39 (18)
5	2,5-Me_2Sel	BT	0.143 (4)
6	2,5-Me_2Sel	DBT	0.439 (47)
7	2-MeSel	2,5-Me_2Sel	1.72 (4)
8	BT	2-MeSel	3.36 (14)
9	DBT	2-MeSel	2.96 (9)
10	2,5-Me_2Sel	PTS	40.2 (17)
11	DBT	PTS	93.1 (32)
12	2,5-Me_2Sel	2,8-Me_2DBT	2.04 (8)
13	DBT	2,8-Me_2DBT	4.64(8)

[a] Numbers in parentheses are average deviations in the least significant digits.

Table 5. Relative Equilibrium Constants (K') for the Ligand Exchange Reactions (Eq 5) of $[CpRu(CO)(PPh_3)(T)]^+$ with L' in CD_2Cl_2 at 25.0 °C

L'	K'_{eq}	L'	K'_{eq}
T	1.0[a]	DBT	74.1[a]
2,5-Me_2T	2.76[a]	2-MeSel	100
2-MeT	4.11[a]	2,5-Me_2Sel	175
3-MeT	6.30[a]	2,8-Me_2DBT	358
Sel	23.8	PTS	7.11×10^3
BT	29.9[a]	THT	$> 7.1 \times 10^6$[a]
Me_4T	57.4[a]		

[a]Ref. 12.

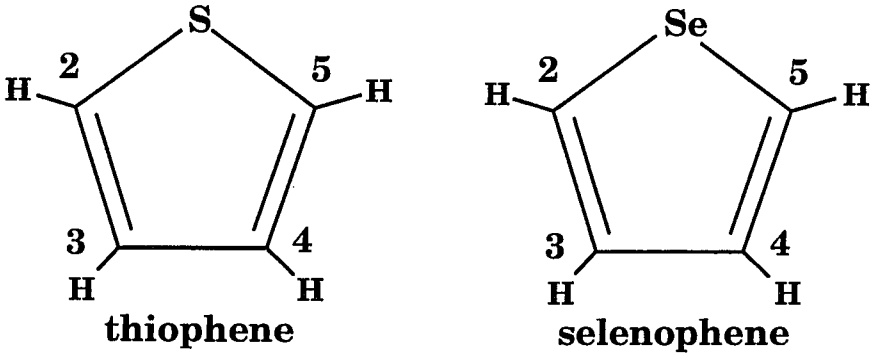

Figure 1. Structures and numbering of thiophene(T) and selenophene(Sel).

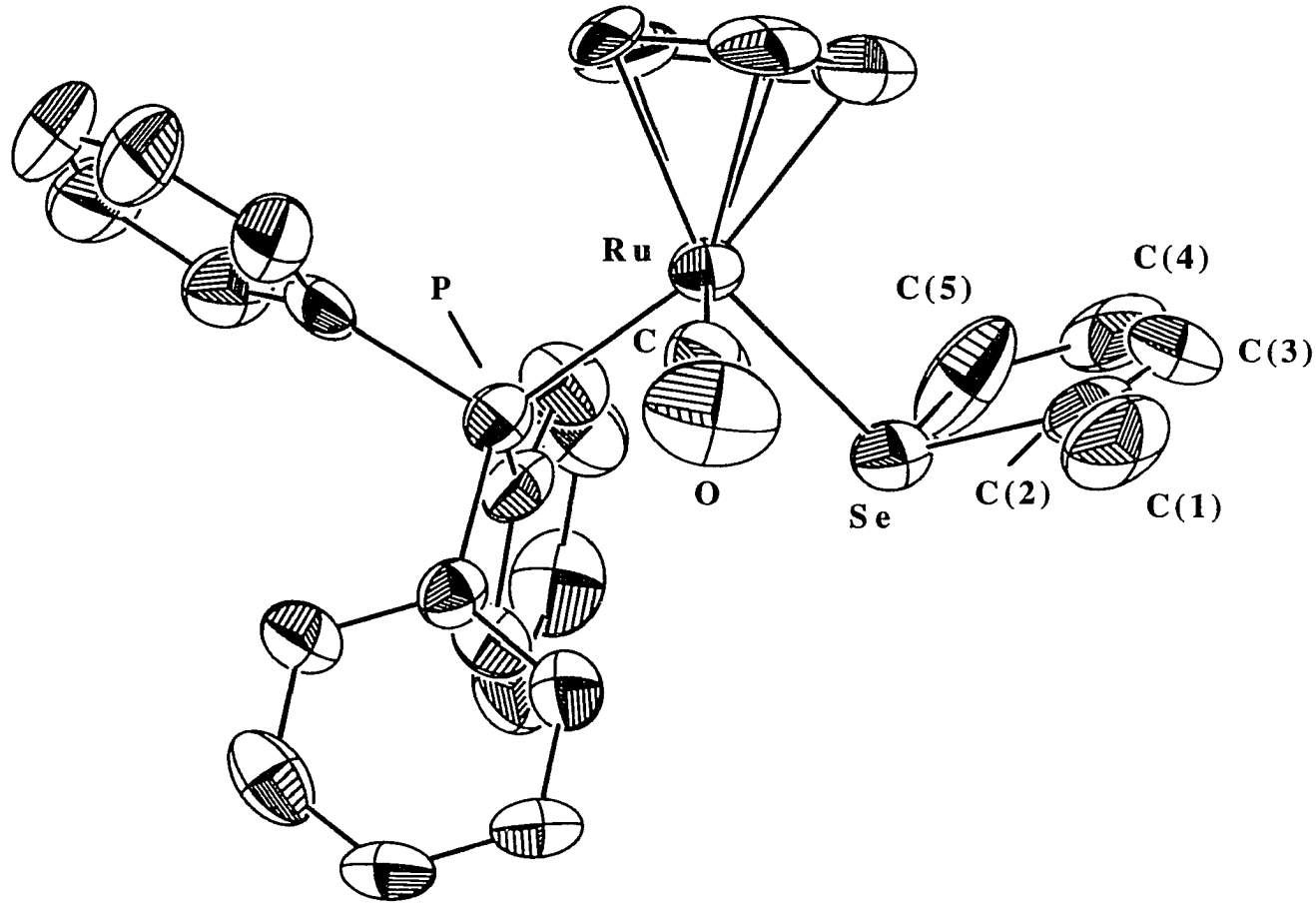

Figure 2. ORTEP drawing of [CpRu(CO)(PPh_3)(η^1(Se)-2-Me_2Sel)]$^+$ (**2**).

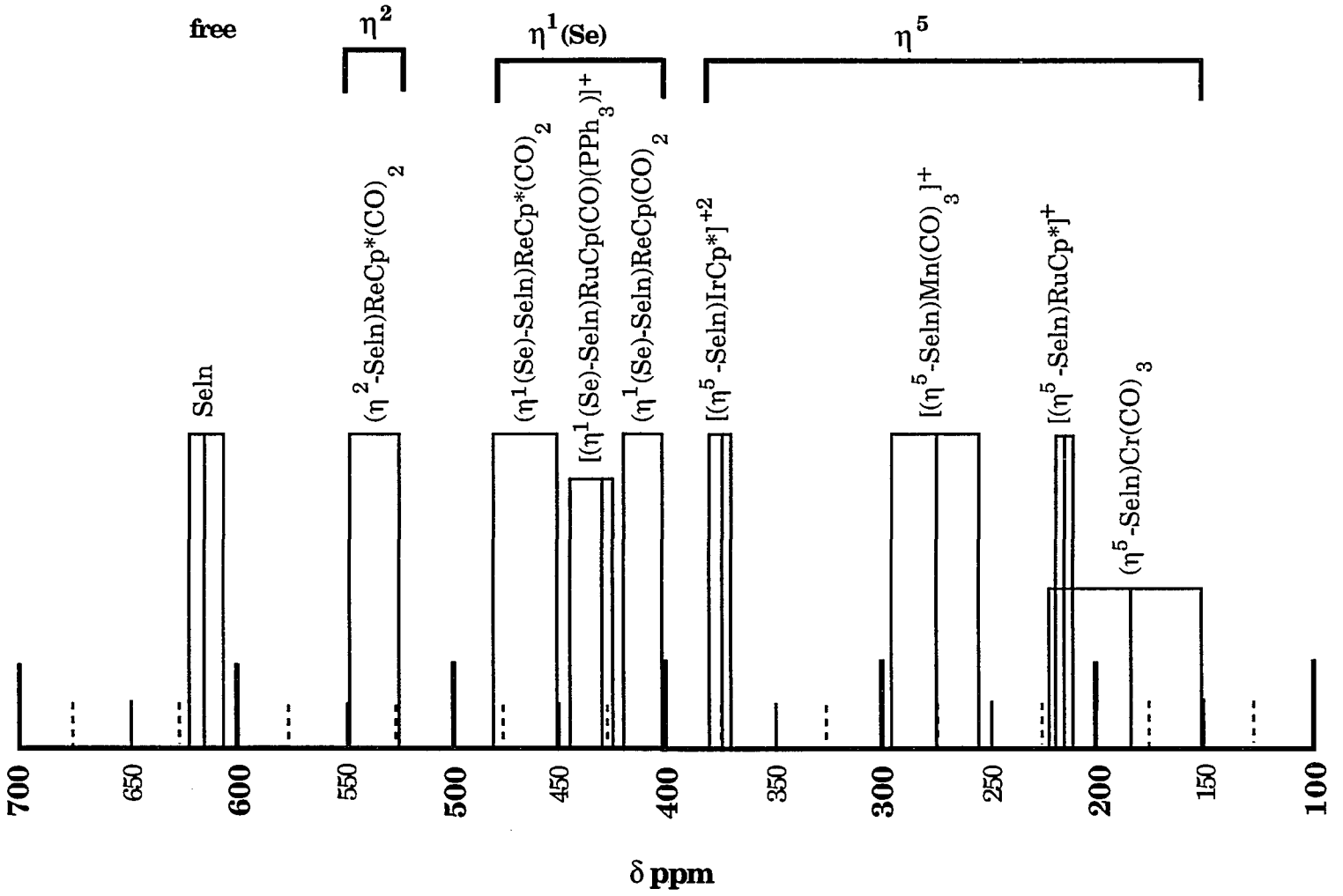

Figure 3. ^{77}Se NMR chemical shifts of selenophene complexes.

SYNTHESIS, STRUCTURE AND REACTIVITY OF THIENYL-, BENZOTHIENYL- AND SELENYLCARBENE COMPLEXES OF RHENIUM: A NEW MECHANISM FOR H/D EXCHANGE DURING HYDRODESULFURIZATION

A paper submitted to *Organometallics*

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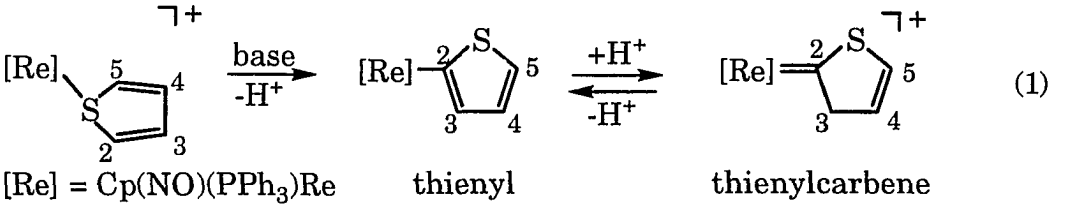
Abstract

A series of η^1(E)-coordinated (E = S or Se) thiophene, benzo[b]thiophene and selenophene complexes $[Cp(NO)(PPh_3)Re(\eta^1(E)\text{-}L)]^+$, Cp = C_5H_5, L = thiophene (T), 2-methylthiophene (2-MeT), 2,5-dimethylthiophene (2,5-Me_2T), benzo[b]thiophene (BT), 3-methylbenzo[b]thiophene (3-MeBT), selenophene (Sel), 2-methylselenophene (2-MeSel), and 2,5-dimethylselenophene (2,5-Me_2Sel) are prepared by the reaction of $[Cp(NO)(PPh_3)Re(ClC_6H_5)]^+$ with the appropriate ligand. The T, 2-MeT, BT, 3-MeBT, Sel, 2-MeSel complexes are deprotonated at C(2) by strong, non-nucleophilic bases to give the neutral $Cp(NO)(PPh_3)Re$(2-L-yl) complexes, where 2-L-yl = 2-thienyl (2-Tyl), 2-(5-methylthienyl) (2-(5-MeTyl)), 2-benzothienyl (2-BTyl), 2-(3-methylbenzothienyl) (2-(3-MeBTyl)), 2-selenyl (2-Selyl), and 2-(5-methylselenyl) (2-(5-MeSelyl)). The pK_a of the base required to effect this deprotonation increases with the L ligand in the complex in the following order: Sel<T<BT. The 2-Tyl, 2-BTyl and 2-Selyl complexes react with either $HBF_4 \bullet Et_2O$ or HO_3SCF_3 at -42°C to give the corresponding carbene complexes $[Cp(NO)(PPh_3)Re$(2-L-ylcarbene)$]^+$ resulting from protonation at C(3). The molecular structure of $[Cp(NO)(PPh_3)Re$(2-

BTylcarbene)]O_3SCF_3, as determined by an X-ray diffraction study, exhibits a Re=C bond distance of 1.992(7)Å. The carbene complexes do not react with nucleophiles; however, those nucleophiles that are sufficiently basic to deprotonate C(3) to give back the L-yl compound. The pK_a of bases that are strong enough to cause deprotonation increase with the L-ylcarbene ligand in the order: Selylcarbene ~ Tylcarbene < BTylcarbene. The carbene complexes $[Cp(NO)(PPh_3)Re(2\text{-}(5\text{-MeTylcarbene})]^+$ and $[Cp(NO)(PPh_3)Re(2\text{-}(5\text{-}$ MeSelylcarbene)]$^+$ are unstable and rearrange to their more stable isomers $[Cp(NO)(PPh_3)Re(\eta^1(S)\text{-}2\text{-MeT})]^+$ and $[Cp(NO)(PPh_3)Re(\eta^1(Se)\text{-}2\text{-MeSel})]^+$. A new mechanism for H/D exchange of thiophene on hydrodesulfurization catalysts is proposed based on deuterium labeling studies of these thiophene complexes.

Introduction

Several different modes of thiophene adsorption to metal sites on catalyst surfaces have been proposed for the hydrodesulfurization (HDS) of thiophene. Of all the possible types of coordination in organometallic model complexes,[1-4] the $\eta^1(S)$ mode was one of the first proposed. It has also been the focus of several recent studies of thiophene, benzothiophene[5,6] and selenophene[7] complexes in this laboratory. The activation of C-S bonds in $\eta^1(S)$-bound thiophene complexes has yet to be demonstrated but has been proposed for the insertion of Rh into the C-S bond in the reaction of thiophene with $(\eta^5\text{-}C_5Me_5)Rh(PMe_3)$.[8] Activation of C-H bonds in $\eta^1(S)$-thiophene has been recently reported[6] in the complex $[Cp(NO)(PPh_3)Re(\eta^1(S)\text{-T})]^+$ which undergoes deprotonation (eq 1) by strong base (KOH/CH_3OH) to give the 2-thienyl complex



(1)

$Cp(NO)(PPh_3)Re$(2-thienyl). Re-protonation of $Cp(NO)(PPh_3)Re$(2-thienyl) with HO_3SCF_3 (triflic acid) does not give back the η^1(S) thiophene complex; instead protonation occurs in the 3-position to form a thienylcarbene product. A similar series of reactions occurred with the analogous benzo[b]thiophene (BT) complex $Cp(NO)(PPh_3)Re(\eta^1(S)\text{-BT})^+$.[6]

In the present study, we report on an improved synthesis of the $[Cp(NO)(PPh_3)Re(\eta^1(S)\text{-thiophene})]^+$ and $Cp(NO)(PPh_3)Re$(2-thienyl) complexes as well as their analogs with benzo[b]thiophene (BT) and selenophene (Seln) ligands. In addition, the thienylcarbene-type complexes of thiophene, benzothiophene and selenophene have been isolated, and their reactions have been explored. The molecular structure of the benzothienylcarbene complex $[Cp(NO)(PPh_3)Re$(2-BTylcarbene)$]O_3SCF_3$ has been determined. These studies offer a new perspective on possible mechanisms for the deuterium exchange of thiophene with D_2 on HDS catalyst surfaces.

Experimental Section

General Procedures. All reactions and manipulations were carried out under an atmosphere of dry N_2 using standard Schlenk techniques unless otherwise stated.[9,10] All solvents were reagent grade or better and were dried and distilled under N_2 by the following methods. Tetrahydrofuran (THF) and

diethyl ether (Et_2O) were distilled from Na/benzophenone. Hexanes and dichloromethane (CH_2Cl_2) and acetonitrile (CH_3CN) were distilled from CaH_2. Acetone and chlorobenzene were dried with potassium carbonate (K_2CO_3) and distilled. The solvents were used immediately after distillation except for acetone and chlorobenzene which were stored over K_2CO_3 under N_2. The neutral alumina (Brockmann, Activity I, ~150 mesh) used for chromatography was deoxygenated at room temperature in high vacuum for 16 h, then deactivated with 5% w/w N_2-saturated deionized distilled water, and stored under N_2.

The ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-300 MHz spectrometer with deuterated solvents as the internal locks and referenced to tetramethylsilane (TMS $\delta = 0.00$) or residual CH_2Cl_2 (δ=5.33). The 2-D $^1H/^1H$ COSY, $^1H/^1H$ NOESY and $^1H/^{13}C$ HETCOR spectra were recorded on the same instrument using standard 2D pulse sequences on a non-spinning, thermostated sample. The $^{77}Se\{^1H\}$ NMR spectra were recorded on the Varian VXR-300 spectrometer at room temperature and referenced to selenophene (δ=605.0 ppm) as the internal standard. Infrared spectra were obtained on a Nicolet 710 FTIR spectrophotometer using a solution cell with NaCl salt plates. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

The following compounds were prepared by literature methods: $Cp(NO)(PPh_3)Re(CH_3)$,[11] selenophene (Sel),[12,13] 2-methylselenophene (2-MeSel),[14] and 2,5-dimethylselenophene (2,5-Me_2Sel).[15] All other reagents were used as received from commercial sources.

General Procedure for the Preparation of [Cp(NO)(PPh3)Re(η^1(E)-L)](BF4) (1-8). Compounds **1-8** containing an η^1(E)-bound ligand were prepared by a method similar to that previously reported by Gladysz and co-workers[16] for the synthesis of other $Cp(NO)(PPh_3)Re(L)^+$ complexes. To a solution of 0.155 g (0.277 mmol) of $Cp(NO)(PPh_3)Re(CH_3)$ in 7.0 mL of chlorobenzene cooled to -42° C in a CH_3CN/N_2(l) bath was added 46.0 μL of $HBF_4 \cdot Et_2O$ (85%, 0.278 mmol). After stirring for 30 minutes, 1.00 mL (~40 fold excess) of the ligand (L) was added and the deep red solution was allowed to slowly warm to room temperature. Within 2 hours a precipitate began to form; after 4 h, 40 mL of hexanes was added to give a light orange precipitate which was filtered and washed with 2 x 10 mL of hexanes followed by 2 x 10 mL of ether. The resulting yellow/orange solid was dried under a stream of N_2 for 10 min then under vacuum. Yield 94-85 %.

Characterization of 1-8. [Cp(NO)(PPh3)Re(η^1(S)-T)](BF4) (1). ^{1}H NMR δ (CD_2Cl_2): 7.22(m, H(2)H(5)), 6.91(m, H(3)H(4)), 5.42(s, Cp), 7.59-7.35(m, Ph), 7.28-7.23(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 138.34(s, C(2) C(5)), 132.42(s, C(3)C(4)), 133.60(d, Ph), 133.53(d, Ph) 132.32(d, Ph), 129.90(d, Ph), 92.38(s, Cp). IR cm^{-1} ν(NO) (CH_2Cl_2): 1724(s).

[Cp(NO)(PPh3)Re(η^1(S)-2-MeT)](BF4) (2). ^{1}H NMR δ (CD_2Cl_2): 7.05 (m, H(3)), 6.92(dd, H(4)), 6.13(d, H(5)), 2.50(s, Me), 5.39 (s, Cp), 7.59-7.35(m, Ph), 7.28-7.20(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 154.52 (s, C(2)), 132.85 (s, C(4)), 132.10 (s, C(5)), 132.42(s, C(3)), 14.43(s, CH_3), 93.37 (s, Cp), 133.60(d, Ph), 133.51(d, Ph)

132.32(d, Ph), 129.90(d, Ph). IR cm^{-1} ν(NO) (CH_2Cl_2): 1723(s). Anal. Calcd for $C_{28}H_{25}BF_4NOPReS$: C, 46.16; H, 3.10. Found: C, 45.96; H, 3.53.

[Cp(NO)(PPh3)Re(η1(S)-2,5-Me2T)](BF4) (3). ^1H NMR δ (CD_2Cl_2): 6.76(s, H(3)H(4)), 2.02 (s, CH_3), 5.37(s, Cp), 7.59-7.35(m, Ph), 7.28-7.20(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 149.74(s, C(2)C(5)), 129.46(C(3)C(4)), 14.81(s, CH_3), 133.60(d, Ph), 133.50(d, Ph) 132.32(d, Ph), 129.90(d, Ph). IR cm^{-1} ν(NO) (CH_2Cl_2): 1723(s).

[Cp(NO)(PPh3)Re(η1(S)-BT)](BF4) (4). ^1H NMR δ (CD_2Cl_2): 7.86 (m, 4H, BT), 6.25(d, 1H, BT), 5.22(s, Cp), 7.59-7.35(m, Ph), 7.28-7.20(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 148.3(s, BT), 138.7(s, BT), 131.8(s, BT), 130.9(s, BT), 129.5(s, BT), 128.3(s, BT), 126.8(s, BT), 124.3(s, BT), 93.6(s, Cp), 133.6(d, Ph), 133.5(d, Ph), 132.3(d, Ph), 129.9(d, Ph). IR cm^{-1} ν(NO) (CH_2Cl_2): 1718(s). Anal. Calcd for $C_{31}H_{26}BF_4NOPReS \cdot 1/4\ CH_2Cl_2$: C, 47.76; H, 3.01. Found: C, 47.75; H, 3.01.

[Cp(NO)(PPh3)Re(η1(S)-3-MeBT)](BF4) (5). ^1H NMR δ (CD_2Cl_2): 7.87(m, 2H, BT), 7.81(m, 2H, BT), 5.79(s, H(2)), 2.30(s, CH_3), 5.29(s, Cp), 7.59-7.35(m, Ph), 7.28-7.20(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 148.25(s, BT), 141.07(s, BT), 139.49(s, C(3)BT),129.41(s, BT), 128.22(s, BT), 124.62(s, BT), 124.52(s, BT), 124.58(s, C(2)BT), 14.80(s, CH_3), 93.65(s, Cp), 133.60(d, Ph), 133.50(d, Ph), 132.32(d, Ph), 129.90(d, Ph). IR cm^{-1} ν(NO) (CH_2Cl_2): 1720(s).

[Cp(NO)(PPh3)Re(η1(Se)-Sel)](BF4) (6). ^1H NMR δ (CD_2Cl_2): 7.45(H(2),H(5)), 7.21(H(3),H(4)), 7.52-7.35(m, Ph), 7.28-7.20(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 141.86(s, C(2)C(5)), 134.37(s, C(3)C(4)), 92.52(s, Cp), 133.60(d, Ph), 133.52(d, Ph),

132.32(d, Ph), 129.90(d, Ph). ^{77}Se NMR δ (CD_2Cl_2): 368.2 (s, br). IR cm^{-1} ν(NO) (CH_2Cl_2): 1719(s). Anal. Calcd for $C_{27}H_{24}BF_4NOPReSe$:C, 42.59; H, 3.18. Found: C, 42.37; H, 3.19.

[Cp(NO)(PPh3)Re(η^1(Se)-2-MeSel)](BF4) (7). ^{1}H NMR δ (CD_2Cl_2): 7.25(H(3)), 6.99(m, H(4)), 6.80(dd, H(5), J_{H-Se} = 16 Hz), 5.30(s, Cp), 7.59-7.35(m, Ph), 7.28-7.20(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 159.10(s, C(2)), 136.33(s, C(4)), 135.52(s, C(3)), 130.17(s, C(5)), 16.74(s, CH_3), 92.71(s, Cp), 133.60(d, Ph), 133.5(d, Ph), 132.32(d, Ph), 129.90(d, Ph). ^{77}Se NMR δ (CD_2Cl_2): 386.5(d, J_{Se-P} = 13 Hz). IR cm^{-1} ν(NO) (CH_2Cl_2): 1716(s). Anal. Calcd for $C_{28}H_{25}BF_4NOPReSe$: C, 43.37; H, 3.38. Found: C, 43.28; H, 3.39.

[Cp(NO)(PPh3)Re(η^1(Se)-2,5-Me2Sel)](BF4) (8). ^{1}H NMR δ (CD_2Cl_2): 6.64(s, H(3)H(4)), 2.05(s, CH_3), 5.22(s, Cp), 7.59-7.35(m, Ph), 7.28-7.20(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 155.42(s, C(2)C(5)), 131.32(s, C(3)C(4)), 17.34(s, Me), 92.72(s, Cp), 133.60(d, Ph), 133.52(d, Ph), 132.32(d, Ph), 129.90(d, Ph). ^{77}Se NMR δ (CD_2Cl_2): 384.2(d, J_{Se-P}= 19.8 Hz). IR cm^{-1} ν(NO) (CH_2Cl_2): 1717(s).

General Procedure for the Preparation of Cp(NO)(PPh3)Re(2-L-yl) (9, 10, 12-15). To a stirred solution of 0.250 mmol of [Cp(NO)(PPh_3)Re(η^1(E)-L)]BF_4 ,where η^1(E)-L = T, 2-MeT, BT, 3-MeBT, Sel, 2-MeSel, in 5.0 mL of CH_2Cl_2, 0.0290 g (0.258 mmol) of 1,4-diazabicyclo[2.2.2]octane (Dabco) was added. The yellow/orange solution turned a deep red/orange within five minutes. The reaction mixture was placed on an alumina/hexanes (1 x 20 cm) column and eluted with 1:1 hexanes:CH_2Cl_2. An orange red band was collected and the

solvent was evaporated from it under vacuum to give an orange red solid. Yield: 90-95%.

Characterization of (9, 10, 12-15). Cp(NO)(PPh_3)Re(2-Tyl) (9). ^1H NMR δ (CD_2Cl_2): 7.08(d, H(5)), 6.70(dd, H(4)), 6.38(d, H(3)), 5.19(s, Cp), 7.40-7.30(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 135.76(d, C(3)), 128.34 (s, C(5)), 127.53 (d, C(2)), 127.32 (s, C(4)), 91.41(s, Cp), 135.76(d, Ph), 134.10(d, Ph), 130.41(d, Ph), 128.48(d, Ph). IR cm^{-1} ν(NO) (CH_2Cl_2): 1653(s).

Cp(NO)(PPh_3)Re(2-(5-MeTyl)) (10). ^1H NMR δ (CD_2Cl_2): 6.27(dd, H(3), J_{H-P} = 1.2 Hz), 5.94(d, H(4)), 2.38(s, CH_3), 5.10(s, Cp), 7.39-7.32(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 142.35 (s, C(5)), 135.51 (s, C(4)), 125.28 (s, C(3)), 123.97 (d, C(2)), 14.56(s, Me), 90.80(s, Cp), 133.18(d, Ph), 134.76(d, Ph), 129.87(d, Ph), 127.92(d, Ph). IR cm^{-1} ν(NO) (CH_2Cl_2): 1654(s). Anal. Calcd for $C_{28}H_{25}NOPReS$: C, 52.49; H, 3.93. Found: C, 52.52; H, 3.97.

Cp(NO)(PPh_3)Re(2-BTyl) (12). ^1H NMR δ (CD_2Cl_2): 7.57(d, BT), 7.23(d, BT), 7.05(td, BT), 6.84 (t, BT), 6.45(s, br, H(3)), 5.27(s, Cp), 7.43-7.32(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 146.7(s, BT), 146.4(s, BT), 136.6(d, C(2)), 131.71(s, C(3)), 122.53(s, BT), 119.76(s, BT), 119.67(s, BT),119.09(s, BT), 91.78(s, Cp), 134.00(d, Ph), 130.68(d, Ph) 132.32(d, Ph), 128.50(d, Ph). IR cm^{-1} ν(NO) (CH_2Cl_2): 1658(s).

Cp(NO)(PPh_3)Re(2-(3-MeBTyl)) (13). ^1H NMR δ (CD_2Cl_2): 7.45-7.32 (m of m, BT and Ph), 7.14(t, BT), 6.87 (t, BT), 2.51(s, CH_3), 5.25(s, Cp). ^{13}C NMR δ (CD_2Cl_2): 16.90(s, Me), 147.31(s, C(3)), 135.44(d, C(2)), 146.5(s, BT), 145.8(s, BT), 122.38(s,

BT), 119.82(s, BT), 119.51(s, BT), 119.01(s, BT), 91.25(s, Cp), 134.04(d, Ph), 130.45(d, Ph), 132.32(d, Ph), 128.47(d, Ph). IR cm^{-1} ν(NO) (CH_2Cl_2): 1656(s).

Cp(NO)(PPh_3)Re(2-Selyl) (14). ^1H NMR δ (CD_2Cl_2): 7.76(d, $J_{H\text{-}Se}$ = 20.1 Hz, H(5)), 6.86(dd, H(4)), 6.54(d, H(3)), 5.20(s, Cp), 7.41-7.34(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 138.33(d, $J_{C\text{-}P}$= 2.5 Hz, C(3)), 136.54 (d, $J_{C\text{-}P}$= 11.5 Hz, C(2)), 132.42 (s, C(5)), 130.21(s, C(4)), 91.82(s, Cp), 135.64(d, Ph), 134.17(d, Ph), 130.50(d, Ph), 128.00(d, Ph). ^{77}Se NMR δ (CD_2Cl_2): 705.1 (s). IR cm^{-1} ν(NO) (CH_2Cl_2): 1653(s). Anal. Calcd for $C_{27}H_{23}NOPReSe$: C, 48.14; H, 3.44. Found: C, 48.10; H, 3.41.

Cp(NO)(PPh_3)Re(2-(5-MeSelyl)) (15). ^1H NMR δ (CD_2Cl_2): 6.23(d, H(4)), 6.42(m, H(3)), 2.55(s, CH_3), 5.19(s, Cp), 7.42-7.35(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 148.45(s, C(5)), 138.74(s, C(4)), 133.74 (d, $J_{C\text{-}P}$= 9.7 Hz, C(2)), 128.91(s, C(3)), 18.11(s, Me), 91.66(s, Cp), 135.83(d, Ph), 134.15(d, Ph), 130.46(d, Ph), 128.46(d, Ph). ^{77}Se NMR δ (CD_2Cl_2): 719.2 (s). IR cm^{-1} ν(NO) (CH_2Cl_2): 1653(s). Anal. Calcd for $C_{28}H_{25}NOPReSe$: C, 48.91; H, 3.66. Found: C, 49.13; H, 3.58.

Preparation of Cp(NO)(PPh_3)Re(3-(2,5-Me_2Tyl)) (11). This compound was prepared as previously described using 0.100 g (0.135 mmol) of [Cp(NO)(PPh_3)Re(η^1(S)-2,5-Me_2T)]BF_4 and 0.011 g (0.200 mmol) KOH in methanol. Yield 0.028 g, 29% as an orange solid. ^1H NMR δ (CD_2Cl_2): 5.54 (s, H(4)), 2.43 (s, CH_3), 2.10 (s, CH_3), 5.15(s, Cp), 7.41-7.33(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 142.32(d, C(4)), 133.24(s, C(2)), 132.59(s, C(5)), 126.07 (d, $J_{C\text{-}P}$= 9.6 Hz, C(3)), 19.03 (s, C(2)-CH_3), 14.82(s, C(5)-CH_3)), 90.62(s, Cp), 136.22(d, Ph), 134.15(d, Ph), 130.22(d, Ph), 128.37(d, Ph). IR cm^{-1} ν(NO) (CH_2Cl_2): 1653(s).

Preparation of Carbene Complexes. [Cp(NO)(PPh_3)Re(2-Tylcarbene)]X (16a, X = BF_4; 16b, X = O_3SCF_3). To a stirred and cooled (-42° C) solution of 0.100 g (0.131 mmol) of Cp(NO)(PPh_3)Re(2-Tyl) in 10.0 mL of Et_2O:CH_2Cl_2 (2:1), one equivalent (0.131 mmol) of acid (**16a,** 21.7 μL of HBF_4•Et_2O 85%; **16b** ,11.6 μL of HO_3SCF_3) was added. The orange-red solution immediately turned bright yellow and within 0.5 h a yellow precipitate began to form. After stirring for 1 h, 60 mL of ether:hexanes (1:1) was added and the resulting precipitate was filtered and washed with 2 x 10 mL of ether:hexanes (1:1). The bright yellow precipitate was dried under a stream of N_2 while being allowed to warm to room temperature. Then it was dried under vacuum to give **16a** (0.084 g, 90%) or **16b** (0.088 g, 86%). ^{1}H NMR δ (CD_2Cl_2): 7.32 (d, H(5)), 6.77(m, H(4)), 4.11(d, br, H(3)), 3.98 (d, br, H(3′)), 5.77(s, Cp), 7.50(s, br, Ph), 7.28-7.22 (m, Ph). ^{13}C NMR δ (CD_2Cl_2): 267.96 (d, J_{C-P}= 7.4 Hz, C(2)), 149.24(s, C(5)), 145.83 (s, C(4)), 55.93 (s, C(3)), 97.10(s, Cp), 134.41(d, Ph), 132.26(d, Ph), 131.64(d, Ph), 128.03(d, Ph). IR cm^{-1} ν(NO) (CH_2Cl_2): 1716(s). FAB (3-nitrobenzyl alcohol matrix): m/z 628 (M^+).

[Cp(NO)(PPh_3)Re(2-BTylcarbene)]X (17a, X = BF_4; 17b, X = O_3SCF_3). Compounds **17a** and **17b** were prepared in the same manner as **16a** and **16b** using 0.100 g (0.148 mmol) of Cp(NO)(PPh_3)Re(2-BTyl) and 24.5 μL of HBF_4•Et_2O (**17a**) or 13.1 μL HO_3SCF_3(**17b**). These reaction yielded **17a** as an orange/yellow powder (0.105 g, 93%) or **17b** as a yellow powder (0.102 g, 83%). ^{1}H NMR δ (CD_2Cl_2): 7.42(BT), 7.35(BT), 7.17 (dd, BT), 7.43(d, BT), 4.78(d, H(3)), 3.53 (d, H(3′)), 5.86(s, Cp), 7.55(s, br, Ph), 7.42-7.22 (m, Ph). ^{13}C NMR δ

(CD_2Cl_2): 277.71 (d, J_{C-P}= 7.9 Hz, C(2)), 66.21 (s, C(3)), 144.00 (s, BT), 142.42 (s, BT), 127.69 (s, BT), 126.28 (s, BT), 123.41(s, BT), 119.80 (s, BT), 98.01(s, Cp), 134.41(d, Ph), 132.41(d, Ph), 132.06(d, Ph), 129.25(d, Ph). IR cm^{-1} ν(NO) (CH_2Cl_2): 1720(s). FAB (3-nitrobenzyl alcohol matrix): m/z 677 (M^+). Anal. Calcd for $C_{31}H_{26}BF_4NOPReS$ • 1/2 CH_2Cl_2: C, 46.88; H, 3.37. Found: C, 46.62; H, 3.59.

[Cp(NO)(PPh$_3$)Re(2-Selylcarbene)]X (18a, X = BF_4; 18b, x = O_3SCF_3). Compounds **18a** and **18b** were prepared in the same manner as **16a** and **16b** using 0.100 g (0.148 mmol) of Cp(NO)(PPh_3)Re(2-Selyl) (**14**) and 24.5 μL of HBF_4•Et_2O (**18a**) or 13.1 μL of HO_3SCF_3(**18b**). From these reactions were isolated **18a** (0.992 g, 88%) or **18b** (0.106 g, 94%) as yellow powders. ^1H NMR δ (CD_2Cl_2): 7.68(d, J_{H-Se}= 17.4 Hz, H(5)), 6.78 (dd, H(4)), 4.25(d, H(3)), 4.15 (d, H(3´)), 5.81(s, Cp), 7.51(s, br, Ph), 7.29-7.18 (m, Ph). ^{13}C NMR δ (CD_2Cl_2): 274.83 (d, J_{C-P}= 6.8 Hz, C(2)), 49.59 (s, C(3)), 152.81(s, C(5)), 146.73 (s, C(4)), 98.00(s, Cp), 132.34(d, Ph), 131.75(d, Ph), 130.52 (d, Ph), 128.64(d, Ph). ^{77}Se NMR δ (CD_2Cl_2): 741.7 (s). IR cm^{-1} ν(NO) (CH_2Cl_2): 1716(s). FAB (3-nitrobenzyl alcohol matrix): m/z 674 (M^+).

[Cp(NO)(PPh$_3$)Re(2-(5-MeTylcarbene)]O_3SCF_3 (19). A 5-mm NMR tube was charged with 0.020 g (0.031 mmol) of Cp(NO)(PPh_3)Re(2-(5-MeTyl) (**10**) and 0.60 mL of CD_2Cl_2. After the tube was cooled to -42° C, 2.8 μL (0.031 mmol) of HO_3SCF_3 was added and the red/orange solution became bright yellow. A ^1H NMR spectrum at -75° C showed a quantitative conversion to **19**. ^1H NMR δ (CD_2Cl_2): 5.98(s, H(4)), 4.32(d, br, H(3)), 2.99 (d, br, H(3´)), 2.08 (s, Me), 5.75(s,

Cp), 7.50(s, br, Ph), 7.31-7.22 (m, Ph). ^{13}C NMR δ (CD_2Cl_2): 280.34 (d, J_{C-P}= 7.1 Hz, C(2)), 146.88 (s, C(5)), 141.33 (s, C(4)), 68.72 (s, C(3)), 14.11(s, CH_3), 97.51(s, Cp), 134.41(d, Ph), 132.27(d, Ph), 131.64(d, Ph), 128.03(d, Ph). IR cm^{-1} ν(NO) (CH_2Cl_2): 1720(s). Compound **19** is not stable and isomerizes to **2** above 0°C as discussed in detail in the Results and Discussion section.

[Cp(NO)(PPh$_3$)Re(2-(5-MeSelylcarbene)]O$_3$SCF$_3$ (20). A 5-mm NMR tube was charged with 0.020 g (0.029 mmol) of Cp(NO)(PPh_3)Re(2-(5-MeSelyl) (**15**) and 0.60 mL of CD_2Cl_2. After the NMR tube was cooled to -42° C, 2.6 μL (0.029 mmol) of HO_3SCF_3 was added and the red/orange solution became bright yellow. A ^1H NMR spectrum at -75° C showed conversion to **20**. ^1H NMR δ (CD_2Cl_2): 5.98(s, H(4)), 4.32(d, br, H(3)), 2.99 (d, br, H(3′)), 2.08 (s, Me), 5.75(s, Cp), 7.50(s, br, Ph), 7.31-7.22 (m, Ph). ^{13}C NMR δ (CD_2Cl_2): 280.34 (d, J_{C-P}=7.1Hz, C(2)), 146.88 (s, C(5)), 141.33 (s, C(4)), 68.72 (s, C(3)), 14.11(s, CH_3), 97.51(s, Cp), 134.41(d, Ph), 132.27(d, Ph), 131.64(d, Ph), 128.03(d, Ph). IR cm^{-1} ν(NO) (CH_2Cl_2): 1720(s). Compound **20** is not stable and rapidly isomerizes to **7** above -30°C as discussed in the Results and Discussion section.

Determination of the Molecular Structure of [Cp(NO)(PPh$_3$)Re(2-BTylcarbene)]O$_3$SCF$_3$ (17b). A single crystal of **17b** suitable for X-ray diffraction was obtained by layering a concentrated CH_2Cl_2 solution of **17b** with Et_2O and cooling at -78° C for several days. A crystal of **17b** with the composition [Cp(NO)(PPh_3)Re(2-BTylcarbene)]O_3SCF_3 • 3 CH_2Cl_2 was attached to the tip of a glass fiber and mounted on the Siemens P4RA diffractometer for data collection at 213 K. The cell constants for the data collection were determined

from reflections found from a rotation photograph. High angle cell constants were determined from a subset of intense reflections in the range of 35.0 to 50.0° 2θ. Pertinent data collection and reduction information is given in Table 1.

Lorentz and polarization corrections were applied. A nonlinear correction based on the decay in the standard reflections was applied to the data. A series of azimuthal reflections was collected for this specimen. A semi-empirical absorption correction based on the azimuthal scans was applied to the data.

The space group was chosen based on systematic absences and intensity statistics. This assumption proved to be correct as indicated by a successful direct-methods solution and subsequent refinement. All non-hydrogen atoms were placed directly from the E-map. All hydrogen atoms were refined as riding-atoms with C-H distance equal to 0.96Å and with individual isotropic displacement parameters.

Selected bond distances and angles are presented in Table 2 and an ORTEP drawing of **17** is given in Figure 1. The final positional and thermal parameters are listed in Table 3.

Deprotonation Studies of 1, 4 and 6. In a small test tube was placed ~ 0.010 g of the compound, and the tube was capped with a septum and degassed with N_2. The solid was dissolved by adding 0.5 mL of CH_2Cl_2; then a 10-fold excess of amine base was added. An infrared spectrum of each solution was taken after 2 min and then again after 1 h. Under the same conditions in the absence of base, complexes **1**, **4**, and **6** were stable for at least 1 h. In cases where

reactions occurred, they were complete within 2 min; the only products of these reactions were **9**, **12**, and **14**. Displacement of the η^1(E)-bound ligand by the amine did not occur to an appreciable extant. The results of these studies along with the pK_a values for the amine bases are presented in Table 4.

Deprotonation Studies of 16, 17 and 18. The complex (~ 0.010 g) was put into a small test tube and capped with a septum. After degassing the tube with N_2, 0.5 mL of CH_2Cl_2 was added to dissolve the complex; then a 10-fold excess of the phosphine was added. An infrared spectrum of each solution was taken after 2 min and again after 1 h. In the cases where reaction occurred, the starting complexes **16**, **17**, and **18** disappeared completely and IR bands for the deprotonated products **9**, **12**, and **14** appeared. In all cases, the reactions were complete within 2 min and no other product formed. Results of these studies along with pK_a values of the phosphine bases are given in Table 5.

Results and Discussion

Synthesis and Characterization of [Cp(NO)(PPh_3)Re(η^1(E)-L)]$^+$ Complexes (1-8). The compounds [Cp(NO)(PPh_3)Re(η^1(S)-Th)]BF_4, where Th = thiophene (T), 2,5-dimethylthiophene (2,5-Me_2T), benzothiophene (BT), and 2-methylbenzothiophene (2-MeBT), were recently[6] synthesized utilizing a method similar to that used for the preparations of [Cp(NO)(PPh_3)Re(L′)]$^+$ complexes, where L′ can be one of several two-electron donor ligands including dialkyl sulfides.[17] The yields (78-39%) were highly dependent on the purity of the reactants and solvents and the temperature sensitive nature of the

intermediate $[Cp(NO)(PPh3)Re(Cl\text{-}CH_2Cl)]^+$. Changing the solvent from CH_2Cl_2 to chlorobenzene[16] allows milder conditions, a smoother reaction and higher yields of product. The application of this route (eq 2) to a variety of thiophenes, benzothiophenes, and selenophenes gives the η^1(E)- complexes

$$Cp(NO)(PPh_3)Re(ClPh)^+ + L \longrightarrow [Cp(NO)(PPh_3)Re(\eta^1(E)\text{-}L)]^+ \quad (2)$$

E = S	E = Se
1, L = T	**6**, L = Sel
2, L = 2-MeT	**7**, L = 2-MeSel
3, L = 2,5-Me_2T	**8**, L = 2,5-Me_2Sel
4, L = BT	
5, L = 3-MeBT	

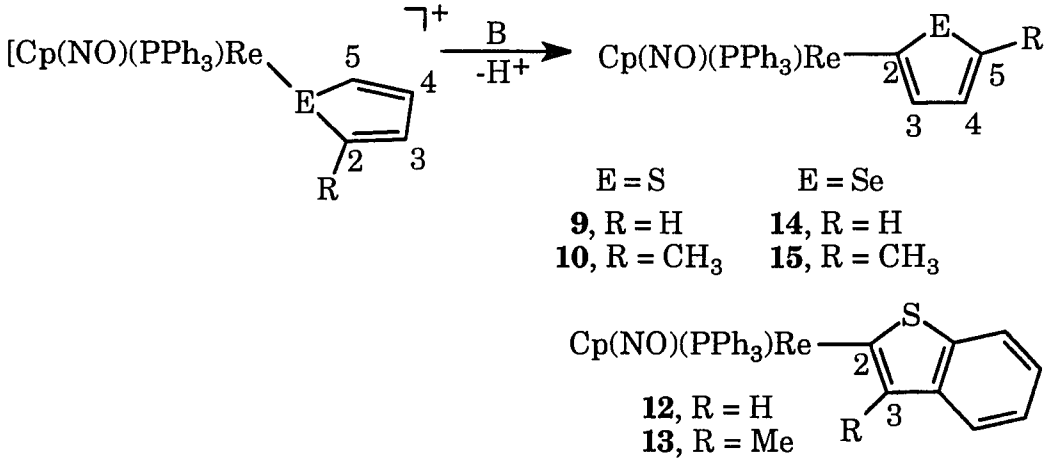
as tan-yellow powders in yields of 94-85%. The compounds **1-8** were characterized by elemental analysis and IR, ^{1}H and ^{13}C NMR spectrometry; ^{77}Se NMR data were obtained for compounds **6-8**. The slightly lower ν(NO) value for the selenophene complex **6** (1719 cm^{-1}) as compared with that for the thiophene complex **1** (1724 cm^{-1}) indicates that selenophene is a better σ-donor ligand than thiophene; the same trend is observed in the ν(CO) values of the sulfur-selenium pairs in the isoelectronic complexes $[Cp(CO)(PPh_3)Ru(\eta^1(E)\text{-}L)]^+$.[7] The ^{1}H NMR resonances of Sel in **6** are not distinguishable in the spectrum because they overlap with those of the PPh_3. The 2-D ^{1}H/^{13}C HETCOR spectrum, however, clearly shows peaks for H(2)H(5) (δ 7.45) and H(3)H(4) (δ 7.21) which are upfield of the corresponding resonances for the free selenophene ligand (H(2)H(5) (δ 7.88), H(3)H(4) (δ 7.23)). η^1(S) coordination of thiophene in **1** and η^1(Se) coordination of selenophene in $[Cp(CO)(PPh_3)Ru(\eta^1(E)\text{-}L)]^+$ result in a similar upfield shift.[7,18] The ^{13}C NMR

spectra of **1** (C(2)C(5) (δ 138.34), C(3)C(4) (δ 132.42)) and **6** (C(2)C(5) (δ 141.86), C(3)C(4) (δ 134.37)) exhibit resonances downfield from those of the free ligand.[7] A similar downfield shift upon η^1(E)-coordination has been reported in the complexes: $[Cp(CO)(PPh_3)Ru(\eta^1(E)\text{-}L)]^+$,[7,18] $Cp(CO)_2Re(\eta^1(E)\text{-}L)$,[19,20] $[Cp(CO)_2Fe(\eta^1(S)\text{-}T)]^+$,[21] and $[Cp(CO)_2Ru(\eta^1(S)\text{-}T)]^+$.[22]

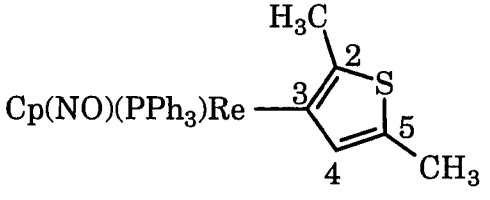
Despite the asymmetry at Re, the H(2) and H(5) protons in **1** (T) and **6** (Sel) and the methyl groups in **3** (2,5-Me_2T) and **8** (2,5-Me_2Sel) occur as single resonances in their room temperature ^{1}H NMR spectra. At low temperature (283 K), the ^{1}H NMR spectra of **3** and **8** in CD_2Cl_2 each show two resonances at δ 2.45, δ 1.59 and δ 2.35, δ 1.91, respectively, for the diastereotopic methyl groups. The free energy of activation for the coalescence of these peaks was calculated to be 37(1) kJ/mol (T_c = 195 K) for **3** and 42(1) kJ/mol (T_c = 215K) for **8** at their coalescence temperatures (T_c).[23] Coalescence of the methyl group signals has been observed in the related complexes $[CpRu(CO)(PPh_3)(\eta^1(E)\text{-}L)]^+$; the 2,5-$Me_2$T complex has a free energy of activation of 40 kJ/mol (T_c = 213 K), while the value is 44 kJ/mol (T_c = 225 K) for the 2,5-Me_2Sel complex. Coalescence in all of these complexes presumably occurs as a result of inversion at the S or Se atom. Such an inversion would be more favorable for S than Se because of greater π-bonding between the sulfur and the diene segment of the thiophene in the planar intermediate. In other organo-sulfur and selenium complexes [24] such as $Re(Cl)(CO)_3(EMe_2)_2$ and $Pt(Br)(Me)(EMe_2)_2$, the inversion barrier is also lower in the S than the Se analog. The low temperature ^{1}H NMR spectra of **1** and **6** in CD_2Cl_2 show only a slight broadening of the proton resonances at the freezing point (178 K) of CD_2Cl_2; this indicates that the T_c values for **1** and **6** are lower than 178 K. The lower T_c

for **1** and **6** compared to **3** and **8** suggests that steric interactions between the methyl groups in the 2,5-positions of the thiophene or selenophene and the bulky triphenylphosphine ligand reduce the rate of inversion at the heteroatom in **3** and **8**.

Synthesis and Characterization of Cp(NO)(PPh$_3$)Re(L-yl) Complexes (9-15). Abstraction of a proton from the η^1(S) complexes [Cp(NO)(PPh$_3$)Re(η^1(S)-Th)]BF_4, where Th = T(**1**), 2,5-Me$_2$T (**3**), or BT (**4**), with KOH in methanol[6] gives the neutral thienyl complexes Cp(NO)(PPh$_3$)Re(2-Tyl) (**9**), Cp(NO)(PPh$_3$)Re(3-(2,5-Me$_2$Tyl)) (**11**), and Cp(NO)(PPh$_3$)Re(2-BTyl) (**12**) in moderate 28-60% yields. There is a side product in these reactions which is proposed to be Cp(NO)(PPh$_3$)Re(OH), based on its IR (ν(NO)(CH_2Cl_2): 1679 cm^{-1}) and ^{1}H NMR ((CD_2Cl_2) δ: 7.52-7.30 (m, 15H, Ph), 5.22 (s, 5H, Cp), 4.9 (br)) spectra; this product results from the displacement of the thiophene ligand by OH^-. The use of a strong, non-nucleophilic, sterically hindered organic base avoids this competing reaction. The reaction of Proton Sponge (1,8-bis(dimethylamino)napthalene), DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), and Dabco (1,4-diazabicyclo[2.2.2]octane) with the cationic complexes **1, 2, 4-7** in CH_2Cl_2 rapidly gives (eq 3) the corresponding deprotonated Cp(NO)(PPh$_3$)Re(2-L-yl) complexes in greater than 90% yield.The cationic amine complex [Cp(NO)(PPh$_3$)Re(amine)]$^+$, resulting from displacement of the thiophene or selenophene ligand, is not observed in IR spectra of the reaction mixtures. Only [Cp(NO)(PPh$_3$)Re(η^1(S)-2,5-Me$_2$T)]$^+$ (**3**) cannot be converted to its L-yl complex Cp(NO)(PPh$_3$)Re(3-(2,5-Me$_2$Tyl)) (**11**) with Dabco; however, KOH/methanol does effect this conversion.[6]



(3)

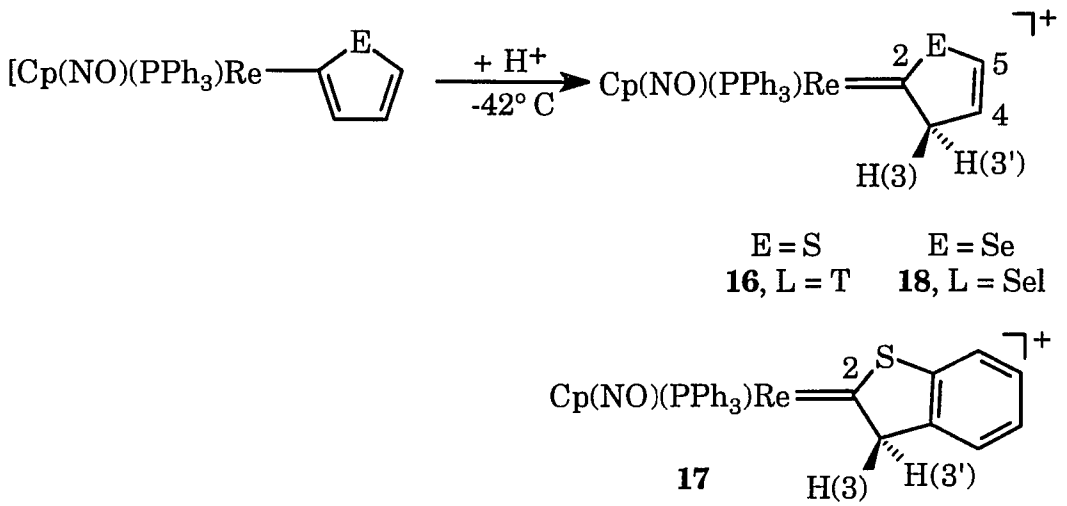


11

The neutral L-yl complexes **9-15** are remarkably stable (> 10 days) to exposure to air in both the solid state and in solution. The ν(NO) values for the compounds **9-15** are ~70cm^{-1} lower than those of their starting cationic complexes. The ^{77}Se NMR resonances for selenyl complexes **14** (2-Selyl: δ 705.1) and **15** (2-(5-MeSelyl): δ 719.2) are more than 300 ppm downfield of those of the cationic starting complexes **6**(Sel: δ 368.2) and **7**(2-MeSel: δ 386.5) and have chemical shift values similar to that of 2-cyanoselenophene (δ 709.3).[25]

Deprotonation of 1, 4 and 6 with Bases of Varying pK_a. In order to determine the base strength required to cause the conversion (eq 3) of **1**, **4**, and **6** to **9**, **12**, and **14**, respectively, a series of bases with a range of pK_a values was used in this reaction. The reactions were monitored by changes in the ν(NO) region of the IR spectrum of the solutions. The results are presented in Table 4. The pK_a of the bases required for deprotonation of the η^1(S)-thiophene complex (**1**) lies between that of 2,6-dimethylpyridine (2,6-Me_2py) (pK_a 6.99) and morpholine (pK_a 8.33). The η^1(S)-benzothiophene complex (**4**) requires a stronger base with a pK_a between Dabco (pK_a 8.7) and (n-Pr_3)N (pK_a 10.71). On the other hand, the η^1(Se)-selenophene complex (**6**) requires a base with a pK_a between pyridine (py) (pK_a 5.25) and 4-Mepy (pK_a 6.02). Thus the required base ranges are as follows: **4** (Sel) (pK_a 5.25-6.02) < **1** (T) (pK_a 6.99-8.33) < **4** (BT) (pK_a 8.7-10.71).

Synthesis and Characterization of L-yl carbene complexes 16, 17, and 18. The reactions of Cp(NO)(PPh_3)Re(2-Tyl) (**9**) and Cp(NO)(PPh_3)Re(2-BTyl) (**12**) with HO_3SCF_3 to form the cationic carbene complexes, [Cp(NO)(PPh_3)Re(2-Tylcarbene)]$^+$ and [Cp(NO)(PPh_3)Re(2-BTylcarbene)]$^+$, respectively, were recently reported.[6] The L-yl complexes Cp(NO)(PPh_3)Re(2-Tyl) (**9**), Cp(NO)(PPh_3)Re(2-BTyl) (**12**), and Cp(NO)(PPh_3)Re(2-Selyl) (**14**) all react with one equivalent of HBF_4•Et_2O or HO_3SCF_3 to give the corresponding cationic carbene complexes [Cp(NO)(PPh_3)Re(2-Tylcarbene)]$^+$ (**16**), [Cp(NO)(PPh_3)Re(2-BTylcarbene)]$^+$ (**17**), and [Cp(NO)(PPh_3)Re(2-Selylcarbene)]$^+$ (**18**) (eq 4). Isolation of the solid carbene complexes was possible by conducting the reaction at low temperature (-42°C) and in a solvent mixture of 2:1 Et_2O:CH_2Cl_2. The isolated bright yellow to bright orange solids are stable in



(4)

air for greater than 3 weeks. In CD_2Cl_2, free from excess acid, **16**, **17** and **18** in an NMR tube, slowly form a green solution within 3-4 days. Bubbling O_2 gas into a solution of **16** does not increase the rate of formation of the green solution. In IR spectra of the three complexes the ν(NO) band is shifted to higher wavenumber **16** (1716 cm^{-1}), **17** (1720 cm^{-1}) and **18** (1716 cm^{-1}) from those of the starting L-yl complexes **9** (1653 cm^{-1}), **12** (1658 cm^{-1}) and **14** (1653 cm^{-1}). Assignments of the ^1H and ^{13}C NMR resonances were made using a combination of 2-D $^1H/^1H$ COSY, $^1H/^1H$ NOESY and $^1H/^{13}C$ HETCOR NMR techniques. Of the diastereotopic protons H(3) and H(3´), H(3´) is upfield of H(3) due to the shielding ring current of the nearby phenyl of the PPh_3 ligand. In the spectrum of **18**, coupling between ^{77}Se and the diastereotopic protons is not observed indicating that protonation is not occurring at C(5). In the room temperature spectrum of **16**, the signals for H(3) and H(3´) are slightly broadened and become sharper when the sample is cooled to -50° C. The broadening of these peaks at room temperature could be due to the onset of

rotation about the metal-carbene bond. Rotation about the metal carbene bond in the carbene $[Cp(NO)(PPh_3)Re(=C(H)(Ph))]^+$ occurs with $t_{1/2}$ = 60 min at 19.0°C; the more stable rotational isomer is favored by a ratio of >99:1.[26] The ^1H NMR spectra of **17** and **18** also exhibit broadening of the H(3) and H(3´) resonances at room temperature, although evidence for the presence of a second isomer is not seen. For all three compounds, no metal hydride resonances are observed at high field (up to -30 ppm) even at -60° C. The ^{13}C NMR spectra exhibit a carbene resonance (**16**, δ 267.96, d, J_{C-P}= 7.4 Hz; **17,** δ 277.71, d, J_{C-P}= 7.9 Hz; **18**, δ 274.83,d, J_{C-P}= 6.8 Hz) that is coupled to the phosphorus; these chemical shifts are similar to those of related carbenes: $[Cp(NO)(PPh_3)Re(=C(H)(SCH_3)]^+$ (δ 274.4),[27] $[Cp(NO)(PPh_3)Re(=C(H)(Ph)]^+$ (δ 288.6).[26] The C(3) resonances of the starting material L-yl complexes (**9**, δ 135.76; **12**, δ 131.71; **14**, δ 138.33) all move upfield approximately 70 ppm upon protonation and formation of the carbene (**16**, δ 55.93; **17**, δ 66.21; **18**, δ 49.59) since this carbon becomes saturated in the reaction. At the same time, the C(4) and C(5) olefin carbons of **16** (δ 145.83 C(4), 149.24 C(5))and **18** (δ 146.73 C(4), 152.81 C(5)) shift slightly downfield of those (**9**, δ 127.32 C(4), 128.34 C(5); **14**, δ 130.21 C(4), 132.42 C(5)) in the L-yl starting complexes.

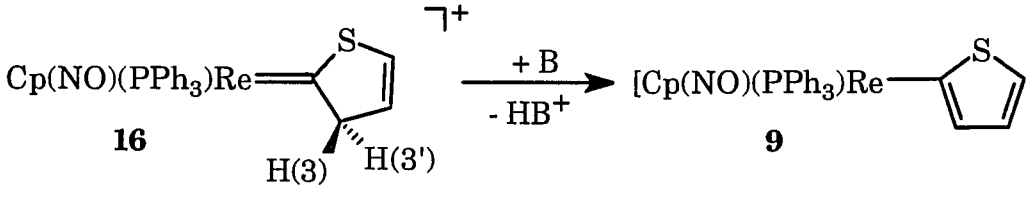
Molecular Structure of $[Cp(NO)(PPh_3)Re(2\text{-}BTylcarbene)](O_3SCF_3)$ (17b). In the structure (Figure 1) of the cation in **17b**, the rhenium carbene carbon bond distance, Re-C(11) (1.992(7)Å), is slightly longer than previously determined Re=C bond distances in similar compounds: $[(Cp(NO)(PPh_3)Re=C(H)(Ph)]^+$ (1.949(6)Å),[26] $Cp^*(NO)(P(OPh)_3Re(=CH_2)$ (1.898(18)Å).[28] The longer Re=C(11) bond is likely due to S-to-C(11) π-bonding which reduces the Re-to-C(11) π-

bonding, as has been observed in other thiocarbene complexes.[29] In the closely related C-pyrrolyl complex, $[CpRe(NO)(PPh_3)Re(C{=}NHCH_2CH{=}CH)]^+$ (2.046(3)Å),[30] the Re-C bond distance is somewhat longer than in **17b**. When compared to the rhenium-carbon single bond distance (2.178(6)Å) in $\{[(Cp)(NO)(PPh_3)Re\text{-}CH_2\text{-}]_2S^+CH_3\}I$,[31] the distance in **17b** is significantly shorter. The torsion angles between P-Re-C(11)-S (86.8°(5)) and P-Re-C(11)-C(12) (-100.2°(6)) indicate that the π-accepting orbitals of C(11) are close to being parallel to the d orbital HOMO of the $Cp(NO)(PPh_3)Re^+$ fragment (Figure 2), which provides further evidence for some Re=C(11) double bond character. The sum of the three angles about C(11) is 360° indicating a trigonal planar geometry. The benzothienyl carbene ligand retains the planarity of the original benzothiophene; the angle between the benzene ring and the thiophene ring is less than 1°. Disruption of the aromaticity of the thiophene ring is evident from the C(11)-C(12) (1.527(11)Å) distance which is ~0.20Å longer than the corresponding bond distance (C(2)-C(3), 1.33(2)Å) in $(C_5Me_5)Re(CO)_2(\eta^1(S)\text{-}3\text{-}MeBT)$.[32] The C(11)-S (1.712(9)Å) bond is 0.066Å shorter than the C(18)-S bond (1.778(7)Å) due to sulfur-to-carbene carbon π-bond donation; such short C-S bond distances are typical of thiocarbene ligands.[29] The benzene portion of the BTylcarbene ligand remains delocalized as indicated by the essentially equal C-C bond lengths (average 1.375Å).

Reaction of $[Cp(NO)(PPh_3)Re(2\text{-}Tylcarbene)]^+$ (16) with Nucleophiles. Nucleophiles typically react with carbene,[33] thiocarbene[34,35] and dithiocarbene[29] complexes by adding to the carbene carbon. Complex **16**, $[Cp(NO)(PPh_3)Re(2\text{-}Tylcarbene)]^+$, in a 5 mm NMR tube with a wide variety of

nucleophiles either does not react (Me_2S, MeSH, $(Co(CO)_4)^-$) or undergoes deprotonation (Me_3N, Me_2HN, H_2MeN, Me_3P, MeS^-, HS^-, H^-, $(Cp(CO)_2Fe)^-$) of C(3) to give the thienyl complex **9** at room temperature. Even warming at 40° C for 48 h, **16** does not react with Me_2S or MeSH. The lack of carbene reactivity is probably due to two factors. First, relatively strong nucleophiles are also strong bases and deprotonation at C(3) is apparently a faster reaction than attack at the carbene carbon. Second, space filling models show that nucleophilic attack is greatly hindered by the PPh_3 on one side of the carbene plane, and nucleophilic attack from the less hindered side of the plane would force the Tylcarbene ligand into the region of the PPh_3, which is also unfavorable.

Deprotonation Studies of 16, 17 and 18. The hydrogens on C(3) of the carbene complex $[Cp(NO)(PPh_3)Re(2\text{-Tylcarbene})]^+$ (**16**) are acidic enough to protonate a variety of amines and phosphines to give the thienyl complex $Cp(NO)(PPh_3)Re(2\text{-Tyl})$ (**9**) in quantitative yield (eq 5). The deprotonation of **16**

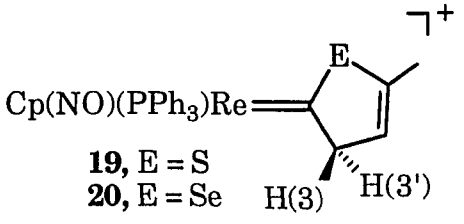


(5)

occurs immediately, the color of the solution turning from bright yellow to orange. The ν(NO) of the carbene (1720 cm^{-1}) shifts by ~70 cm^{-1} to the lower wavenumber of the thienyl complex (1654 cm^{-1}). The pK_a values of complexes **16**, **17**, and **18** were estimated from their reactions with a variety of bases; the

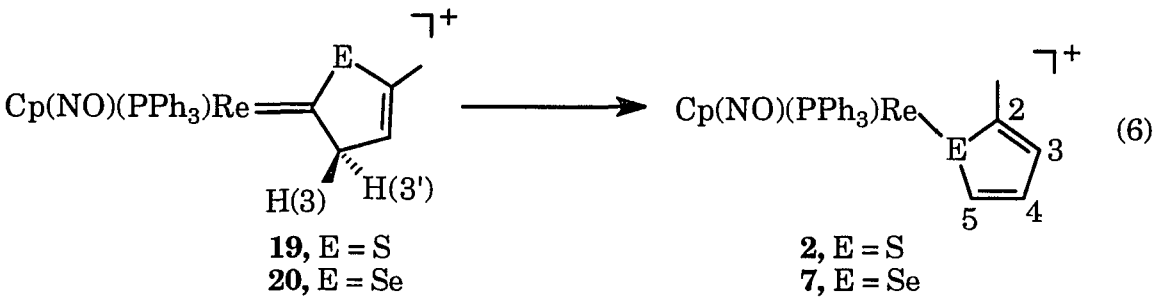
results are given in Table 5. The benzothienylcarbene (**17**) is the most acidic with a pK_a between that of $(p\text{-}FC_6H_4)_3P$ (pK_a 1.97) and Ph_3P (pK_a 2.73). The thienylcarbene (**16**) and the selenylcarbene(**18**) are less acidic than **17** and both have a pK_a between $(m\text{-}MeC_6H_4)_3P$ (pK_a 3.30) and $(p\text{-}MeC_6H_4)_3P$ (pK_a 3.84). Deuterated **16**, **17** and **18** were prepared by reaction of **9**, **12** and **14** with DO_3SCF_3 ; the isolated carbene solids contain equal amounts of D in both the H(3) and H(3´) positions as determined by integration of the ^2H and ^1H NMR spectra. Deprotonation with Dabco in CD_2Cl_2 gives the respective L-yl complex (**9**, **12**, and **14**) back with approximately equal amounts of the complexes with deuterium or hydrogen on C(3) based on integrations of the ^1H NMR spectra. When **17** and DO_3SCF_3 are dissolved in CD_2Cl_2, exchange of D into the H(3) or H(3´) positions is not observed.

Synthesis and Thermal Isomerism of the Carbenes 19 and 20. The reactions of $Cp(NO)(PPh_3)Re$(2-(5-methylthienyl)) (**10**) and $Cp(NO)(PPh_3)Re$(2-(5-methylselenyl)) (**15**) in CD_2Cl_2 with triflic acid at -42° C in 5 mm NMR tubes gives the corresponding carbene compounds [$Cp(NO)(PPh_3)Re$(2-(5-methylthienyl)carbene)]$^+$ (**19**) and [$Cp(NO)(PPh_3)Re$(2-(5-methylselenyl)carbene)]$^+$ (**20**) in quantitative yield. The IR, ^1H and ^{13}C NMR



19, E = S
20, E = Se

spectra closely resemble those of the isoloated thienyl- and selenylcarbene complexes **16**, and **18**. However, upon warming the samples above -10° C for **19** and -30° C for **20**, the ^1H NMR resonances for the carbene complexes disappear and peaks for the η^1(E) complexes **2** and **7** appear (eq 6). The reaction is



19, E = S
20, E = Se

2, E = S
7, E = Se

(6)

complete within 1 h with no evidence in the ^1H or ^{13}C NMR spectra for other products. Attempts to isolate **19** at low temperature (-78° C) gave only the rearranged η^1(S) isomer. The reaction of DO_3SCF_3 with **10** gives the deutero carbene (**19D**) with deuterium approximately equally distributed in the H(3) and H(3′) positions as determined by ^2D NMR studies. Upon warming, the isomerization reaction (eq 6) occurs, which yields **2** with deuterium not only into the 4- and 5-positions of the thiophene ring, but also in the ortho positions of the phenyl rings of the PPh_3. No evidence is found in the upfield region (up to -30 ppm) for a metal hydride intermediate in either the ^1H or ^2H NMR spectrum of the reaction mixture. The mechanism for the rearrangement (eq 6) is unclear at this time. However, the fact that it occurs demonstrates that the η^1(E) isomers (**2** and **7**) are thermodynamically more stable than the carbene forms.

While protonation of the Tyl complex **9** gives (eq 4) the stable Tylcarbene complex **16** and protonation of the 2-MeTyl complex **10** yields (eq 6) the unstable but detectable carbene **19**, protonation of $Cp(NO)(PPh_3)Re(3\text{-}(2,5\text{-}Me_2Tyl))$ (**11**) produces $[Cp(NO)(PPh_3)Re(\eta^1(S)\text{-}2,5\text{-}Me_2T)]^+$ (**3**) in quantitative yield. An ^1H NMR study of the latter reaction at -60° C shows no evidence for a carbene intermediate. If it were to form, it would likely be very unstable because the carbene carbon would not be stablized by an adjacent sulfur or selenium heteroatom, which undoubtedly contributes to the stabilities of the other carbene complexes (**16** - **20**).

Comments on the Mechanism of Deuterium Exchange of Thiophenes over HDS Catalysts. Catalytic reactor studies[36-40] of the deuterium exchange of thiophene with D_2 over HDS catalysts have shown that deuterium is readily incorporated into the 2- and 5-positions and to a lesser extent in the 3- and 4-positions. This exchange has been previously modeled in the η^5-thiophene complex $CpRu(\eta^5\text{-}T)^+$,[41,42] with the rate of deuterium incorporation into the 2,5-positions being much faster than into the 3,4-positions. These studies form the basis for a mechanism for deuterium exchange into thiophene that involves η^5-adsorbed thiophene.[41] An alternative mechanism[5,6] involves $\eta^1(S)$-adsorbed thiophene that is deprotonated by a basic oxide, sulfide or hydride species to give a surface bound thienyl group (Scheme 1); this step is similar to the reaction in eq 3. Transfer of D^+ from an acidic site on the surface to C(2) of the thienyl group would give the 2-deuterated $\eta^1(S)$-bound thiophene(Scheme 1, path **a**); the formation of 2-deutero-benzothiophene in the reaction[5] of $Cp(CO)(PPh_3)Ru(2\text{-}BTyl)$ with DO_3SCF_3 serves as an organometallic model for

this step, which was originally proposed by Cowley.[43] The thienyl species could also undergo D^+ addition at C(3) to form the surface-bound carbene(Scheme 1, path **b**); this step is modeled by the reaction in eq 4. The carbene could then rearrange thermally to either the 2-deuterated or the 3-deuterated η^1(S)-bound thiophene as was observed (eq 6) for the 2-(5-methylthienylcarbene) (**19**) compound. Thus, the 2-thienyl intermediate is key to producing 2-deutero-thiophene via direct M-C(2) cleavage (path **a**)and to forming both 2- and 3-deutero-thiophene via the carbene intermediate (path **b**). Therefore, the new organometallic model reactions described in the present work provide new ways of thinking about deuterium exchange into thiophene and benzothiophene on HDS catalysts.

Acknowledgments. The authors would like to thank Dr. Victor G. Young, Jr. of the ISU Molecular Structure Laboratory for solving the molecular structure of **17b**. We also would like to thank Dr. Karen Ann Smith and Dr. Dave Scott of ISU Instrument Services for their help with and discussions about multi-dimensional NMR.

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Table 1. Crystal and Data Collection Parameters for [Cp(NO)(PPh_3)Re(2-BTylcarbene)]O_3SCF_3 (17b)

formula	$C_{35}H_{32}Cl_6F_3NOPReS$
fw	1081.6
space group	P 1
a	10.4897(8) Å
b	12.554(2) Å
c	17.046(2) Å
α	79.73(1)°
β	73.95(1)°
γ	75.49(1)°
V,Å^3	2054.8(4)
Z	2
d_{calc}, mg/m^3	1.748
crystal size (mm)	0.32 x 0.18 x 0.08
m(CuKα), cm^{-1}	1.54178Å
diffractometer used	Siemens P4RA
radiation	CuKα(λ = 1.54178 Å)
orientation reflections: no., range (2θ)	25, 2.00° plus Kα separation
temp (K)	213
scan method	2θ-θ
data collection range, 2θ, deg	4.0 to 115.0°
no data collected	5863
no unique data	5500 (R_{int} = 2.74%)
no data with ($F_o > 4.0\sigma(F_o^2)$)	4639
no of parameters refined	511
transmission factors: min,max	0.3165 / 1.0000
final R indices (obs. data)	R = 4.37 %, wR = 4.70 %
R indices (all data)	R = 5.47 %, wR = 4.84 %
goodness-of-fit	1.58
largest peak e/ Å	1.76
largest shift/eds. final cycle	0.009, 0.000

Table 2. Selected Bond Distances (Å) and Bond Angles in [Cp(NO)(PPh_3)Re(2-BTylcarbene)]O_3SCF_3 (17b)

Bond	Distance (Å)[a]	Bond	Distance (Å)[a]
Re-N	1.762(8)	C(12)-C(13)	1.522(11)
Re-C(11)	1.992(7)	C(13)-C(14)	1.373(11)
Re-P	2.392(2)	C(13)-C(18)	1.365(13)
N-O	1.191(11)	C(14)-C(15)	1.374(13)
S-C(11)	1.712(9)	C(15)-C(16)	1.378(16)
S-C(18)	1.778(7)	C(16)-C(17)	1.368(12)
C(11)-C(12)	1.527(11)	C(17)-C(18)	1.393(12)

Atoms	Angle (degrees)[a]	Atoms	Angle (degrees)[a]
Re-C(11)-S	125.2(5)	C(14)-C(13)-C(18)	118.9(8)
Re-C(11)-C(12)	124.2(6)	C(13)-C(14)-C(15)	119.5(10)
S-C(11)-C(12)	110.3(5)	C(14)-C(15)-C(16)	120.7(9)
C(11)-S-C(18)	94.6(4)	C(15)-C(16)-C(17)	121.1(9)
S-C(18)-C(13)	112.4(6)	C(16)-C(17)-C(18)	116.8(9)
S-C(18)-C(17)	124.7(7)	C(13)-C(18)-C(17)	122.9(7)
C(11)-C(12)-C(13)	108.6(7)	N-Re-C(11)	94.3(3)
C(12)-C(13)-C(14)	127.6(9)	N-Re-P	90.2(2)
C(12)-C(13)-C(18)	113.5(7)	C(11)-Re-P	93.2(2)
		Re-N-O	174.7(6)

[a] Estimated standard deviations are given in parentheses.

Table 3. Atomic Coordinates (x10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 x 10^3) for [Cp(NO)(PPh_3)Re(2-BTylcarbene)]O_3SCF_3 (17b).

Atom	x	y	z	U_{eq} [a]
Re	-1637(1)	312(1)	3399(1)	22(1)
C(1)	-2312(9)	-1349(7)	3861(5)	33(3)
C(2)	-863(8)	-1585(7)	3607(5)	34(3)
C(3)	-365(9)	-1123(7)	4121(5)	39(4)
C(4)	-1485(9)	-564(8)	4686(5)	38(4)
C(5)	-2684(9)	-725(8)	4533(5)	39(4)
N	-913(7)	1458(6)	3335(4)	30(3)
O	-334(6)	2172(6)	3308(4)	54(3)
S	-4819(2)	732(2)	3304(1)	33(1)
C(11)	-3457(8)	1234(7)	3326(5)	26(3)
C(12)	-3873(7)	2481(6)	3378(5)	26(3)
C(13)	-5411(8)	2830(7)	3526(5)	28(3)
C(14)	-6215(9)	3844(7)	3706(6)	43(4)
C(15)	-7596(9)	4011(8)	3821(7)	53(5)
C(16)	-8181(9)	3169(7)	3763(6)	41(4)
C(17)	-7406(8)	2151(8)	3582(5)	37(4)
C(18)	-6010(8)	2003(7)	3480(5)	26(3)
P	-851(2)	299(2)	1943(1)	23(1)
C(21)	-1714(8)	1480(7)	1351(5)	27(3)
C(22)	-2491(8)	1350(7)	849(5)	32(3)
C(23)	-3168(9)	2265(8)	443(6)	43(4)
C(24)	-3087(9)	3309(8)	526(6)	48(4)

C(25)	-2306(9)	3452(8)	1026(5)	38(4)
C(26)	-1608(8)	2529(7)	1432(5)	33(3)
C(31)	931(7)	333(7)	1570(5)	25(3)
C(32)	1448(8)	839(8)	795(5)	39(4)
C(33)	2822(9)	869(9)	521(6)	49(4)
C(34)	3688(9)	379(9)	1028(6)	52(5)
C(35)	3198(9)	-134(9)	1797(6)	49(4)
C(36)	1831(8)	-148(8)	2066(5)	37(4)
C(41)	-1063(8)	-930(7)	1611(4)	28(3)
C(42)	22(8)	-1639(7)	1163(5)	30(3)
C(43)	-172(9)	-2592(7)	966(5)	36(4)
C(44)	-1418(9)	-2842(8)	1188(5)	39(4)
C(45)	-2524(9)	-2147(8)	1641(5)	39(4)
C(46)	-2346(8)	-1196(7)	1840(5)	32(3)
S(50)	-3954(2)	1843(2)	-3996(1)	32(1)
O(51)	-2831(6)	995(5)	-3820(3)	39(2)
O(52)	-4953(6)	2219(6)	-3278(4)	52(3)
O(53)	-4484(6)	1663(5)	-4641(4)	48(3)
C(50)	-3190(10)	3023(8)	-4438(6)	44(4)
F(51)	-2651(6)	3330(5)	-3912(4)	67(3)
F(52)	-2203(5)	2815(5)	-5111(3)	56(2)
F(53)	-4092(7)	3905(5)	-4657(4)	76(3)
C(60)	7507(12)	5708(13)	3543(9)	79(7)
Cl(61)	9161(4)	5617(3)	3489(4)	154(3)
Cl(62)	7271(4)	4985(3)	2842(3)	101(2)

C(70)	1735(13)	3725(17)	1640(8)	98(8)
Cl(71)	3504(3)	3535(3)	1369(2)	93(2)
Cl(72)	1048(3)	4229(3)	781(2)	82(2)
C(80)	4267(11)	6119(12)	2000(7)	70(6)
Cl(81)	2544(3)	6569(3)	1959(2)	84(2)
Cl(82)	5353(3)	6320(2)	1020(2)	61(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Deprotonation of 1, 4 and 6 with Bases of Varying pK_a (eq 3)

Base	pK_a (aq)[a]	**1** (T)	**4** (BT)	**6** (Sel)
pyridine (py)	5.25	no rxn	no rxn	no rxn
4-Mepy	6.02	no rxn	no rxn	rxn
2,6-Me_2py	6.99	no rxn	no rxn	rxn
morpholine	8.33	rxn	no rxn	rxn
Dabco	8.7	rxn	no rxn	rxn
$(n\text{-}Pr)_3N$	10.71	rxn	rxn	rxn
Proton Sponge	12.37	rxn	rxn	rxn
DBU	24.32 [b]	rxn	rxn	rxn

[a] CRC Handbook of Chemistry and Physics; 66th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1985, pp D159-161. [b] Measured in CH_3CN, Schwesinger, R.; Schlemper, H. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1167.

Table 5. Deprotonation of Carbene Complexes 16, 17 and 18 with Bases of Varying pK_a (eq 5)

Base	pK_a (aq)	16	17	18
$(p\text{-}ClC_6H_4)_3P$	1.03[a]	no rxn	no rxn	no rxn
$(p\text{-}FC_6H_4)_3P$	1.97[a]	no rxn	no rxn	no rxn
Ph_3P	2.73[a]	no rxn	rxn	no rxn
$(o\text{-}MeC_6H_4)_3P$	3.08[a]	no rxn	rxn	no rxn
$(m\text{-}MeC_6H_4)_3P$	3.30[a]	no rxn	rxn	no rxn
$(p\text{-}MeC_6H_4)_3P$	3.84[a]	rxn	rxn	rxn
$(p\text{-}MeOC_6H_4)_3P$	4.57[a]	rxn	rxn	rxn
aniline	4.63[b]	rxn	rxn	rxn
pyridine	5.21[b]	rxn	rxn	rxn

[a] Bush, R. C., Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 681. [b] CRC Handbook of Chemistry and Physics; 66th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1985, pp D159-161.

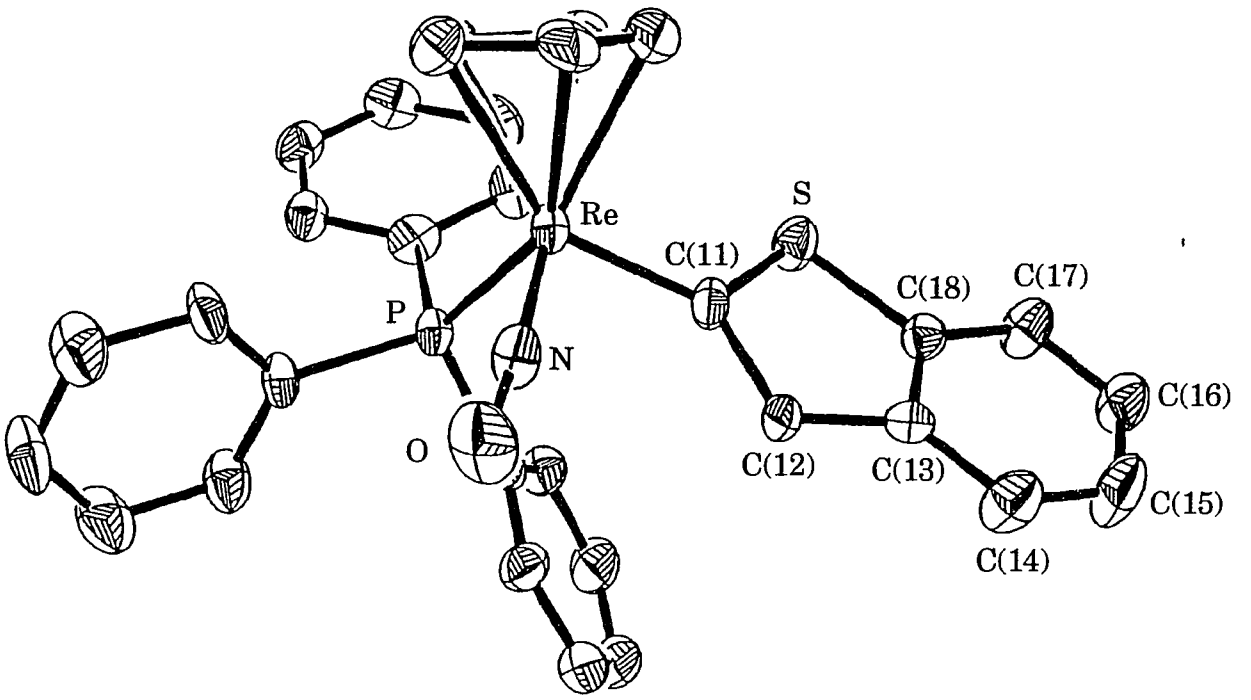


Figure 1. ORTEP Drawing of the cation $[Cp(NO)(PPh_3)Re(2\text{-}BTylcarbene)]^+$ in **17b**.

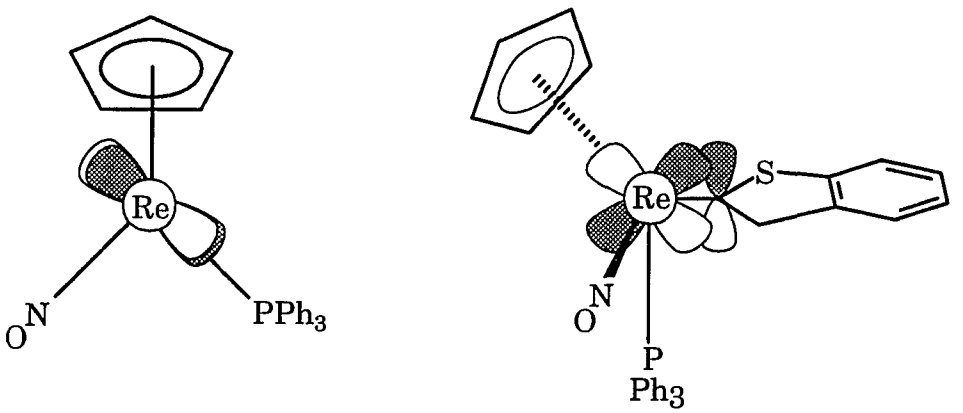
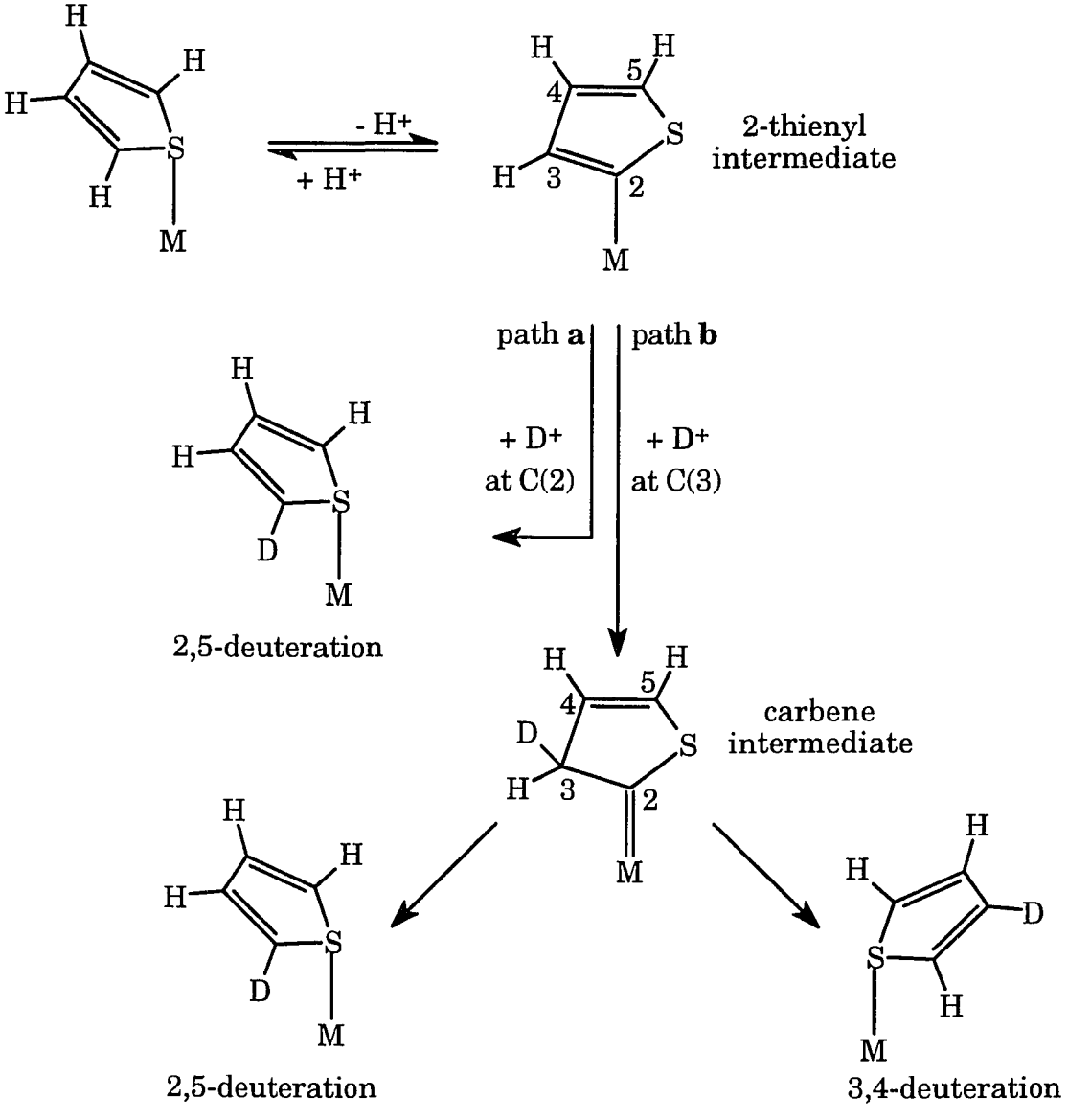


Figure 2. The HOMO (left) for the fragment $[Cp(NO)(PPh_3)Re]^+$ and its bonding with the carbene in **17** (right).

Scheme 1


- H+
+ H+
2-thienyl intermediate
path a
path b
+ D+ at C(2)
+ D+ at C(3)
2,5-deuteration
carbene intermediate
2,5-deuteration
3,4-deuteration

General Summary

This research shows that selenophene transition metal complexes have a chemistry that is similar to their thiophene analogs. Selenophene coordination has been demonstrated and confirmed by molecular structure in both the η^5- and the η^1(Se)- coordination modes. The reaction chemistry of selenophene complexes closely resembles that of the analogous thiophene complexes. One major difference, however, is that selenophene is a better donor ligand than thiophene making the selenophene complexes more stable than the corresponding thiophene complexes.

The ^{77}Se NMR chemical shift values for selenophene complexes fall within distinct regions primarily depending on the coordination mode of the selenophene ligand. Within each region, the chemical shift is further influenced by the charge of the complex, and the other ligands attached to the metal. The separation between the chemical shift region for η^5-selenophene and the region for η^1(Se)-selenophene is over 150 ppm when the charge of the complex is considered. The successful use of ^{77}Se NMR for studies of the hydrodesulfurization surface is highly dependent on the use of isotopic labeling of selenophene. Even though ^{77}Se is a more sensitive nucleus than ^{13}C, the small amount of surface binding sites and the potential for surface induced signal broadening limits the experimental application.

In the final paper, the C-H bond activation of η^1(S)-bound thiophenes, η^1(S)-benzothiophene and η^1(Se)-bound selenophenes has been demonstrated. The deprotonation and rearrangement of the η^1(E)- bound ligand to the carbon bound L-yl complex readily occurs in the presence of base. Reprotonation with

a strong acid gives a carbene complex that is unreactive towards nucleophilic attack at the carbene carbon and is stable towards exposure to air. The molecular structure of [Cp(NO)(PPh_3)Re(2-benxothienylcarbene)]O_3SCF_3 was determined and contains a Re-C bond with substantial double bond character. Methyl substitution of the thienylcarbene or selenylcarbene gives a carbene that rearranges thermally to give back the η^1(E)- bound complex. Based on these model reactions, a new mechanism for the H/D exchange of thiophene over the hydrodesulfurization catalyst has been proposed.