Selenophene transition metal complexes

Carter James White
Iowa State University

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Selenophene transition metal complexes

White, Carter James, Ph.D.
Iowa State University, 1994
Selenophene transition metal complexes

by

Carter James White

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.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>v</td>
</tr>
<tr>
<td>GENERAL INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>Dissertation Organization</td>
<td>1</td>
</tr>
<tr>
<td>Significance and Goals of Research</td>
<td>1</td>
</tr>
<tr>
<td>References</td>
<td>4</td>
</tr>
<tr>
<td>OVERVIEW OF SELENOPHENE AND SELENOPHENE TRANSITION METAL CHEMISTRY</td>
<td>8</td>
</tr>
<tr>
<td>Introduction</td>
<td>8</td>
</tr>
<tr>
<td>Structure and Bonding in Selenophene</td>
<td>8</td>
</tr>
<tr>
<td>Spectroscopy of Selenophene</td>
<td>12</td>
</tr>
<tr>
<td>Synthesis and Chemical Reactions of Selenophene</td>
<td>17</td>
</tr>
<tr>
<td>Transition Metal Complexes of Selenophene</td>
<td>21</td>
</tr>
<tr>
<td>Summary</td>
<td>24</td>
</tr>
<tr>
<td>References</td>
<td>24</td>
</tr>
<tr>
<td>SYNTHESIS, REACTIONS AND $^{77}$Se NMR STUDIES OF $\eta^5$-</td>
<td>29</td>
</tr>
<tr>
<td>SELENOPHENE (Seln) COMPLEXES OF CHROMIUM, MANGANESE, RUTHENIUM AND IRIDIUM</td>
<td></td>
</tr>
<tr>
<td>Abstract</td>
<td>29</td>
</tr>
<tr>
<td>Introduction</td>
<td>30</td>
</tr>
<tr>
<td>Experimental Section</td>
<td>32</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>42</td>
</tr>
<tr>
<td>References</td>
<td>53</td>
</tr>
</tbody>
</table>
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.

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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 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 pre-treatment 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 feedstocks 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 H₂S and a mixture of C₄ hydrocarbons.2 Often 1,3-butadiene in not observed, evidence15 supports the suggestion that it is the initial desulfurization product. Although significant insight into the HDS process 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 benzene18
and ethylene\textsuperscript{19-22} to catalytic surfaces with moderate success. These studies have relied on isotopic \textsuperscript{13}C enrichment and large chemical shifts in the \textsuperscript{13}C resonances caused by the binding of the molecule to the surface.\textsuperscript{23-25}

Unfortunately, analogous studies using \textsuperscript{13}C enriched thiophene have not been conducted due to the high cost of \textsuperscript{13}C isotopic enrichment of thiophene and the small chemical shift differences found between unbound thiophene and metal bound thiophene.\textsuperscript{14}

Selenophene, the selenium analogue of thiophene, has a structure and chemistry similar to that of thiophene (Figure 1).\textsuperscript{26-31} Selenium compounds

![Figure 1. Structure and numbering of thiophene and selenophene.](image)

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

**References**


(15) Benson, J. W.; Schrader, G. L.; Angelici, R. J. J. Catal. submitted for publication,


OVERVIEW OF SELENOPHENE AND SELENOPHENE TRANSITION METAL CHEMISTRY

Introduction

Selenophene was first described in the literature in 1928; however, references to its derivatives were reported earlier. 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.

Several earlier reviews 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 and thiophene
Table 1. Molecular Geometries of Thiophene and Selenophene

<table>
<thead>
<tr>
<th>Bond Length (Å)</th>
<th>Thiophene X=S ¹</th>
<th>Selenophene X=Se ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-C(2)</td>
<td>1.714</td>
<td>1.855</td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td>1.370</td>
<td>1.369</td>
</tr>
<tr>
<td>C(3)-C(4)</td>
<td>1.423</td>
<td>1.433</td>
</tr>
<tr>
<td>C(2)-H</td>
<td>1.078</td>
<td>1.070</td>
</tr>
<tr>
<td>C(3)-H</td>
<td>1.081</td>
<td>1.079</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Angle (degrees) Thiophene</th>
<th>Angle (degrees) Selenophene</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(2)-X-C(5)</td>
<td>92.17</td>
<td>87.76</td>
</tr>
<tr>
<td>X-C(2)-C(3)</td>
<td>111.47</td>
<td>111.56</td>
</tr>
<tr>
<td>C(2)-C(3)-C(4)</td>
<td>112.45</td>
<td>114.55</td>
</tr>
<tr>
<td>X-C(2)-H</td>
<td>119.85</td>
<td>121.73</td>
</tr>
<tr>
<td>C(2)-C(3)-H</td>
<td>123.28</td>
<td>122.59</td>
</tr>
</tbody>
</table>

¹ Reference 10   ² 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 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

<table>
<thead>
<tr>
<th>Compound</th>
<th>A&lt;sup&gt;a&lt;/sup&gt;</th>
<th>B&lt;sup&gt;a&lt;/sup&gt;</th>
<th>ΣΔN&lt;sub&gt;a,b&lt;/sub&gt;</th>
<th>J&lt;sup&gt;a&lt;/sup&gt;</th>
<th>N&lt;sup&gt;c&lt;/sup&gt;</th>
<th>μ&lt;sub&gt;m&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>furan</td>
<td>7.67</td>
<td>1.72</td>
<td>1.42</td>
<td>0.87</td>
<td>43</td>
<td>1.03</td>
</tr>
<tr>
<td>thiophene</td>
<td>11.56</td>
<td>3.85</td>
<td>0.90</td>
<td>0.91</td>
<td>66</td>
<td>1.35</td>
</tr>
<tr>
<td>selenophene</td>
<td>10.44</td>
<td>2.94</td>
<td>1.02</td>
<td>0.91</td>
<td>59</td>
<td>1.29</td>
</tr>
<tr>
<td>tellurophene</td>
<td>8.50</td>
<td>1.85</td>
<td>1.30</td>
<td>0.88</td>
<td>48</td>
<td>1.17</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reference 42  <sup>b</sup> Sum of bond C-C bond order.  <sup>c</sup> Reference 17

on either the dilution shift method (A)<sup>18,19</sup> or the uniformity of the methyl effects on the aromatic proton chemical shifts (B).<sup>20</sup> The next three indices, the sum of the differences in bond orders for the three C-C bonds (ΣΔN), Julg's (J) parameter<sup>21</sup> and the aromaticity index (N)<sup>17</sup> 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<sub>m</sub>), which is related to the π-electron delocalization, and has been proposed as a criterion for measuring aromaticity of delocalized rings.<sup>22</sup> 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 and thiophene 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 \( \nu_3 \) and antisymmetric \( \nu_{17} \) stretching of the C(2)-X-C(5) and the ring deformation modes \( \nu_8, \nu_{18}, \) and \( \nu_{21} \) have been attributed to
Table 3. Fundamental Vibrational Frequencies (in cm⁻¹) for Thiophene and Selenophene

<table>
<thead>
<tr>
<th>Vibration</th>
<th>Approximate description</th>
<th>Point Group: ( C_{2v} )</th>
<th>Thiophene(^a) (cm⁻¹)</th>
<th>Selenophene(^b) (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( v_1 )</td>
<td>C-H stretch</td>
<td>( A_1 )</td>
<td>3110</td>
<td>3110</td>
</tr>
<tr>
<td>( v_2 )</td>
<td>C-H stretch</td>
<td></td>
<td>3086</td>
<td>3083</td>
</tr>
<tr>
<td>( v_5 )</td>
<td>ring stretch</td>
<td></td>
<td>1408</td>
<td>1419</td>
</tr>
<tr>
<td>( v_4 )</td>
<td>ring stretch</td>
<td></td>
<td>1360</td>
<td>1341</td>
</tr>
<tr>
<td>( v_6 )</td>
<td>C-H scissoring</td>
<td></td>
<td>1081</td>
<td>1080</td>
</tr>
<tr>
<td>( v_7 )</td>
<td>C-H scissoring</td>
<td></td>
<td>1033</td>
<td>1010</td>
</tr>
<tr>
<td>( v_3 )</td>
<td>ring stretch</td>
<td></td>
<td>833</td>
<td>758</td>
</tr>
<tr>
<td>( v_8 )</td>
<td>ring breathing</td>
<td></td>
<td>606</td>
<td>456</td>
</tr>
<tr>
<td>( v_9 )</td>
<td>C-H wagging</td>
<td>( A_2 )</td>
<td>900</td>
<td>905</td>
</tr>
<tr>
<td>( v_{10} )</td>
<td>C-H wagging</td>
<td></td>
<td>686</td>
<td>685</td>
</tr>
<tr>
<td>( v_{11} )</td>
<td>ring twisting</td>
<td></td>
<td>565</td>
<td>544</td>
</tr>
<tr>
<td>( v_{12} )</td>
<td>C-H stretch</td>
<td>( B_1 )</td>
<td>3110</td>
<td>3100</td>
</tr>
<tr>
<td>( v_{13} )</td>
<td>C-H stretch</td>
<td></td>
<td>3073</td>
<td>3054</td>
</tr>
<tr>
<td>( v_{14} )</td>
<td>ring stretch</td>
<td></td>
<td>1506</td>
<td>1515</td>
</tr>
<tr>
<td>( v_{15} )</td>
<td>C-H scissoring</td>
<td></td>
<td>1250</td>
<td>1243</td>
</tr>
<tr>
<td>( v_{16} )</td>
<td>C-H scissoring</td>
<td></td>
<td>1081</td>
<td>1080</td>
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<tr>
<td>( v_{17} )</td>
<td>ring deformation</td>
<td></td>
<td>871</td>
<td>820</td>
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<tr>
<td>( v_{18} )</td>
<td>ring breathing</td>
<td></td>
<td>750</td>
<td>623</td>
</tr>
<tr>
<td>( v_{20} )</td>
<td>C-H wagging</td>
<td>( B_2 )</td>
<td>864</td>
<td>870</td>
</tr>
<tr>
<td>( v_{19} )</td>
<td>C-H wagging</td>
<td></td>
<td>712</td>
<td>700</td>
</tr>
<tr>
<td>( v_{21} )</td>
<td>ring twisting</td>
<td></td>
<td>453</td>
<td>394</td>
</tr>
</tbody>
</table>

\(^a\) Reference 23 \(^b\) Reference 4
the changes in geometry and mass of the different heteroatoms.

**1H NMR Spectroscopy**

1H NMR parameters for selenophene and thiophene are given in Table 4. A solvent induced change in the resonances is seen by changing the solvent 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 1H 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 1H NMR spectrum because of the small value of $^3J_{\text{Se-H}}$ and the difficulty in resolving the satellite peaks.

Tabulations of the 1H NMR chemical shifts and coupling constants for 2- and 3-substituted selenophenes are available. Extrapolation to infinite dilution of the 1H NMR chemical shifts in deuteroacetone 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

---

**Table 4. 1H NMR Parameters for Selenophene and Thiophene**

<table>
<thead>
<tr>
<th>Compound</th>
<th>H(2), H(5) $^\delta$</th>
<th>H(3), H(4) $^\delta$</th>
<th>J$_{2,3}$ (Hz)</th>
<th>J$_{2,4}$ (Hz)</th>
<th>J$_{2,5}$ (Hz)</th>
<th>J$_{3,4}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selenophene</td>
<td>7.88</td>
<td>7.23</td>
<td>5.40</td>
<td>1.46</td>
<td>2.34</td>
<td>3.74</td>
</tr>
<tr>
<td>Thiophene</td>
<td>7.18</td>
<td>6.99</td>
<td>4.90</td>
<td>1.04</td>
<td>2.84</td>
<td>3.50</td>
</tr>
</tbody>
</table>

*In d$_6$-acetone. Reference 4*
the $^1$H NMR chemical shift of the ring protons and the electron donating ability of the substituent.\textsuperscript{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 $\delta$ 131.0 (C(2), C(5)) and the other with $\delta$ 129.8 (C(3), C(4)) (Table 5). Assignment of the resonances has been made based on the one bond $^{1}$J$_{C-H}$ 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.\textsuperscript{7} Confirmation of the assignments have been made using 2-D $^1$H/$^{13}$C NMR techniques.\textsuperscript{26} Comparison of the chemical shift values of selenophene and thiophene shows that the selenophene C(2),C(5) resonances 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.\textsuperscript{25,27} As was done with the $^1$H NMR chemical shifts,

<table>
<thead>
<tr>
<th>Compound</th>
<th>C(2), C(5) ($\delta$)</th>
<th>$^1$J$_{C-H}$ (Hz)</th>
<th>C(3), C(4) ($\delta$)</th>
<th>$^1$J$_{C-H}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selenophene</td>
<td>131.0</td>
<td>189</td>
<td>129.8</td>
<td>166</td>
</tr>
<tr>
<td>Thiophene</td>
<td>125.6</td>
<td>185</td>
<td>127.3</td>
<td>168</td>
</tr>
</tbody>
</table>

\textsuperscript{a} In d$_6$-acetone. \textsuperscript{b} Reference 24
the $^{13}$C NMR chemical shifts of C(5) have been correlated with the electron-donating or withdrawing ability of the substituent.\textsuperscript{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 $R$)\textsuperscript{28} gives a linear correlation for both 2- and 3-substituted selenophenes.\textsuperscript{25}

**Heteroatom NMR Spectroscopy**

The heteroatom in both selenophene and thiophene contain NMR active isotopes. Several good references to $^{77}$Se \textsuperscript{29,30} and $^{33}$S NMR\textsuperscript{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.\textsuperscript{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 $\delta$ 500 to 700 ($\delta$ Me$_2$Se = 0.0) with linewidths less

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>NMR frequency (MHz)</th>
<th>Nuclear spin</th>
<th>Natural Abundance (%)</th>
<th>Relative receptivity</th>
<th>Chemical Shift Standard ($\delta = 0.00$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H</td>
<td>100</td>
<td>1/2</td>
<td>99.98</td>
<td>1</td>
<td>Me$_4$Si</td>
</tr>
<tr>
<td>$^{13}$C</td>
<td>25.19</td>
<td>1/2</td>
<td>1.11</td>
<td>1.8 x 10^-4</td>
<td>Me$_4$Si</td>
</tr>
<tr>
<td>$^{33}$S</td>
<td>7.67</td>
<td>3/2</td>
<td>0.74</td>
<td>1.7 x 10^-5</td>
<td>(NH$_4$)$_2$SO$_4$</td>
</tr>
<tr>
<td>$^{77}$Se</td>
<td>19.135</td>
<td>1/2</td>
<td>7.58</td>
<td>5.2 x 10^-4</td>
<td>Me$_2$Se</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reference 29
than 4 Hz. In contrast, $^{33}\text{S}$ chemical shifts for thiophene compounds range from $\delta$ -111 to -197 ($\delta(\text{NH}_4\text{SO}_4) = 0.0$) with linewidths of 600-1600 Hz due to the quadrapole of the nucleus.

An extensive study of the $^{77}\text{Se}$ NMR chemical shifts of substituted selenophenes has been reported. A correlation of the Swain and Lupton reactivity parameters ($F$ and $R$) for 3-substituted selenophenes with the change in the $^{77}\text{Se}$ chemical shift ($\Delta\delta = \delta(\text{Sel}) - \delta(\text{sample})$) gave the equation: $\Delta\delta = 8.5 + 17.5F + 170.9R$ with a $\sigma = 13.1$ and $r = 0.96$. This equation is similar to that for the correlation of the same reactivity parameters with the $^{13}\text{C}$ 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. (eq 1) Addition of sand or deactivated

\[
\begin{align*}
\text{H} & \\
\text{C} & \\
\text{C} & \\
\text{H} & \\
\text{C} & \\
\text{H} & \\
\end{align*}
\]

\[
\text{Se} + \text{tube furnace} \quad 400^\circ \text{C, under N}_2 \rightarrow \quad \text{C}_2\text{H}_2\text{Se} + \text{other products} \quad (1)
\]

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 N₂ 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. Substitution occurs almost exclusively in the 2,5-positions making the 3,4-substituted selenophenes difficult to prepare. The synthesis of 2-methylselenophene and 2,5-dimethylselenophene is best accomplished using a series of formylation and reduction reactions (Figure 2). 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-Me₂Sel](image)
replacement of the oxygen in furan with selenium using \( \text{H}_2\text{Se} \).\(^{38}\) This method is impracticable and time-consuming due to the difficult method of generating \( \text{H}_2\text{Se} \) in the lab from the reaction of \( \text{Al}_2\text{Se}_3 \) 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,\(^4^3\) 2,5-dimethoxyselenophene is attacked by butyllithium (eq 2) at the selenium heteroatom. This is followed by ring opening and
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. 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. 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.

Selenophene is reported to decompose in strong organic and mineral acids. Nevertheless, acid-catalyzed isotopic exchange occurs for deuterated selenophene in a mixture of 4:1 acetic : trifluoroacetic acids. 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.\(^\text{46,47}^\) Selenophene (Sel) coordination in transition metal complexes, in contrast has been limited to a handful of examples. The potential metal binding modes of selenophene, \(\eta^5\), \(\eta^4\), \(\eta^2\), and \(\eta^1(\text{Se})\), (Figure 3) are similar to those exhibited in thiophene.\(^\text{48,49}^\)

Reported in 1966 by Karl Öfele\(^\text{50}^\), the \(\eta^5\)-selenophene complex, \((\eta^5\text{-Sel})\text{Cr(CO)}_3\), 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 \(\text{Cr(CO)}_3(\text{NC}_5\text{H}_5)_3\) and \(\text{BF}_3\) (eq 4). Recently an alternative route for
the synthesis of (η⁵-Sel)Cr(CO)₃ using the direct reaction of selenophene with Cr(CO)₆ has been reported by our research group.²⁶ The complex (η⁵-Sel)Cr(CO)₃ has been characterized by IR, UV, ¹H and ¹³C 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 (η⁵-T)Cr(CO)₃ shows the selenophene ligand to be slightly more electron donating than thiophene. In the ¹H NMR spectrum of (η⁵-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 complexes of chromium tricarbonyl.⁵² The ¹³C 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 η⁵-coordination of the selenophene ring.⁵³,⁵⁴

Both η¹(Se)- or η²-coordination selenophene (Figure 3) have been observed in the complexes CpRe(CO)₂(η¹(Se)-Sel) and Cp*Re(CO)₂(η¹(Se)-Sel).⁵⁵-⁵⁷ Selenophene is η²-coordinated through one of the C=C double bonds in the electron rich complex Cp*Re(CO)₂(Sel) (Cp* = η⁵-C₅H₅). In the analogous 2,5-dimethylselenophene (2,5-Me₂Sel) complex Cp*(CO)₂Re(2,5-Me₂Sel) the ligand is coordinated through the Se atom. The intermediate methyl substituted ligand, 2-methylselenophene (2-MeSel) exhibits an equilibrium of the η¹(Se) and η² isomers. (eq 5) The equilibrium amount of the η¹(Se) isomer increases when the Cp* ligand is replaced by the less electron-donating ligand Cp(η⁵-C₅H₅) as in CpRe(CO)₂(Sel). In the analogous
Table 7. Spectroscopic Data for (η⁵-Sel)Cr(CO)₃ and (η⁵-T)Cr(CO)₃

<table>
<thead>
<tr>
<th>Compound</th>
<th>UV (cm⁻¹)a,b</th>
<th>log ε</th>
<th>IR vCO (cm⁻¹)a,b</th>
<th>¹H NMR δ c,d</th>
<th>¹³C NMR δ c,d</th>
</tr>
</thead>
<tbody>
<tr>
<td>(η⁵-Sel)Cr(CO)₃</td>
<td>18,800</td>
<td>2.90</td>
<td>1897</td>
<td>5.95 (m, H(2), H(5)) 91.63 (C(2),C(5))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>23,800</td>
<td>3.74</td>
<td>1917</td>
<td>5.79 (m, H(3),H(4))  91.91 (C(3),C(4))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>26,670</td>
<td>3.86</td>
<td>1985</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>38,600</td>
<td>4.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>44,640</td>
<td>4.44</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(η⁵-T)Cr(CO)₃</td>
<td>19,200</td>
<td>3.00</td>
<td>1897</td>
<td>5.37 (m, H(2),H(5)) 85.87 (C(2),C(5))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>24,450</td>
<td>3.83</td>
<td>1914</td>
<td>5.59 (m, H(3), H(4)) 91.24 (C(3),C(4))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>31,250</td>
<td>3.82</td>
<td>1985</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>38,500</td>
<td>4.13</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>44,450</td>
<td>4.49</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Reference 50 and 51  b Cyclohexane  c Reference 26  d CDCl₃
thiophene (Th) complexes, Cp'\text{Re}(\text{CO})_2(\text{Th}) (\text{Cp'} = \text{Cp} \text{ or Cp}^\ast), only the $\eta^1$(S) isomer is observed regardless of the electron richness of the metal or the methyl substitution of thiophene.\textsuperscript{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. Finally, selenophene is a better electron donating ligand and therefore will form more stable transition metal complexes than thiophene.

**References**


(2) Paal, C. *Ber.* 1885, 17, 2756.


SYNTHESIS, REACTIONS AND $^{77}$Se NMR STUDIES OF $\eta^5$-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 $\eta^5$-selenophene transition metal complexes ($\eta^5$-Seln)Cr(CO)$_3$ (1-3), [(\$\eta^5$-Seln)Mn(CO)$_3$]SO$_2$CF$_3$ (4-6), [(\$\eta^5$-Seln)RuCp*]SO$_2$CF$_3$ (7-9), and [(\$\eta^5$-Seln)IrCp*](BF$_4$)$_2$ (10-12), where Seln = selenophene(Sel), 2-methylselenophene (2-MeSel), or 2,5-dimethylselenophene(2,5-Me$_2$Sel), were synthesized and characterized by $^1$H, $^{13}$C, and $^{77}$Se NMR and IR spectroscopy. The molecular structure of (\$\eta^5$-2,5-Me$_2$Sel)Cr(CO)$_3$ (3) was determined.

Reactions of [(\$\eta^5$-Sel)Mn(CO)$_3$]SO$_2$CF$_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 [(\$\eta^5$-Sel)RuCp*]SO$_2$CF$_3$ (7) with H~, however, results in cleavage of the C-Se bond to form a butadiene selenide complex ([\$\eta^5$-SeCH=CH-CH=CH$_2$]RuCp*) (7a). Still another type of product results from the reaction of [(\$\eta^5$-2,5-Me$_2$Sel)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$_2$Sel)IrCp* (12a). All of these reactions are similar to those of the analogous $\eta^5$-thiophene complexes. The $^{77}$Se NMR chemical shift values for the $\eta^5$-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 \(\pi\)-system (\(\eta^5\)) or through the sulfur atom (\(\eta^1(S)\)) only. Reactions of the \(\eta^5\) 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 (\(\eta^2\)) or through both C=C bonds (\(\eta^4\)).\(^6\)\(^,\)\(^7\)

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 \(\text{Cp'}\text{Re(CO)}_2(\text{Seln})\).\(^12\)\(^,\)\(^13\) In the electron-rich complex \(\text{Cp'}\text{Re(CO)}_2(\text{Seln})\) (\(\text{Cp'} = \eta^5\)-C\(_5\)Me\(_5\)), the selenophene (Sel) ligand is 2,3-\(\eta^2\)-coordinated through two of the carbons of Sel, while in the analogous 2,5-dimethylselenophene (2,5-Me\(_2\)Sel) complex \(\text{Cp'}(\text{CO})_2\text{Re(2,5-Me}_2\text{Sel})\) the ligand is coordinated through the Se atom. For the analogous 2-methylselenophene (2-MeSel) complexes, the \(\eta^1(\text{Se})\) and 2,3-\(\eta^2\) isomers are in equilibrium (eq 1).
Not only does the selenophene binding mode depend on the number of methyl groups in the SeIn, but the equilibrium amount of the $\eta^1(Se)$ isomer increases when the Cp* ligand is replaced by the less electron-donating Cp ($\eta^5$-C$_5$H$_5$) in CpRe(CO)$_2$(SeIn). Lowering the electron density on Re favors the $\eta^1(Se)$ isomer, in which the Se acts as a two electron donor to the Re. The 2,3-$\eta^2$ isomer becomes less favored in this case because the lower electron density on Re makes it less capable of $\pi$-back-bonding to the olefin. In the analogous thiophene (Th) complexes, Cp'Re(CO)$_2$(Th), only the $\eta^1(S)$ 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 $\eta^1(Se)$ and 2,3-$\eta^2$ isomers of the CpRe(CO)$_2$(SeIn) 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 ($\eta^5$-SeIn)Cr(CO)$_3$ (SeIn = 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 $\eta^5$ coordination from $\eta^1(Se)$ coordination based on the chemical shift. In the investigations reported
herein, we determine the \(^{77}\text{Se}\) NMR chemical shifts in the following series of complexes, \((\eta^5-\text{Seln})\text{Cr(CO)}_3\), \([\eta^5-\text{Seln}]\text{Mn(CO)}_3^+\), \([\eta^5-\text{Seln}]\text{RuCp}^*\]^+, and \([\eta^5-\text{Seln}]\text{IrCp}^*\)^2+ (where \text{Seln} = \text{Sel, 2-MeSel, 2,5-Me}_2\text{Sel}) 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 \((\eta^5-2,5\text{-Me}_2\text{Sel})\text{Cr(CO)}_3\) determined by x-ray crystallography is compared with the recently published structure of the analogous \(\eta^5\)-thiophene complex \((\eta^5-2,5\text{-Me}_2\text{T})\text{Cr(CO)}_3\)^{17}

**Experimental Section**

**General Procedures.** All reactions and manipulations were carried out under an atmosphere of \(\text{N}_2\) using standard Schlenk techniques unless otherwise stated.\(^{18,19}\) Solvents were reagent grade and dried under \(\text{N}_2\) by the following methods. Tetrahydrofuran (THF) and diethyl ether (Et\(_2\)O) were distilled from Na/benzophenone. Hexanes, CH\(_2\)Cl\(_2\), and MeCN were distilled from CaH\(_2\). Acetone was dried with potassium carbonate (K\(_2\)CO\(_3\)) 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 \(\text{N}_2\). 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 \(\text{N}_2\)-saturated water, and stored under \(\text{N}_2\).

The \(^1\text{H}\) and \(^{13}\text{C}\) 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 VX-300 spectrometer at room temperature and referenced to selenophene ($\delta=605.0$ ppm). Electrong-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)$_3$, Mn(CO)$_5$(OTf) (OTf = SO$_3$CF$_3$), [Cp*Ru(MeCN)$_3$]OTf$^{25}$ [Cp*IrCl$_2$]$_2$, Sel, 2,2-MeSel, 2,5-Me$_2$Sel. All other compounds were purchased from commercial sources and used as received.

($\eta^5$-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$_2$Cl$_2$/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$_2$O; 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 (CDCl₃): 5.95 (m, J_H-Se = 18.8 Hz, H(2),H(5)), 5.79 (m, H(3),H(4)). ¹³C NMR δ (CDCl₃): 91.82 (s, C(3), C(4)), 91.53 (s, C(2), C(5)), 233.03 (s, CO). ⁷⁷Se NMR δ (CDCl₃): 152.3 (s). IR ν(CO) cm⁻¹ (hexanes): 1984 (s), 1918 (s), 1897 (s). Anal. Calcd for C₇H₄O₃CrSe: C, 31.48; H, 1.51. Found: C, 30.87; H, 1.27.

(η⁵-2-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 (CDCl₃): 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, CH₃). ¹³C NMR δ (CDCl₃): 113.77 (s, C(2)), 92.64 (s,C(4)), 92.59 (s, C(3)), 90.96 (s, C(5)), 18.09 (s, CH₃), 233.2 (s, CO). ⁷⁷Se NMR δ (CDCl₃): 186.1 (s). IR ν(CO) cm⁻¹ (hexanes): 1978 (s), 1912 (s), 1893 (s). Anal. Calcd for C₈H₆O₃CrSe: C, 34.18; H, 2.14. Found: C, 33.99; H, 2.11.

(η⁵-2,5-Me₂Sel)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-Me₂Sel (1.6 g, 10 mmol). 3 (0.77 g, 52% based on Cr(CO)₆) was isolated as a red solid. ¹H NMR δ (CDCl₃): 5.39 (s, H(3), H(4)), 2.29 (s, CH₃). ¹³C NMR δ (CDCl₃): 113.55 (s, C(2),C(5)), 93.31 (s, C(3),C(4)), 18.11 (s, CH₃), 233.9 (s, CO). ⁷⁷Se NMR δ (CDCl₃): 222.2 (s). IR ν(CO) cm⁻¹ (hexanes): 1972 (s), 1905 (s), 1887 (s). Anal. Calcd for C₉H₈O₃CrSe: C, 36.63; H, 2.73. Found: C, 36.58; H, 2.74.

[(η⁵-Sel)Mn(CO)₃](OTf) (4). To a solution of Mn(CO)₅(OTf) (0.0880 g, 0.250 mmol) in Et₂O (50 mL) was added selenophene (0.16 g, 1.2 mmol); the solution was
refluxed under N₂ in the dark for 48 h. The solution turned brown/red and a yellow precipitate formed. After filtration, the yellow precipitate was washed with Et₂O (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 (CD₃NO₂): 7.32 (m, J_H-Se = 18.3 Hz, H(2),H(5)), 6.98 (m, H(3),H(4)). ¹³C NMR δ (CD₃NO₂): 108.10 (s, C(3),C(4)), 101.55 ppm (s, C(2),C(5)), 231.17 (s, CO). ⁷⁷Se NMR δ (CD₃NO₂): 255.9 (s). IR ν(CO) cm⁻¹ (CH₃NO₂): 2075 (s), 2016 (s), 2014 (sh).


[(η⁵-2-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 (CD₃NO₂): 6.91 (d, H(5)), 6.87 (t, H(4)), 6.68 (d, H(3)), 2.58 (s, CH₃). ¹³C NMR δ (CD₃NO₂): 115.4 (s, C(2)), 106.1 (s, C(4)), 101.3 (s, C(3)), 100.6 (s, C(5)), 14.5 (s, CH₃), 232.1 (s, CO). ⁷⁷Se NMR δ (CD₃NO₂): 274.7 (s). IR ν(CO) cm⁻¹ (CH₃NO₂): 2071 (s), 2009 (s).

[(η⁵-2,5-Me₂Sel)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-Me₂Sel (0.16 g, 1.0 mmol). Pale yellow microcrystals of 6 (0.0871 g, 76%) were isolated after drying under vacuum. ¹H NMR δ (CD₃NO₂): 6.45 (s, H(3), H(4)), 2.41 (s, CH₃). ¹³C NMR δ (CD₃NO₂): 128.9 (s, C(2), C(5)), 100.1 (s, C(3), C(4)), 18.0 (s, CH₃), 230.2 (s, CO). ⁷⁷Se NMR δ (CD₃NO₂): 295.1 (s). IR ν(CO) cm⁻¹ (CH₃NO₂): 2068 (s), 2003 (s). Anal. Calcd for C₁₀H₈O₆MnSeSF₃: 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 CH₂Cl₂ (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 Et₂O (20 mL) yielding a yellow crystalline powder (0.056 g, 55%). ¹H NMR δ (d₆-acetone): 6.39 (m, J_H-Se = 17.8 Hz, H(2),H(5)), 5.94 (m, H(3),H(4)), 2.02 (s, CH₃-Cp*). ¹³C NMR δ (d₆-acetone): 89.82 (s, C(3),C(4)), 87.31 (s, C(2), C(5)), 96.76 (s, C-Cp*), 11.05 (s, CH₃-Cp*). ⁷⁷Se NMR δ (CD₃NO₂): 211.9 (s). FAB/MS (CH₂Cl₂/3-nitrobenzyl alcohol matrix): m/e 369 (M⁺). The product was sometimes tan colored, but was purified by adding a CH₂Cl₂ solution of 7 onto a short column of neutral Al₂O₃ (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 CH₂Cl₂ 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 (CDCl₃): 6.51 (d, H(5)), 5.89 (t, H(4)), 5.71 (d, H(3)), 2.28 (s, CH₃), 1.99 (s, CH₃-Cp*). ¹³C NMR δ (CDCl₃): 103.9 (s, C(2)), 89.8 (s, C(4)), 88.6 (s, C(3)), 86.9 (s, C(5)), 15.9 (s, CH₃), 95.6 (s, C-Cp*), 10.9 (CH₃-Cp*). ⁷⁷Se NMR δ (CD₃NO₂): 218.2 (s). FAB/MS (CH₂Cl₂/3-nitrobenzyl alcohol matrix): m/e 383 (M⁺). Anal. Calcd for C₁₆H₂₁RuSeSO₃F₃: C, 36.23; H, 3.99. Found: C, 36.25; H, 3.97.
\[ \text{Cp}^*\text{Ru}(\eta^5-2,5-\text{Me}_2\text{Sel})(\text{OTf}) \ (9) \]. This complex was prepared in the same manner as for 7 from \([\text{Cp}^*\text{Ru}(\text{MeCN})_3](\text{OTf})\) (0.15 g, 0.29 mmol) and 2,5-\text{Me}_2\text{Sel} (0.16 g, 1.0 mmol). Pale yellow microcrystals of 9 (0.096 g, 60%) were isolated after drying under vacuum. \(^1\text{H} \text{NMR} \delta (\text{CDCl}_3): \ 5.69 \ (s, H(3), H(4)), \ 2.26 \ (s, \ CH_3), \ 1.96 \ (s, \ CH_3-\text{Cp}^*). \ 13\text{C} \text{NMR} \delta (\text{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-\text{Cp}^*), \ 9.89 \ (s, \ CH_3-\text{Cp}^*). \ 77\text{Se} \text{NMR} \delta (\text{CD}_3\text{NO}_2): \ 219.8 \ (s). \ \text{FAB/MS} (\text{CH}_2\text{Cl}_2/3\text{-nitrobenzyl alcohol matrix}): m/e 397 (M^+). \ \text{Anal. Calcd for C}_{17}\text{H}_{23}\text{RuSeSO}_3\text{F}_3: C, 37.50; H, 4.26. Found: C, 37.77; H, 4.32.

\[ \text{Cp}^*\text{Ir}(\eta^5-\text{Sel})](\text{BF}_4)_2 \ (10). \] To a solution of \([\text{Cp}^*\text{IrCl}_2]_2\) (0.44 g, 0.55 mmol) in acetone (5.0 mL) was added \(\text{AgBF}_4\) (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 \(\text{Et}_2\text{O}\) (20 mL) which produced a gray-white solid. The solid was filtered from the solution and then redissolved in \(\text{MeNO}_2\) (5 mL). The \(\text{MeNO}_2\) solution was filtered to remove a black insoluble impurity; upon addition of \(\text{Et}_2\text{O}\) (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\text{H} \text{NMR} \delta (\text{CD}_3\text{NO}_2): \ 7.99 \ (dd, J_H-\text{Se} = 16.9 \text{ Hz}, H(2), H(5)), \ 7.70 \ (dd, H(2), H(4)), \ 2.50 \ (s, \ CH_3-\text{Cp}^*). \ 13\text{C} \text{NMR} \delta (\text{CD}_3\text{NO}_2): \ 101.2 \ (s, C(3), C(4)), \ 100.3 \ (s, C(2), C(5)), \ 107.2 \ (s, \ C-\text{Cp}^*), \ 10.7 \ (s, \ CH_3-\text{Cp}^*). \ 77\text{Se} \text{NMR} \delta (\text{CD}_3\text{NO}_2): \ 371.2 \ (s). \ \text{FAB/MS} (3\text{-nitrobenzyl alcohol matrix}): m/e 547 (parent dication + BF_4^-).
[\text{Cp}^*\text{Ir}(\eta^5\text{-2-MeSel})(\text{BF}_4)_2] (11). This compound was prepared from [\text{Cp}^*\text{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 (CD$_3$NO$_2$): 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*). ^13C NMR (CD$_3$NO$_2$): 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*). ^77Se NMR (CD$_3$NO$_2$): 374.7 (s). Anal. Calcd for C$_{15}$H$_{21}$B$_2$F$_8$IrSe: C, 27.88; H, 3.28. Found: C, 27.54; H, 3.13.

[Cp$^*$Ir($\eta^5$-2,5-Me$_2$Sel)](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$_2$Sel (1.40 g, 2.58 mmol). White solid 12 (0.359 g, 49.2%) was obtained. ^1H NMR (CD$_3$NO$_2$): 7.31 (s, H(3), H(4)), 2.74 (s, CH$_3$), 2.42 (s, CH$_3$-Cp*). ^13C NMR (CD$_3$NO$_2$): 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*). ^77Se NMR (CD$_3$NO$_2$): 379.8 (s). Anal. Calcd for C$_{16}$H$_{23}$B$_2$F$_8$IrSe: C, 29.11; H, 3.51. Found: C, 28.83; H, 3.53.

**Reaction of [(\eta^5\text{-Sel})\text{Mn(CO)}_3](\text{OTf}) (4) with Hydride (H$^-$) Sources. Method A. Reaction with NaBH$_4$.** A solution of [(\eta^5\text{-Sel})\text{Mn(CO)}_3](\text{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$_2$SO$_4$. After filtering the yellow solution was chromatographed on an Al$_2$O$_3$/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 $\delta$ (CDCl$_3$): 6.95 (m, $J_{H-Se}$ = 17.4 Hz, H(5)), 6.02 (t, H(4)), 4.00 (dd, $J_{H-Se}$ = 11.7 Hz, H(2, endo)), 3.41 (m, H(3)), 3.07 (d, H(2, exo)). $^{13}$C NMR $\delta$ (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 $\delta$ (CDCl$_3$): -162.3 (s). IR $\nu$(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$_3$OC$_2$H$_4$)$_2$AlH$_2$]). A solution of 0.050 g (0.12 mmol) of [(r$_5$-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 vacuum 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 [(r$_5$-Sel)Mn(CO)$_3$(OTf)] (4) with NaCN. A solution of [(r$_5$-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 Na₂SO₄; the volatiles were removed from this solution under vacuum. The resulting yellow/orange oil was redissolved in hexanes and put onto a hexanes/Al₂O₃ 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 (d₆-acetone): 7.05 (t, Jₕ-Se = 16.4 Hz, H(5)), 6.28 (dd, H(4)), 4.86 (d, Jₕ-Se = 11.8 Hz, H(2, endo)), 3.59 (m, H(3)). ¹³C NMR δ (d₆-acetone): 92.75 (s, C(4)), 78.44 (s, C(5)), 52.13 (s, C(3)), 43.05 (s, C(2)). ⁷⁷Se NMR δ (d₆-acetone): 24.3 (s). IR ν(CO) cm⁻¹ (hexanes): 2028(s), 1954(vs), 1941(s).

**Reaction of [(η⁵-Se₅)RuCp*]OTf (7) with Red-Al (Na[(CH₃OC₂H₄O)₂AlH₂]).** To a suspension of 0.100 g (0.194 mmol) of [(η⁵-Se₅)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 Al₂O₃/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 (CDCl₃): 6.38 (d, Jₕ-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*). ¹³C NMR δ
(CDCl₃): 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, CH₃-Cp*). ⁷⁷Se NMR δ (CDCl₃): 227.3 (s). EIMS exact mass calculated for C₁₄H₂₀⁸₀Se¹⁰²Ru: 369.97735. Found for M⁺: 369.97737

**Reaction of [(η⁵-2,5-Me₂Sel)IrCp*]OTf₂ (12) with Red-Al(Na[(CH₃OC₂H₄O)₂AlH₂]).** To a cooled (0° C) suspension of 0.100 g (0.15 mmol) of [(η⁵-2,5-Me₂Sel)IrCp*]OTf₂ (12) in 10 mL of THF was added dropwise 1.00 mL (0.17 mmol) of a 0.17 M Red-Al (Na[(CH₃OC₂H₄O)₂AlH₂])/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 Al₂O₃/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 (CDCl₃): 7.59 (d, H(3)), 7.49 (d, H(4)), 3.26 (s, CH₃), 2.84 (s, CH₃), 1.87 (s, CH₃-Cp*). ¹³C NMR δ (CDCl₃): 134.9 (s), 132.1 (s), 129.8 (s), 123.3(s), 8.5 (s, CH₃), 8.4 (s, CH₃), 90.7 (s, Cp*), 10.4 (s, CH₃-Cp*). ⁷⁷Se NMR δ (CDCl₃): 905.4 (s).

**X-ray Structure Determination of (η⁵-2,5-Me₂Sel)Cr(CO)₃ (3).** A single crystal of 3 suitable for X-ray diffraction was obtained by vapor diffusion of hexanes into a saturated Et₂O 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 $\eta^5$-Seln Complexes. The complexes ($\eta^5$-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

$$\text{Cr(CO)}_6 + 3 \text{MeCN} \rightarrow \text{Cr(CO)}_3(\text{MeCN})_3 \rightarrow \text{(}$\eta^5$-Seln)Cr(CO)$_3$ $$

1. Seln = Sel
2. Seln = 2-Me$_2$Sel
3. Seln = 2,5-Me$_2$Sel
Cr(CO)$_3$(MeCN)$_3$ with selenophenes are more straightforward and give higher yields of ($\eta^5$-Seln)Cr(CO)$_3$. The pure moderately air-stable red ($\eta^5$-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 $^1$H, $^{13}$C and $^{77}$Se NMR spectral data for 1 are given in Table 4. The $^1$H 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 $^1$H NMR resonances for the analogous thiophene complex ($\eta^5$-T)Cr(CO)$_3$ in CDCl$_3$ [$\delta$ 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$_3$ [$\delta$ 5.95 (m, H(2), H(5)), 5.79 (m, H(3), H(4))].

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

$$\text{Mn(CO)}_5(\text{OTf}) + \text{Seln} \xrightarrow{\text{ether, reflux 48 h in dark}} [(\eta^5\text{-Seln})\text{Mn(CO)}_3]\text{(OTf)} \quad (3)$$

4, Seln = Sel
5, Seln = 2-Me$_2$Sel
6, Seln = 2,5-Me$_2$Sel
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 \([(\eta^5-\text{Th})\text{Mn}(\text{CO})_3]\text{OTf}). 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 $^1\text{H}$ NMR spectrum (Table 4) the selenophene protons in 4 are slightly downfield (-0.2 ppm) as compared with those in the analogous thiophene complex, \([(\eta^5-\text{Th})\text{Mn}(\text{CO})_3]^+ \delta 6.90 (\text{H(2), H(5)}), 6.77 (\text{H(3), H(4)})].\)

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

\[
\begin{align*}
[(\text{MeCN})_3\text{RuCp}^*)\text{OTf} + \text{Seln} & \xrightarrow{\text{CH}_2\text{Cl}_2 - 3 \text{MeCN}} [(\eta^5-\text{Seln})\text{RuCp}^*)\text{(OTf)} \\
7, \text{Seln} = \text{Sel} & \\
8, \text{Seln} = 2-\text{MeSel} & \\
9, \text{Seln} = 2,5-\text{Me}_2\text{Sel} &
\end{align*}
\] (4)

thiophene complexes \([(\eta^5-\text{Th})\text{RuCp}^*)\text{OTf}].\) As was the case for 1 and 4, the $^1\text{H}$ NMR resonances of the Sel in 7 (Table 4) are slightly deshielded as compared with those in the analogous thiophene compound \([(\eta^5-\text{Th})\text{RuCp}^*)^+] in acetone-$d_6 [\delta 6.22 (\text{m, H(3), H(4)}), 6.19 (\text{m, H(2), H(5)}), 2.07 (\text{s, Cp}^*)].\)

Selenophene compounds of the type \([(\eta^5-\text{Seln})\text{IrCp}^*](\text{BF}_4)_2 ((10), (11), and (12)) are prepared by the same method (eq 5) used for the thiophene analogs. These complexes are isolated as white air-stable solids in yields of 41 to 49%. The $^1\text{H}$ NMR chemical shift values for the Sel ligand in 10 (Table
45

\[
[Cp^*\text{Ir}(\text{Cl})_2]_2 + 4 \text{AgOTf} + 2 \text{Seln} \xrightarrow{\text{acetone}} 2 \left[\eta^5-\text{Seln} \text{IrCp}^*\right] \left(\text{OTf}\right)_2
\]

(5)

10, Seln = Sel
11, Seln = 2-MeSel
12, Seln = 2,5-Me Sel

4) are slightly downfield of those of the thiophene analog \([(\eta^5-T)\text{IrCp}^*]^2^+\) 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 \(^1\text{H}, \quad ^{13}\text{C}\) and \(^{77}\text{Se}\) NMR Spectra of 1, 4, 7 and 10. In all of these complexes, the H(2) and H(5) protons are assigned to the \(^1\text{H}\) NMR peaks that exhibit satellites due to \(^1\text{H}-^{77}\text{Se}\) coupling. These coupling constants, \(J_{\text{H-Se}}\), are in a narrow range, 16.9-18.8 Hz (Table 4). No coupling between \(^{77}\text{Se}\) and the protons on C(3) and C(4) is observed in any of the complexes. Peaks in the \(^{13}\text{C}\) 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, \(^1\text{H}\) 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 \(\pi\)-bound in complexes with 0 and +1 charges.

Since \(^{13}\text{C}\) NMR chemical shifts are more sensitive to factors other than complex charge, it is not surprising 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 \(^1\text{H}\) 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\textsuperscript{36} and π-thiophene\textsuperscript{17,24} complexes.

\textbf{\textsuperscript{77}Se NMR Studies of $\eta^5$-Sel.} A goal of the studies described in this report is to determine the usefulness of \textsuperscript{77}Se NMR spectroscopy for establishing the mode of selenophene binding in transition metal complexes and on catalyst surfaces. The \textsuperscript{77}Se nucleus has a natural abundance of 7.58\% and a relative receptivity that is 2.98 times larger than \textsuperscript{13}C, with a chemical shift range of more than 3000 ppm\textsuperscript{20}. The \textsuperscript{77}Se NMR chemical shift values of the $\eta^5$-Sel complexes are given in Table 4 and Figure 4. It is evident that the \textsuperscript{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 \textsuperscript{77}Se chemical shift of the coordinated selenophene ring; increasing the number of methyl groups in the 2- and 5-positions causes the \textsuperscript{77}Se chemical shift to move downfield. A similar trend occurs for the free ligands in CDCI\textsubscript{3}: Sel(\delta 605) > 2-MeSel (\delta 612) > 2,5-Me\textsubscript{2}Sel (\delta 621)\textsuperscript{20,21}.

\textbf{Molecular Structure of $(\eta^5$-2,5-Me\textsubscript{2}Sel)Cr(CO)\textsubscript{3}.} The ORTEP drawing of $(\eta^5$-2,5-Me\textsubscript{2}Sel)Cr(CO)\textsubscript{3} (3) is given in Figure 2. The 2,5-Me\textsubscript{2}Sel complex was chosen for the structural study in order to avoid the disorder previously found in the analogous thiophene complex $(\eta^5$-T)Cr(CO)\textsubscript{3}\textsuperscript{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 (η⁵-T)Cr(CO)₃\(^3\) and (η⁵-2,5-Me₂T)Cr(CO)₃\(^1\). 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 (η⁵-2,5-Me₂T)Cr(CO)₃. Other dihedral angles for thiophene rings are reported for the following complexes: Ru(Me₄T)₂²⁺ (5.0(0.5)° and 3.7(1.5)°), and \{[(η⁵-Me₄T)RuCl]₃S\}⁺ (11.8(1.9)°, 13.4(1.9)°, and 13.7(1.9)°).\(^3\) The C-Se bond distances (1.899(8) and 1.912(7) Å) in the 2,5-Me₂Sel ring in 3 are slightly longer than that (1.855(7) Å) in free selenophene.\(^1\) The C-Se distances in 3 are approximately 0.15 Å longer than the C-S distances in (η⁵-2,5-Me₂T)Cr(CO)₃ due to the larger size of the selenium heteroatom. The ring C-C bond distances in the coordinated 2,5-Me₂Sel are within experimental error the same as in (η⁵-2,5-Me₂T)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 (η⁵-2,5-Me₂T)Cr(CO)₃, again presumably due to the larger size of Se. The Cr-Se distances in Cr(CO)₄(CN(Et)₂)(SeC₆H₄F)\(^3\) (2.562(2) Å) and [CrCp(NO)(μ²-SeC₆H₅)]₂\(^4\) (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 (η⁵-2,5-Me₂T)Cr(CO)₃ are the same within experimental error.

**Reactions of η⁵-Sel Complexes.** Previously, it was reported\(^1,2\) that the η⁵-thiophene ligand in (η⁵-T)Mn(CO)₃⁺ is attacked at the 2-position by a hydride donor (BH₄⁻, HFe(CO)₄⁻) to give the product (η⁴-T•H)Mn(CO)₃ in which three
carbons and the sulfur are coordinated to the Mn. The same reaction of [(η⁵-Sel)Mn(CO)₃]⁺ (4) with one equivalent of NaBH₄ or Red-Al as the hydride source gives the analogous product (η⁴-Sel•H)Mn(CO)₃ (4a) which is isolated in 80-90% (Scheme 1). The ¹H NMR spectrum of 4a in CDCl₃ contains signals for the five hydrogens on the ring as follows: δ 6.95 (m, J_H-Se = 17.4 Hz, H(5)), 6.02 (t, H(4)), 4.00 (dd, J_H-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 (η⁴-T•H)Mn(CO)₃ in d₆-acetone (not in CDCl₃ as originally reported²⁴): 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 ⁷⁷Se to H(2, endo) (²J_H-Se = 11.7 Hz) and H(5) (²J_H-Se = 17.4 Hz) indicates that the ring C-Se bonds remain intact. Coupling is not seen between ⁷⁷Se and H(2, exo) presumably due to the angle between the atoms. Integration of the ²H NMR spectrum of the product resulting from the reaction of 4 with NaBD₄ shows a of 6.4:1.0 ratio of products resulting from exo and endo attack. In the corresponding reaction of [(η⁵-T)Mn(CO)₃]⁺ with NaBD₄ the ratio of exo to endo attack was 3.6:1.0.¹¹ It is interesting to note that the ⁷⁷Se 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 CH₂Cl₂ results in the loss of H⁻ to give back complex 4 in quantitative yield.

Other nucleophiles (CN⁻, PR₃ 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. The reaction of 4 with NaCN, carried out in the same manner as described for the analogous reaction of \( (\eta^5-T)\text{Mn(CO)}_3^+ \) with NaCN, gives a yellow oil (4b) after evaporation under vacuum. The \(^1\text{H NMR}\) spectrum of 4b in d\(_6\)-acetone [\( \delta \) 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 \(^{77}\text{Se}\) 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 \( (\eta^4-T\cdot\text{CN})\text{Mn(CO)}_3 \) in d\(_6\)-acetone [\( \delta \) 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 \(^{13}\text{C NMR}\) spectrum of 4b in d\(_6\)-acetone [\( \delta \) 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 \( (\eta^4-T\cdot\text{CN})\text{Mn(CO)}_3 \) in d\(_6\)-acetone (\( \delta \) 93.08, 69.89, 53.10, 50.77). An upfield shift of 231 ppm for the Sel\( \cdot \)CN ligand in 4b (\( \delta \) 24.3) is observed in the \(^{77}\text{Se}\) NMR spectrum when compared to the chemical shift of the starting material 4 (\( \delta \) 255.9). Thus, the NMR results suggest that 4b is \( (\eta^4-\text{Sel}\cdot\text{CN})\text{Mn(CO)}_3 \) in which the CN\(^-\) nucleophile has added to the 2-exo-position of Sel (Scheme 1). Comparison of the IR spectrum of 4b (\( \nu\text{(CO)} \) (hexanes): 2028 (s), 1954 (vs), 1941 (s) cm\(^{-1}\)) with that of \( (\eta^4-T\cdot\text{CN})\text{Mn(CO)}_3 \) (\( \nu\text{(CO)} \) (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 \( ((M^+) \text{ m/z} = 297) \).

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•PR₃)Mn(CO)₃⁺ which were not sufficiently stable to be isolated. The analogous reaction of 4 with P(n-Bu)₃ gave (η⁴-Sel•PBu₃)Mn(CO)₃⁺ (4c) which decomposed upon attempted isolation. The ¹H NMR spectrum of 4c in d₆-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 (v(CO); 2019 (vs), 1938 (s), 1923 (s) cm⁻¹) are very similar to those previously reported for (η⁴-T•PBu₃)Mn(CO)₃⁺. The ⁷⁷Se NMR spectrum of 4c shows a doublet at δ -60 (Jₜₛₑ-P = 5 Hz) due to the coupling of ⁷⁷Se to ³¹P. Other basic phosphines such as PMe₃ and PEt₃ 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 [(η⁵-T)Mn(CO)₃]⁺, hydride addition at C(2) in [(η⁵-T)RuCp]⁺ results in cleavage of a C-S bond. The analogous reaction of [(η⁵-Sel)RuCp⁺]⁺ (7) with hydride (Na[(H₃COC₂H₄O)₂AlH₂]) also causes C-Se bond cleavage to give the complex (SeCH=CHCH=CH₂)RuCp⁺ (7a) in 30% yield (Scheme 1). The ¹H NMR spectrum of 7a in CDCl₃ shows five resonances assignable to the protons of the coordinated selenide/diene ligand (δ 6.38 (d, Jₜₛₑ = 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=CH₂)RuCp⁺. 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 ⁷⁷Se. However, coupling is observed between the proton on C(5) and ⁷⁷Se, with Jₜₛₑ (16.5 Hz) approximately the same as that (Jₜₛₑ = 17.4 Hz) for the proton on C(5) in 4a. In the ¹³C 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 [(η⁵-2,5-Me₂T)IrCp*]²⁺ with Na[(CH₃OC₂H₄O)₂AlH₂] or the reducing agent Cp₂Co gives the neutral complex (η⁴-2,5-Me₂T)IrCp*, in which the η⁴-2,5-Me₂T ligand is coordinated to the metal only through the four carbon atoms. This η⁴-complex rearranges in the presence of base to give the ring-opened product (C,S-2,5-Me₂T)IrCp* in which the Ir is inserted into a C-S bond to give a planar 6-membered ring. The analogous reaction of [(η⁵-2,5-Me₂Sel)IrCp]²⁺ (12) with two equivalents of Na[(CH₃OC₂H₄O)₂AlH₂] gives the ring-opened complex (C,Se-2,5-Me₂Sel)IrCp*(12a) (Scheme 1) as the only isolable product in low yield (17%). The ¹H NMR spectrum of 12a in CDCl₃ 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-Me₂T)IrCp*, which has a planar 6-membered π-delocalized ring that has been described as an iridathiabenzene. The ¹³C NMR spectrum of 12a in CDCl₃ 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 ⁷⁷Se 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 ((SeCH-CH-CH-CH)⁺). This similarity in ⁷⁷Se NMR chemical shift further supports the description of the six-membered ring in 12a as a delocalized π-system making 12a an iridaselebenzene compound. The ¹H, ¹³C and ⁷⁷Se 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-Me2T)IrCp*.

Conclusions

The synthesis of several new η5-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 η5-Th complexes. The 1H and 13C NMR and IR spectroscopic data for the η5-Seln complexes (1-12) are very similar to those of the analogous η5-Th complexes. Reactions of the η5-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 η5-T complexes. Differences between the structures of (η5-2,5-Me2Sel)Cr(CO)3 and (η5-2,5-Me2T)Cr(CO)3 are mostly due to the larger size of the Se as compared to S. The 77Se chemical shifts of these η5-Seln complexes all fall within the region between δ 375 and 150, the more positive the charge on the complex the more downfield the 77Se signal. The observation that the 77Se 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 77Se NMR spectroscopy may be a useful probe for detecting η5-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 RuCl3 and IrCl3.
References


(33) Spies, G. H.; Angelici, R. J. *Organometallics* 1987, 6, 1897.


Table 1. Crystal and Data Collection Parameters for 
$(\eta^5$-2,5-Me2Sel)Cr(CO)$_3$ (3)

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$R_w^b$ 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 (\(\eta^5\)-2,5-Me\(_2\)Sel)Cr(CO)\(_3\) (3)

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\(^a\) Numbers in parentheses are estimated standard deviations in the least significant digits.
Table 3. Positional and Thermal Parameters for (η^5-2,5-Me2Sel)Cr(CO)_3 (3)

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<tbody>
<tr>
<td>Cr</td>
<td>0.50022(1)</td>
<td>0.20323(6)</td>
<td>0.33291(5)</td>
<td>2.83(1)</td>
</tr>
<tr>
<td>Se</td>
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<td>0.19014(4)</td>
<td>0.43137(4)</td>
<td>3.62(1)</td>
</tr>
<tr>
<td>C(1)</td>
<td>0.7793(7)</td>
<td>-0.0172(4)</td>
<td>0.3195(4)</td>
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<tr>
<td>C(2)</td>
<td>0.7586(6)</td>
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<td>0.3093(4)</td>
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</tr>
<tr>
<td>C(3)</td>
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<td>0.2177(4)</td>
<td>3.7(1)</td>
</tr>
<tr>
<td>C(4)</td>
<td>0.6987(7)</td>
<td>0.2731(4)</td>
<td>0.2323(4)</td>
<td>4.1(1)</td>
</tr>
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<td>C(5)</td>
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<tr>
<td>C(6)</td>
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<td>0.4211(4)</td>
<td>0.3809(5)</td>
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</tr>
<tr>
<td>C(7)</td>
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<td>0.3011(4)</td>
<td>0.4134(4)</td>
<td>3.8(1)</td>
</tr>
<tr>
<td>C(8)</td>
<td>0.2733(7)</td>
<td>0.2132(4)</td>
<td>0.2251(4)</td>
<td>3.5(1)</td>
</tr>
<tr>
<td>C(9)</td>
<td>0.3770(6)</td>
<td>0.0914(4)</td>
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<td>3.5(1)</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.3321(5)</td>
<td>0.3648(3)</td>
<td>0.4626(3)</td>
<td>5.68(9)</td>
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<tr>
<td>O(2)</td>
<td>0.1280(5)</td>
<td>0.2170(3)</td>
<td>0.1580(3)</td>
<td>5.12(9)</td>
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<tr>
<td>O(3)</td>
<td>0.2934(5)</td>
<td>0.0203(3)</td>
<td>0.4140(3)</td>
<td>5.20(9)</td>
</tr>
</tbody>
</table>

^a Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: \(4/3 \times [a^2 \times B(1,1) + b^2 \times B(2,2) + c^2 \times B(3,3) + ab \times \cos \gamma \times B(1,2) + ac \times \cos \beta \times B(1,3) + bc \times \cos \alpha \times B(2,3)]\).
Table 4. Spectroscopic Data for $\eta^5$-Coordinated Selenophene (Sel) in $(\eta^5$-Sel)Cr(CO)$_3$ (1),

[(η⁵-Sel)Mn(CO)₃]+ (4), [(η⁵-Sel)RuCp*]+ (7), and [(η⁵-Sel)IrCp*]²⁺ (10)

<table>
<thead>
<tr>
<th>Compound (Solvent)</th>
<th>$^1$H NMR (δ in ppm)</th>
<th>$^{13}$C NMR (δ in ppm)</th>
<th>$^{77}$Se NMR (δ in ppm)</th>
<th>IR (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (CDCl₃)</td>
<td>5.95 (m, H(2), H(5))ᵃ</td>
<td>91.53 (s, C(2), C(5))</td>
<td>152.3</td>
<td>1984(s)</td>
</tr>
<tr>
<td></td>
<td>5.79 (m, H(3), H(4))</td>
<td>91.82 (s, C(3), C(4))</td>
<td></td>
<td>1918(s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>233.03 (CO)</td>
<td></td>
<td>1897(s)</td>
</tr>
<tr>
<td>4 (CD₃NO₂)</td>
<td>7.32 (s, H(2), H(5))ᵇ</td>
<td>101.55 (s, C(2), C(5))</td>
<td>255.9</td>
<td>2075(s)</td>
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<tr>
<td></td>
<td>6.98 (s, H(3), H(4))</td>
<td>108.10 (s, C(3), C(4))</td>
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<td>2016(s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>231.17 (CO)</td>
<td></td>
<td>2014(sh)</td>
</tr>
<tr>
<td>7 (d₆-acetone)</td>
<td>6.39 (m, H(2), H(5))ᶜ</td>
<td>87.31 (s, C(2), C(5))</td>
<td>211.9</td>
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<tr>
<td></td>
<td>5.94 (m, H(3), H(4))</td>
<td>89.82 (s, C(3), C(4))</td>
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</tr>
<tr>
<td></td>
<td>2.02 (s, CH₃-Cp*)</td>
<td>96.76 (Cp*), 11.05 (Cp*)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 (CD₃NO₂)</td>
<td>7.99(dd, H(2),H(5))ᵈ</td>
<td>100.3 (s, C(2), C(5))</td>
<td>371.2</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td>7.70(dd, H(3), H(4))</td>
<td>101.2 (s, C(3), C(4))</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.50(s, CH₃-Cp*)</td>
<td>107.2 (Cp*), 10.7 (Cp*)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sel (CDCl₃)</td>
<td>7.88(d, H(2),H(5))</td>
<td>129.4 (s, C(2), C(5))</td>
<td>605.0</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td>7.23(d, H(3), H(4))</td>
<td>130.4 (s, C(3), C(4))</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ᵃ JH-Se = 18.8 Hz. ᵇ JH-Se = 18.3 Hz. ᶜ JH-Se = 17.8 Hz. ᵈ JH-Se = 16.9 Hz.
Figure 1. Structures and numbering of thiophene and selenophene.
Figure 2. ORTEP Drawing of (η^5-2,5-Me2Sel)Cr(CO)_3 (3)
Figure 3. $^1$H and $^{13}$C NMR Chemical shifts of selenophene in complexes (1), (4), (7), and (10).
Figure 4. NMR Chemical shift data for \( \eta^5 \)-Selen complexes (1-12).

\[
\text{ppm}
\]

\[
(\eta^5\text{-Selen})\text{Cr(CO)}_3
g (\eta^5\text{-Selen})\text{Ru(Cp)}^*\]

\[
(\eta^5\text{-Selen})\text{Mn(CO)}_3^+
g (\eta^5\text{-Selen})\text{Ir(Cp)}^*\]

\[
(\eta^5\text{-Selen})\text{Cr(CO)}
g \text{Selen}
\]
Scheme 1

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

7a
12b
SYNTHESIS, EQUILIBRIUM BINDING AND $^{77}$Se NMR STUDIES OF $\eta^{1}$-SELENOPHENE (SELN) COMPLEXES: [CpRu(CO)(PPh$_3$)($\eta^{1}$(Se)-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$_5$H$_5$) with Ag$^+$ and selenophenes (SEln) produce the stable selenium-bound ($\eta^{1}$(Se)) selenophene complexes [Cp(CO)(PPh$_3$)Ru($\eta^{1}$(Se)-SEln)]$^+$ (SEln = selenophene (Sel), 2-methylselenophene(2-MeSel) and 2,5-dimethylselenophene (2,5-Me$_2$Sel)). The molecular structure of Cp(CO)(PPh$_3$)Ru($\eta^{1}$(Se)-2-MeSel)$^+$ was determined and $^1$H, $^{13}$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-dimethyl dibenzothiophene (2,8-Me$_2$DBT), and $p$-tolyl sulfide (PTS) increase in the order: T(1.00) < 2,5-Me$_2$T (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$_2$Sel (175) < 2,8-Me$_2$DBT (358) < PTS (7.11 x 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$_2$DBT. A $^{77}$Se NMR study of free selenophenes and their complexes establishes $^{77}$Se chemical
shift ranges that are characteristic of $\eta^1$(Se), $\eta^2$, and $\eta^5$ 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. Based on studies of model organometallic complexes, two modes for thiophene (T) binding, $\eta^5$ and $\eta^1$(S), are most common. Equilibrium studies of the adsorption of thiophenes on a Co/Mo/Al$_2$O$_3$ 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$_2$T. In the organometallic model complexes [CpRu($\eta^5$-Th)]$^+$, where Th is thiophene or its methyl-substituted derivatives, equilibrium constants for $\eta^5$ binding of Th increase in the same order, which is consistent with $\eta^5$ binding on the Co/Mo/Al$_2$O$_3$ catalyst. Support for this mode of adsorption can also be found in the results of reactivity studies conducted on $\eta^5$-thiophene complexes.

The $\eta^1$(S)-thiophene coordination mode occurs in several complexes including [CpRu(CO)(PPh$_3$)($\eta^1$(S)-Th)]$^+$, [CpRu(CO)$_2$($\eta^1$(S)-Th)]$^+$, and CpRe(CO)$_2$($\eta^1$(S)-Th). Equilibrium constants ($K'$) for thiophene ligand exchange in [CpRu(CO)$_2$($\eta^1$(S)-Th)]$^+$ show that $\eta^1$(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$_2$T. This is essentially the same order as that for thiophene adsorption on the Co/Mo/Al$_2$O$_3$ catalyst. Thus, equilibrium constants for the binding of both $\eta^5$- and $\eta^1$(S)-thiophenes...
follow the same trend as that observed on the HDS catalyst. Kinetic studies of 
\( \eta^1(S) \)-thiophene dissociation from \([\text{CpRu(CO)}_2(\eta^1(S)-\text{Th})]^+\), and 
\([\text{CpRe(CO)}_2(\eta^1(S)-\text{Th})]^{13}\) show that the rate of Th dissociation increases as the 
number of methyl groups decreases: 2,5-Me\(_2\)T < 2-MeT < 3-MeT < T. All of 
these studies indicate that \( \eta^1(S) \)-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 \( \sigma \)-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 \(^{77}\text{Se} \) NMR chemical shifts of a series of \( \eta^5 \)-selenophene 
complexes: \((\eta^5-\text{Sel})\text{Cr(CO)}_3\),\(^{16,17}\) \([\eta^5-\text{Sel}]*\text{Mn(CO)}_3]^+\), \([\text{Cp}^*\text{Ru}(\eta^5-\text{Sel})]^+ \), and 
\([\text{Cp}^*\text{Ir}(\eta^5-\text{Sel})]^2^+\). The \( \eta^5 \)-Sel complexes are structurally and chemically very 
similar to the analogous \( \eta^5 \)-thiophene complexes. \(^{77}\text{Se} \) NMR chemical shift 
values for \( \eta^5 \)-coordinated Sel fall into the region between \( \delta \) 370 and \( \delta \) 150. 
Within this range the \(^{77}\text{Se} \) 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 \( \text{Cp'}\text{Re(CO)}_2(\text{Seln}) \) (Cp' = Cp or Cp*).\(^{14,18}\) 
In the electron-rich complex \( \text{Cp}^*\text{Re(CO)}_2(\text{Seln}) \) (Cp* = \( \eta^5-C_5\text{Me}_5 \)), selenophene 
(Sel) is \( \eta^2 \)-coordinated through a C=C double bond. In the 2,5-
dimethylselenophene (2,5-Me\(_2\)Sel) complex \( \text{Cp}^*\text{Re(CO)}_2(2,5-\text{Me}_2\text{Sel}) \), the ligand 
is coordinated through the Se atom in an \( \eta^1(\text{Se}) \)-manner. When the 
selenophene ligand is 2-methylselenophene (2-MeSel), both the \( \eta^1(\text{Se}) \) and \( \eta^2 \)
isomers are observed and they are in equilibrium with each other (eq 1).
Replacement of the Cp* ligand with the less electron donating Cp (η5-C5H5) ligand increases the equilibrium amount of the η1(Se) isomer and decreases the amount of the η2 isomer. This shift in isomer distribution is reasonable since a decrease in the electron-density on the metal would reduce π backbonding to the olefin in the η2 isomer but would strengthen selenium to rhenium donation in the η1(Se) isomer.19,20

In this paper, we present the synthesis and characterization of several new η1(Se)-selenophene complexes [CpRu(CO)(PPh3)(η1(Se)-Seln)]BF4 (Seln = selenophene (Sel), 2-methylselenophene (2-MeSel), or 2,5-dimethylselenophene (2,5-Me2Sel)). The X-ray-determined structure of [CpRu(CO)(PPh3)(η1(Se)-2-MeSel)]BF4 is described and compared with that of the analogous thiophene complex. Equilibrium constants for the ligand replacement reaction (eq 2)

\[
[CpRu(CO)(PPh3)(L)]^+ + L' \xrightarrow{25^\circ C} L + [CpRu(CO)(PPh3)(L')]^+ \quad (2)
\]

are reported and are compared with those of the analogous η1(S)-thiophene complexes [CpRu(CO)(PPh3)(η1(S)-Th)]+.11 Finally, 77Se NMR chemical shift
values for the new $\eta^1$(Se)-Seln complexes are discussed in relation to those of selenophene in its $\eta^5$ and $\eta^2$ 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. 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$_2$O) were distilled from Na/benzophenone. Hexanes and dichloromethane (CH$_2$Cl$_2$) were distilled from CaH$_2$. Acetone was dried with potassium carbonate (K$_2$CO$_3$) and distilled. The solvents were used immediately after distillation except for acetone which was stored over K$_2$CO$_3$ 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 $^1$H 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$_2$Cl$_2$ ($\delta = 5.33$). The $^{77}$Se NMR spectra were recorded on the Varian VXR-300 spectrometer at room temperature and referenced to selenophene ($\delta = 605.0$ 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: 

\[ \text{CpRu(CO)(PPh}_3\text{Cl)} \] \[ \text{[CpRu(CO)(PPh}_3\text{)(Th)]BF}_4 \] (Th = thiophene (T), 2-methylthiophene (2-MeT), 2,5-dimethylthiophene (2,5-Me₂T), benzothiophene (BT), and dibenzothiophene (DBT)), \[ \text{selenophene (Sel)} \], \[ \text{2-MeSel} \], \[ \text{2,5-Me}_2\text{Sel} \], \[ \text{p-tolyl sulfide (PTS)} \], \[ \text{2,8-dimethyl dibenzothiophene (2,8-Me}_2\text{DBT)} \]. All other compounds were used as received from commercial sources.

\[ \text{[Cp(CO)(PPh}_3\text{)Ru(\eta^1(Se)-Sel)](BF}_4 \] (1). To a stirred solution of 1.00 mL of Sel and 0.103 g (0.209 mmol) of Cp(CO)(PPh₃)RuCl in 20 mL of CH₂Cl₂ was added 0.056 g (0.288 mmol) of AgBF₄. 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 CH₂Cl₂; upon addition of 20 mL of Et₂O, product 1 precipitated as a yellow powder. The powder was filtered and washed with 10 mL of Et₂O three times and dried under vacuum. Yield of 1: 0.167 g, 86%. ¹H NMR δ (CD₂Cl₂) 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). ¹³C NMR δ (CD₂Cl₂): 200.74 (d, J_C-P = 18.33 Hz, CO), 141.60 (d, J_C-P = 2.3 Hz, 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-C = 1.34 Hz, Cp). ⁷⁷Se NMR δ (CD₂Cl₂): 411.6 (d, J_Se-P = 12 Hz). IR cm⁻¹ (CH₂Cl₂): 1991. Anal. Calcd for C₂₈H₂₄O₃RuSeBF₄: 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 CH₂Cl₂ layered with a 5-7 fold excess of Et₂O at -20 °C overnight; this yielded bright yellow crystals.

\[ \text{[Cp(CO)(PPh₃)Ru(\eta^1(Se)-2-MeSel)](BF₄)} \] (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)(PPh₃)RuCl and 0.056 g (0.29 mmol) of AgBF₄. Yellow crystals of 2 were obtained (0.161 g, 81%). ¹H NMR δ (CD₂Cl₂): 7.35(H(5)), 7.10(m, H(4)), 6.89(m, H(3)), 2.47(s, CH₃), 4.87(s, Cp), 7.65-7.30(m, Ph). ¹³C NMR δ (CD₂Cl₂): 200.6(d, Jc-P = 17.42 Hz, CO), 157.93(d, Jc-P = 4.6 Hz, 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). ⁷⁷Se NMR δ (CD₂Cl₂): 427.4(d, JSe-P = 12 Hz). IR cm⁻¹ (CH₂Cl₂): 1988. FAB Mass Spectrum 601.0 (M⁺), 456.9 (M⁺ - 2-MeSel). Anal. Calcd for C₂₉H₂₆O₃RuSeBF₄: C, 50.44; H, 3.81. Found: C, 49.97; H, 3.78.

\[ \text{[Cp(CO)(PPh₃)Ru(\eta^1(Se)-2,5-Me₂Sel)](BF₄)} \] (3). Compound 3 was synthesized in the same manner as 1 using 1.00 mL of 2,5-Me₂Sel, 0.103 g (0.209 mmol) of Cp(CO)(PPh₃)RuCl and 0.056 g (0.288 mmol) of AgBF₄. Yellow crystals of 3 were obtained (0.170 g, 84%). ¹H NMR δ (CD₂Cl₂): 6.64(s, H(3), H(4)), 2.22 (s, CH₃), 4.88(s, Cp), 7.63-7.35(m, Ph). ¹³C NMR δ (CD₂Cl₂): 201.4(d, Jc-P = 19.23 Hz, CO), 154.2(d, Jp-C = 19.2 Hz, C(2), C(5)), 131.13(s, C(3), C(4)), 17.50(CH₃), 133.33(d, Ph), 132.75(s, Ph), 132.03(d, Ph), 129.71(d, Ph), 88.0(Cp). ⁷⁷Se NMR δ (CD₂Cl₂): 444.0(d, JSe-P = 12 Hz). IR cm⁻¹ (CH₂Cl₂): 1987. FAB Mass Spectrum: 616.8 (M⁺), 456.9 (M⁺ - 2,5-Me₂Sel). Anal. Calcd for C₃₀H₂₈O₃RuSeBF₄: C, 51.30; H, 4.02. Found: C, 50.82; H, 4.09.
[Cp(CO)(PPh3)Ru(\eta^1(S)-2,8-Me2DBT)]BF4 (4). Compound 4 was made using the same method previously published\textsuperscript{11} for the synthesis of [Cp(CO)(PPh3)Ru(\eta^1(S)-DBT)]S03CF3 substituting 2,8-Me2DBT for DBT. The reaction utilized 0.100 g (0.203 mmol) of CpRu(CO)(PPh3)Cl, 0.129 g (0.609 mmol) of 2,8-Me2DBT, and 0.400g (0.205 mmol) of AgBF4. The product 4 was isolated as a yellow solid. Yield: 0.126 g, 76%. \textsuperscript{1}H NMR (CD2Cl2): 7.87(s, DBT), 2.52(s, CH3), 7.59-7.35(m, PPhs), 4.72(s, Cp). IR cm\textsuperscript{-1} (CH2Cl2): 1992. Anal. Calcd for C38H35OPRUSBF4 • 0.2 CH2Cl2; C, 60.01; H, 4.16. Found: C, 60.21; H, 4.15.

[Cp(CO)(PPh3)Ru(\eta^1(S)-(p-H3CC6H4)2S)]S03CF3 (5). A solution of 0.100 g (0.203 mmol) of CpRu(CO)(PPh3)Cl and 0.053 g (0.21 mmol) AgOTf in 20 mL of CH2Cl2 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-H3CC6H4)2S) (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 CH2Cl2; 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 N2 and finally under vacuum. Yield: 0.153 g (92%, based on Ru). \textsuperscript{1}H NMR δ (CD2Cl2): 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, CH3). IR cm\textsuperscript{-1} (CH2Cl2): 1992. Anal. Calcd for C39H37O4PRuS2F3: C, 57.14; H, 4.18. Found: C, 57.95; H, 4.52.
X-ray Structure Determination of [CpRu(CO)(PPh3)(η1-Se)-2-MeSe]BF4 (2). A single crystal of 2 suitable for X-ray diffraction study was obtained by vapor diffusion of Et2O into a saturated CH2Cl2 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)(PPh3)Ru(L)]+ complex was placed in a 5 mm NMR tube, then dissolved in 0.5 mL of CD2Cl2 and an equimolar amount of the incoming ligand (L') was added under N2. 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; CD₂Cl₂ 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 ICp are the Cp peak integrals of Cp(CO)(PPh₃)Ru(L')⁺ and

\[
K = \frac{\left( \frac{I'_Cp}{5} \right)^2}{\left( \frac{I_Cp}{5} \right) \left( \frac{I_{Me}}{x} \right)} = \frac{[Cp(CO)(PPh₃)Ru(Th')⁺][Th]}{[Cp(CO)(PPh₃)Ru(Th')][Th']}
\]

Cp(CO)(PPh₃)Ru(L)⁺, respectively; IMe 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-Me₂T, 2,5-Me₂Sel, 2,8-Me₂DBT, 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)(PPh₃)(η¹(Se)-Seln)]⁺ Complexes (1-3).** The compounds [CpRu(CO)(PPh₃)(η¹(Se)-Seln)]BF₄ (Seln = Sel (1), 2-
MeSel (2), or 2,5-Me₂Sel (3)) were synthesized from CpRu(CO)(PPh₃)Cl, AgBF₄ and the appropriate ligand in CH₂Cl₂ (eq 4). The halide extraction method has

\[ \text{CpRu(CO)(PPh₃)Cl} + \text{Seln} \rightarrow \text{[CpRu(CO)(PPh₃)(η¹(Se)-Seln)]}^+ + \text{AgCl} \]  

\[ \text{eq 4} \]

been used previously to make a variety of cationic ruthenium complexes [CpRu(CO)(PPh₃)(L)]⁺ (L = PR₃, CO²⁴, Th¹¹,¹²). 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)(PPh₃)(η¹(S)-T)]BF₄. 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 CD₂Cl₂ 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)(PPh₃)(η¹(S)-2,5-Me₂T)]⁺ 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\textsuperscript{31} such as ReCl(CO\textsubscript{3})(EMe\textsubscript{2})\textsubscript{2} and PtBr(Me)(EMe\textsubscript{2})\textsubscript{2} the inversion barrier is also lower in the S than the Se analog. A low temperature \textsuperscript{1}H NMR spectrum of 1 in CD\textsubscript{2}Cl\textsubscript{2} shows only a slight broadening of the proton resonances at the freezing point (178 K) of CD\textsubscript{2}Cl\textsubscript{2}; this indicates that the T\textsubscript{c} for 1 is lower than 178 K. The lower T\textsubscript{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 \textsuperscript{1}H/\textsuperscript{13}C HETCOR NMR spectrum. It was necessary to use this 2D technique because of overlapping \textsuperscript{1}H resonances from the PPh\textsubscript{3} and the 2-MeSel ligands.

The \textsuperscript{13}C NMR spectra of 1-3 were assigned using the 2D \textsuperscript{1}H/\textsuperscript{13}C HETCOR NMR technique because resonances for both the Seln and the PPh\textsubscript{3} ligands occurred in the same region. The \textsuperscript{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 \textsuperscript{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.\textsuperscript{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.\textsuperscript{11}

The ν(CO) band in the IR spectra of 1-3 is consistently 8-10 cm\textsuperscript{-1} smaller than in the corresponding thiophene complexes,\textsuperscript{11} which suggests that
selenophene is a better sigma donor ligand than thiophene.

**Molecular Structure of** [CpRu(CO)(PPh3)(η¹(Se)-2-MeSel)]BF₄ **(2).** The X-ray determined molecular structure of the cation [CpRu(CO)(PPh₃)(η¹(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)(PPh₃)(η¹(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 (η⁵-2,5-Me₂Sel)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)(PPh₃)(η¹(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)(PPh₃)(η¹(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 \([\text{CpRu(CO)(PPh}_3\text{(L)}]^+\) 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 \(\text{Th}^{11}\) 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\(^{11}\)

\[
\text{CpRu(CO)(PPh}_3\eta^1\text{(S)-T})^+ + L' \xrightleftharpoons{25^\circ \text{C}}^{\text{CD}_2\text{Cl}_2} \text{CpRu(CO)(PPh}_3\text{L'})^+ + \text{Th} \tag{5}
\]

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\(_2\)T (2.76) < 2-MeT (4.11) < 3-MeT (6.30) < Me\(_4\)T (57.4) < BT (29.9) < DBT (74.1) << THT (>7.1\times10^6). 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 \(\sigma\)-donor to the Ru. However, two methyl groups in the 2 and 5 positions reduce the coordinating ability of the 2,5-Me\(_2\)T, as
compared with 2-MeT and 3-MeT, due to steric crowding between one of the methyl groups and the bulky PPh₃ ligand. The addition of two more methyl groups in the uncrowded 3 and 4 positions of 2,5-Me₂T makes Me₄T 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-Me₂Sel (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-Me₂Sel presumably results from the larger size of Se, as compared with S, which moves the 2,5-methyl groups away from the bulky PPh₃, as noted in the discussion of the structure of [CpRu(CO)(PPh₃)(2-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-Me₂Sel binds 63.4 times more strongly than 2,5-Me₂T due to crowding in the 2,5-Me₂T complex.

For the dibenzothiophene-related ligands, the K' values increase in the order: DBT (74.1) < 2,8-Me₂DBT (358) < PTS (7.11 x 10³). The larger K' for 2,8-Me₂DBT 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-Me₂DBT. The DBT and 2,8-Me₂DBT 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-Me₂DBT as compared with
PTS. It is also possible that PTS is a less bulky ligand than 2,8-Me2DBT because of its ability to rotate around the S-tolyl bonds.

**77Se NMR Studies of Coordinated Selenophenes.** As part of an investigation of 77Se chemical shifts of selenophenes and their complexes, we determined the 77Se chemical shifts of the $\eta^1$(Se)-selenophene complexes $[\text{CpRu(CO)}(\text{PPh}_3)(\eta^1(\text{Se})-\text{Seln})]^{\dagger}$; these values are reported in the Experimental Section. They are also plotted in Fig. 3 with those of the free selenophenes, and their $\eta^2$, $\eta^1$(Se) and $\eta^5$ complexes. In general, the various modes of selenophene coordination define certain 77Se chemical shift regions. The free selenophenes $^{15,33}$ are furthest downfield with a chemical shift range from $\delta 621$ for 2,5-Me2Sel to $\delta 605$ for Sel. Somewhat upfield are the $\eta^2$ complexes in which the Seln is coordinated only through two carbon atoms; at this time only two compounds, Cp*Re(CO)$_2$(\eta$^2$-Sel) (δ 524) and Cp*Re(CO)$_2$(\eta$^2$-2-MeSel) (δ 549),$^{18}$ are known with the $\eta^2$ structure. Upfield from the $\eta^2$ compounds are those with $\eta^1$(Se)-Seln ligands, which have chemical shifts in the range $\delta 480$-402. Finally, the most upfield selenophenes are those that are $\eta^5$-coordinated to transition metals. These chemical shifts$^{15}$ cover a broad range and increase in the order: $[(\eta^5\text{-Seln})\text{IrCp}^\ast]^2 < [(\eta^5\text{-Seln})\text{Mn(CO)}_3]^+ < [(\eta^5\text{-Seln})\text{RuCp}^\ast]^+ < (\eta^5\text{-Seln})\text{Cr(CO)}_3$. In general, the 77Se chemical shifts of the $\eta^5$-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 RuCl₃.

References

(5) Ligand abbreviations are as follows: thiophene (T); 2-methylthiophene (2-MeT); 3-methylthiophene (3-MeT); 2,5-dimethylthiophene (2,5-Me₂T); benzo(b)thiophene (BT); dibenzothiophene (DBT); 2,8-dimethyldibenzothiophene (2,8-Me₂DBT); p-tolyl sulfide (PTS).

(8) Sauer, N. N.; Angelici, R. J. Organometallics 1987, 6, 1146.


(20) Choi, M. G.; Angelici, R. J. Organometallics 1991, 10, 2436.


Table 1. Crystal and Data Collection Parameters for [CpRu(CO)(PPh₃)(η¹(Se)-2-MeSel)]BF₄ (2)

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a R = Σ |Fₑ| - |Fₑ| / Σ |Fₑ|.
b Rₑw = [Σw(|Fₑ| - |Fₑ|)² / Σw|Fₑ|²]¹/₂, w = 1/σ²(|Fₑ|).
c quality-of-fit = [Σw(|Fₑ| - |Fₑ|)² / (Nobs - Nparam)]¹/₂.
### Table 2. Selected Bond Distances and Angles for \([\text{CpRu(CO)(PPh}_3](\eta^1(\text{Se})-2-\text{MeSel})\text{BF}_4\,(2)\]

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\(^a\)Estimated standard deviations are given in parentheses.
Table 3. Positional Parameters and B(eq) for [CpRu(CO)(PPh₃)(η¹(Se)-2-MeSel)]BF₄ (2)

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<th>atom</th>
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<td>C(13)</td>
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<td>0.085(1)</td>
<td>0.328(2)</td>
<td>5(1)</td>
</tr>
<tr>
<td>C(14)</td>
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<td>C(15)</td>
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</tr>
<tr>
<td>C(16)</td>
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<tr>
<td>C(21)</td>
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<td>-0.054(2)</td>
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<td>C(25)</td>
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<tr>
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<tr>
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</tr>
<tr>
<td>B(1)</td>
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<td>0.288(2)</td>
<td>0.639(2)</td>
<td>6(1)</td>
</tr>
<tr>
<td>F(1)</td>
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<td>0.772(1)</td>
<td>12(1)</td>
</tr>
<tr>
<td>F(2)</td>
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<td>0.342(1)</td>
<td>0.664(2)</td>
<td>10.6(9)</td>
</tr>
<tr>
<td>F(3)</td>
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<td>0.336(1)</td>
<td>0.573(1)</td>
<td>9.5(8)</td>
</tr>
<tr>
<td>F(4)</td>
<td>1.021(1)</td>
<td>0.2052(8)</td>
<td>0.561(1)</td>
<td>8.4(7)</td>
</tr>
</tbody>
</table>

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$_2$Cl$_2$ at 25.0° C

<table>
<thead>
<tr>
<th>reaction no.</th>
<th>L</th>
<th>L'</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sel</td>
<td>2-MeT</td>
<td>0.179 (9)</td>
</tr>
<tr>
<td>2</td>
<td>Sel</td>
<td>2,5-Me$_2$T</td>
<td>0.112 (8)</td>
</tr>
<tr>
<td>3</td>
<td>Sel</td>
<td>2-MeSel</td>
<td>4.22 (20)</td>
</tr>
<tr>
<td>4</td>
<td>Sel</td>
<td>2,5-Me$_2$Sel</td>
<td>7.39 (18)</td>
</tr>
<tr>
<td>5</td>
<td>2,5-Me$_2$Sel</td>
<td>BT</td>
<td>0.143 (4)</td>
</tr>
<tr>
<td>6</td>
<td>2,5-Me$_2$Sel</td>
<td>DBT</td>
<td>0.439 (47)</td>
</tr>
<tr>
<td>7</td>
<td>2-MeSel</td>
<td>2,5-Me$_2$Sel</td>
<td>1.72 (4)</td>
</tr>
<tr>
<td>8</td>
<td>BT</td>
<td>2-MeSel</td>
<td>3.36 (14)</td>
</tr>
<tr>
<td>9</td>
<td>DBT</td>
<td>2-MeSel</td>
<td>2.96 (9)</td>
</tr>
<tr>
<td>10</td>
<td>2,5-Me$_2$Sel</td>
<td>PTS</td>
<td>40.2 (17)</td>
</tr>
<tr>
<td>11</td>
<td>DBT</td>
<td>PTS</td>
<td>93.1 (32)</td>
</tr>
<tr>
<td>12</td>
<td>2,5-Me$_2$Sel</td>
<td>2,8-Me$_2$DBT</td>
<td>2.04 (8)</td>
</tr>
<tr>
<td>13</td>
<td>DBT</td>
<td>2,8-Me$_2$DBT</td>
<td>4.64 (8)</td>
</tr>
</tbody>
</table>

$^a$ 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 $[\text{CpRu(CO)}(\text{PPh}_3)(T)]^+$ with $L'$ in CD$_2$Cl$_2$ at 25.0°C

<table>
<thead>
<tr>
<th>$L'$</th>
<th>$K'_{eq}$</th>
<th>$L'$</th>
<th>$K'_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>1.0$^a$</td>
<td>DBT</td>
<td>74.1$^a$</td>
</tr>
<tr>
<td>2,5-Me$_2$T</td>
<td>2.76$^a$</td>
<td>2-MeSel</td>
<td>100</td>
</tr>
<tr>
<td>2-MeT</td>
<td>4.11$^a$</td>
<td>2,5-Me$_2$Sel</td>
<td>175</td>
</tr>
<tr>
<td>3-MeT</td>
<td>6.30$^a$</td>
<td>2,8-Me$_2$DBT</td>
<td>358</td>
</tr>
<tr>
<td>Sel</td>
<td>23.8</td>
<td>PTS</td>
<td>$7.11 \times 10^3$</td>
</tr>
<tr>
<td>BT</td>
<td>29.9$^a$</td>
<td>THT</td>
<td>$&gt;7.1 \times 10^6$$^a$</td>
</tr>
<tr>
<td>Me$_4$T</td>
<td>57.4$^a$</td>
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<td></td>
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</tbody>
</table>

$^a$Ref. 12.
Figure 1. Structures and numbering of thiophene (T) and selenophene (Sel).
Figure 2. ORTEP drawing of [CpRu(CO)(PPh₃)(η¹(Se)-2-Me₂Sel)]⁺ (2).
Figure 3. $^{77}$Se NMR chemical shifts of selenophene complexes.
SYNTHESIS, STRUCTURE AND REACTIVITY OF THIENYL-, BENZOTHIENYL- AND SELENYL CARBENE COMPLEXES OF Rhenium: A NEW MECHANISM FOR H/D EXCHANGE DURING HYDRODESULFURIZATION

A paper submitted to Organometallics
Carter J. White and Robert J. Angelici

Abstract

A series of $\eta^1(E)$-coordinated (E = S or Se) thiophene, benzo[b]thiophene and selenophene complexes [Cp(NO)(PPh$_3$)Re($\eta^1(E)$-L)]$, \text{Cp} = \text{C}_5\text{H}_5$, L = thiophene (T), 2-methylthiophene (2-MeT), 2,5-dimethylthiophene (2,5-Me$_2$T), benzo[b]thiophene (BT), 3-methylbenzo[b]thiophene (3-MeBT), selenophene (Sel), 2-methylselenophene (2-MeSel), and 2,5-dimethylselenophene (2,5-Me$_2$Sel) are prepared by the reaction of [Cp(NO)(PPh$_3$)Re(ClC$_6$H$_5$)]$^+$ 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$_4$•Et$_2$O or HO$_3$SCF$_3$ 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$_3$SCF$_3$, 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-(5-MeTylcarbene))]$^+$ and [Cp(NO)(PPh$_3$)Re(2-(5-MeSelylcarbene))]$^+$ are unstable and rearrange to their more stable isomers [Cp(NO)(PPh$_3$)Re(η$^1$(S)-2-MeT)]$^+$ and [Cp(NO)(PPh$_3$)Re(η$^1$(Se)-2-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, the η$^1$(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 η$^1$(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 (η$^5$-C$_5$Me$_5$)Rh(PMe$_3$).$^8$ Activation of C-H bonds in η$^1$(S)-thiophene has been recently reported$^6$ in the complex [Cp(NO)(PPh$_3$)Re(η$^1$(S)-T)]$^+$ which undergoes deprotonation (eq 1) by strong base (KOH/CH$_3$OH) to give the 2-thienyl complex.
Cp(NO)(PPh₃)Re(2-thienyl). Re-protonation of Cp(NO)(PPh₃)Re(2-thienyl) with HO₃SCF₃ (triflic acid) does not give back the η¹(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)(PPh₃)Re(η¹(S)-BT)+.⁶

In the present study, we report on an improved synthesis of the [Cp(NO)(PPh₃)Re(η¹(S)-thiophene)]⁺ and Cp(NO)(PPh₃)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)(PPh₃)Re(2-BTylcarbene)]O₃SCF₃ has been determined. These studies offer a new perspective on possible mechanisms for the deuterium exchange of thiophene with D₂ on HDS catalyst surfaces.

**Experimental Section**

**General Procedures.** All reactions and manipulations were carried out under an atmosphere of dry N₂ using standard Schlenk techniques unless otherwise stated.⁹,¹⁰ All solvents were reagent grade or better and were dried and distilled under N₂ by the following methods. Tetrahydrofuran (THF) and
diethyl ether (Et₂O) were distilled from Na/benzophenone. Hexanes and dichloromethane (CH₂Cl₂) and acetonitrile (CH₃CN) were distilled from CaH₂. Acetone and chlorobenzene were dried with potassium carbonate (K₂CO₃) and distilled. The solvents were used immediately after distillation except for acetone and chlorobenzene which were stored over K₂CO₃ under N₂. 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 N₂-saturated deionized distilled water, and stored under N₂.

The ¹H and ¹³C NMR spectra were recorded on a Varian VXR-300 MHz spectrometer with deuterated solvents as the internal locks and referenced to tetramethylsilane (TMS δ = 0.00) or residual CH₂Cl₂ (δ=5.33). The 2-D ¹H/¹H COSY, ¹H/¹H NOESY and ¹H/¹³C HETCOR spectra were recorded on the same instrument using standard 2D pulse sequences on a non-spinning, thermostated sample. The ⁷⁷Se(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)(PPh₃)Re(CH₃),¹¹ selenophene (Sel),¹²,¹³ 2-methylselenophene (2-MeSel),¹⁴ and 2,5-dimethylselenophene (2,5-Me₂Sel).¹⁵ All other reagents were used as received from commercial sources.
General Procedure for the Preparation of [Cp(NO)(PPh3)Re(η¹(E)-L)](BF4) (1-8). Compounds 1-8 containing an η¹(E)-bound ligand were prepared by a method similar to that previously reported by Gladysz and co-workers for the synthesis of other Cp(NO)(PPh3)Re(L)+ complexes. To a solution of 0.155 g (0.277 mmol) of Cp(NO)(PPh3)Re(CH3) in 7.0 mL of chlorobenzene cooled to -42°C in a CH3CN/N2(l) bath was added 46.0 μL of HBF4·Et2O (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 N2 for 10 min then under vacuum. Yield 94-85 %.

Characterization of 1-8. [Cp(NO)(PPh3)Re(η¹(S)-T)](BF4) (1). ¹H NMR δ (CD2Cl2): 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). ¹³C NMR δ (CD2Cl2): 138.34(s, C(2) C(5)), 132.42(s, C(3)), 133.53(d, Ph), 133.60(d, Ph) 132.32(d, Ph), 129.90(d, Ph), 92.38(s, Cp). IR cm⁻¹ ν(NO) (CH2Cl2): 1724(s).

[Cp(NO)(PPh3)Re(η¹(S)-2-MeT)](BF4) (2). ¹H NMR δ (CD2Cl2): 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). ¹³C NMR δ (CD2Cl2): 154.52 (s, C(2)), 132.85 (s, C(4)), 132.10 (s, C(5)), 132.42(s, C(3)), 14.43(s, CH3), 93.37 (s, Cp), 133.60(d, Ph), 133.51(d, Ph)
132.32(d, Ph), 129.90(d, Ph). IR cm⁻¹ v(NO) (CH₂Cl₂): 1723(s). Anal. Calcd for C₂₈H₂₅BF₄NOPrēS: C, 46.16; H, 3.10. Found: C, 45.96; H, 3.53.

[Cp(NO)(PPh₃)Re(η¹(S)-2,5-MegT)](BF₄) (3). ¹H NMR δ (CD₂Cl₂): 6.76(s, H(3)H(4)), 2.02 (s, CH₃), 5.37(s, Cp), 7.59-7.35(m, Ph), 7.28-7.20(m, Ph). ¹³C NMR δ (CD₂Cl₂): 149.74(s, C(2)C(5)), 129.46(C(3)C(4)), 14.81(s, CH₃), 133.60(d, Ph), 133.50(d, Ph) 132.32(d, Ph), 129.90(d, Ph). IR cm⁻¹ v(NO) (CH₂Cl₂): 1723(s).

[Cp(NO)(PPh₃)Re(η¹(S)-BT)](BF₄) (4). ¹H NMR δ (CD₂Cl₂): 7.86 (m, 4H, BT), 6.25(d, 1H, BT), 5.22(s, C₂), 7.59-7.35(m, Ph), 7.28-7.20(m, Ph). ¹³C NMR δ (CD₂Cl₂): 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, C₂), 133.6(d, Ph), 133.5(d, Ph), 132.3(d, Ph), 129.9(d, Ph). IR cm⁻¹ v(NO) (CH₂Cl₂): 1718(s). Anal. Calcd for C₃₁H₂₆BF₄NOPrēS · 1/4 CH₂Cl₂: 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 (CD₂Cl₂): 7.87(m, 2H, BT), 7.81(m, 2H, BT), 5.79(s, H(2)), 2.30(s, CH₃), 5.29(s, C₂), 7.59-7.35(m, Ph), 7.28-7.20(m, Ph). ¹³C NMR δ (CD₂Cl₂): 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, CH₃), 93.65(s, C₂), 133.60(d, Ph), 133.50(d, Ph), 132.32(d, Ph), 129.90(d, Ph). IR cm⁻¹ v(NO) (CH₂Cl₂): 1720(s).

[Cp(NO)(PPh₃)Re(η¹(Se)-Sel)](BF₄) (6). ¹H NMR δ (CD₂Cl₂): 7.45(H(2),H(5)), 7.21(H(3),H(4)), 7.52-7.35(m, Ph), 7.28-7.20(m, Ph). ¹³C NMR δ (CD₂Cl₂): 141.86(s, C(2)C(5)), 134.37(s, C(3)C(4)), 92.52(s, C₂), 133.60(d, Ph), 133.52(d, Ph),
132.32(d, Ph), 129.90(d, Ph). $^{77}$Se NMR $\delta$ (CD$_2$Cl$_2$): 368.2 (s, br). IR cm$^{-1}$ v(NO) (CH$_2$Cl$_2$): 1719(s). Anal. Calcd for C$_{27}$H$_{24}$BF$_4$NOPReSe: C, 42.59; H, 3.18. Found: C, 42.37; H, 3.19.

$[\text{Cp(NO)}(PPh$_3$)Re\{\eta^1(\text{Se}-2\text{-MeSel})\}]$(BF$_4$) (7). $^1$H NMR $\delta$ (CD$_2$Cl$_2$): 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 $\delta$ (CD$_2$Cl$_2$): 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), 133.52(d, Ph), 132.32(d, Ph), 129.90(d, Ph). $^{77}$Se NMR $\delta$ (CD$_2$Cl$_2$): 386.5(d, J$_{Se,P}$ = 13 Hz). IR cm$^{-1}$ v(NO) (CH$_2$Cl$_2$): 1716(s). Anal. Calcd for C$_{28}$H$_{25}$BF$_4$NOPReSe: C, 43.37; H, 3.38. Found: C, 43.28; H, 3.39.

$[\text{Cp(NO)}(PPh$_3$)Re\{\eta^1(\text{Se}-2,5\text{-Me$_2$Sel})\}]$(BF$_4$) (8). $^1$H NMR $\delta$ (CD$_2$Cl$_2$): 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 $\delta$ (CD$_2$Cl$_2$): 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 $\delta$ (CD$_2$Cl$_2$): 384.2(d, J$_{Se,P}$= 19.8 Hz). IR cm$^{-1}$ v(NO) (CH$_2$Cl$_2$): 1717(s).

**General Procedure for the Preparation of Cp(NO)(PPh$_3$)Re(2-L)$_y$** (9, 10, 12-15).

To a stirred solution of 0.250 mmol of $[\text{Cp(NO)}(PPh$_3$)Re\{\eta^1(\text{E})-\text{L}\}]$BF$_4$, where $\eta^1(\text{E})$-L = T, 2-MeT, BT, 3-MeBT, Sel, 2-MeSel, in 5.0 mL of CH$_2$Cl$_2$, 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$_2$Cl$_2$. 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)(PPh₃)Re(2-Tyl) (9).** ¹H NMR δ (CD₂Cl₂): 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). ¹³C NMR δ (CD₂Cl₂): 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) (CH₂Cl₂): 1653(s).

**Cp(NO)(PPh₃)Re(2-(5-MeTyl)) (10).** ¹H NMR δ (CD₂Cl₂): 6.27(dd, H(3), Jₜₚ = 1.2 Hz), 5.94(d, H(4)), 2.38(s, CH₃), 5.10(s, Cp), 7.39-7.32(m, Ph). ¹³C NMR δ (CD₂Cl₂): 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) (CH₂Cl₂): 1654(s). Anal. Calcd for C₂₈H₂₅NOPReS: C, 52.49; H, 3.93. Found: C, 52.52; H, 3.97.

**Cp(NO)(PPh₃)Re(2-BTyl) (12).** ¹H NMR δ (CD₂Cl₂): 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). ¹³C NMR δ (CD₂Cl₂): 146.7(s, BT), 146.4(s, BT), 136.6(d, 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) (CH₂Cl₂): 1658(s).

**Cp(NO)(PPh₃)Re(2-(3-MeBTyl)) (13).** ¹H NMR δ (CD₂Cl₂): 7.45-7.32 (m of m, BT and Ph), 7.14(t, BT), 6.87 (t, BT), 2.51(s, CH₃), 5.25(s, Cp). ¹³C NMR δ (CD₂Cl₂): 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\(^{-1}\) v(NO) (CH\(_2\)Cl\(_2\)): 1656(s).

**Cp(NO)(PPh\(_3\))Re(2-Selyl) (14).** \(^1\)H NMR \(\delta\) (CD\(_2\)Cl\(_2\)): 7.76(d, \(J_{H-Se} = 20.1\) 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 \(\delta\) (CD\(_2\)Cl\(_2\)): 138.33(d, \(J_{C-p} = 2.5\) Hz, C(3)), 136.54 (d, \(J_{C-p} = 11.5\) 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 \(\delta\) (CD\(_2\)Cl\(_2\)): 705.1 (s). IR cm\(^{-1}\) v(NO) (CH\(_2\)Cl\(_2\)): 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).** \(^1\)H NMR \(\delta\) (CD\(_2\)Cl\(_2\)): 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 \(\delta\) (CD\(_2\)Cl\(_2\)): 148.45(s, C(5)), 138.74(s, C(4)), 133.74 (d, \(J_{C-p} = 9.7\) 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 \(\delta\) (CD\(_2\)Cl\(_2\)): 719.2 (s). IR cm\(^{-1}\) v(NO) (CH\(_2\)Cl\(_2\)): 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\(_2\)Tyl)) (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\(_2\)T)]BF\(_4\) and 0.011 g (0.200 mmol) KOH in methanol. Yield 0.028 g, 29% as an orange solid. \(^1\)H NMR \(\delta\) (CD\(_2\)Cl\(_2\)): 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 \(\delta\) (CD\(_2\)Cl\(_2\)): 142.32(d, C(4)), 133.24(s, C(2)), 132.59(s, C(5)), 126.07 (d, \(J_{C-p} = 9.6\) 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\(^{-1}\) v(NO) (CH\(_2\)Cl\(_2\)): 1653(s).
Preparation of Carbene Complexes. [Cp(NO)(PPh3)Re(2-Tylcarbene)]X (16a, X = BF₄; 16b, X = O₃SCF₃). To a stirred and cooled (−42°C) solution of 0.100 g (0.131 mmol) of Cp(NO)(PPh3)Re(2-Tyl) in 10.0 mL of Et₂O:CH₂Cl₂ (2:1), one equivalent (0.131 mmol) of acid (16a, 21.7 μL of HBF₄•Et₂O 85%; 16b, 11.6 μL of HO₃SCF₃) 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 N₂ 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%). ¹H NMR δ (CD₂Cl₂): 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). ¹³C NMR δ (CD₂Cl₂): 267.96 (d, Jc-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) (CH₂Cl₂): 1716(s). FAB (3-nitrobenzyl alcohol matrix): m/z 628 (M⁺).

[Cp(NO)(PPh₃)Re(2-B'Tylcarbene)]X (17a, X = BF₄; 17b, X = O₃SCF₃). Compounds 17a and 17b were prepared in the same manner as 16a and 16b using 0.100 g (0.148 mmol) of Cp(NO)(PPh₃)Re(2-BTyl) and 24.5 μL of HBF₄•Et₂O (17a) or 13.1 μL HO₃SCF₃(17b). These reaction yielded 17a as an orange/yellow powder (0.105 g, 93%) or 17b as a yellow powder (0.102 g, 83%). ¹H NMR δ (CD₂Cl₂): 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). ¹³C NMR δ
(CD₂Cl₂): 277.71 (d, Jₜₛₜ= 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)
(CH₂Cl₂): 1720 (s).


[Cp(NO)(PPh₃)Re(2-Selylcarbene)]X (18a, X = BF₄; 18b, x = O₃SCF₃).

Compounds 18a and 18b were prepared in the same manner as 16a and 16b using 0.100 g (0.148 mmol) of Cp(NO)(PPh₃)Re(2-Selyl) (14) and 24.5 µL of HBF₄•Et₂O (18a) or 13.1 µL of HO₃SCF₃ (18b). From these reactions were isolated 18a (0.992 g, 88%) or 18b (0.106 g, 94%) as yellow powders. ¹H NMR δ (CD₂Cl₂): 7.68 (d, Jₜₛₜ= 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). ¹³C NMR δ (CD₂Cl₂): 274.83 (d, Jₜₛₜ= 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). ⁷⁷Se NMR δ (CD₂Cl₂): 741.7 (s). IR cm⁻¹ ν(NO) (CH₂Cl₂): 1716 (s). FAB (3-nitrobenzyl alcohol matrix): m/z 674 (M⁺).

[Cp(NO)(PPh₃)Re(2-(5-MeTylcarbene))O₃SCF₃ (19). A 5-mm NMR tube was charged with 0.020 g (0.031 mmol) of Cp(NO)(PPh₃)Re(2-(5-MeTyl)) (10) and 0.60 mL of CD₂Cl₂. After the tube was cooled to -42° C, 2.8 µL (0.031 mmol) of HO₃SCF₃ 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 (CD₂Cl₂): 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 $\delta$ (CD$_2$Cl$_2$): 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$^{-1}$ v(NO) (CH$_2$Cl$_2$): 1720 (s). Compound 19 is not stable and isomerizes to 2 above 0°C as discussed in detail in the Results and Discussion section.

$[\text{Cp} (\text{NO})(\text{PPh}_3)\text{Re}(2-(5-\text{MeSelyl carbene})])O_3\text{SCF}_3$ (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$_2$Cl$_2$. After the NMR tube was cooled to -42° C, 2.6 $\mu$L (0.029 mmol) of HO$_3$SCF$_3$ was added and the red/orange solution became bright yellow. A $^1$H NMR spectrum at -75° C showed conversion to 20. $^1$H NMR $\delta$ (CD$_2$Cl$_2$): 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 $\delta$ (CD$_2$Cl$_2$): 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$^{-1}$ v(NO) (CH$_2$Cl$_2$): 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 $[\text{Cp} (\text{NO})(\text{PPh}_3)\text{Re}(2-B\text{Tylcarbene})]O_3\text{SCF}_3$ (17b).** A single crystal of 17b suitable for X-ray diffraction was obtained by layering a concentrated CH$_2$Cl$_2$ solution of 17b with Et$_2$O and cooling at -78° C for several days. A crystal of 17b with the composition $[\text{Cp} (\text{NO})(\text{PPh}_3)\text{Re}(2-\text{BTylcarbene})]O_3\text{SCF}_3 \cdot 3 \text{CH}_2\text{Cl}_2$ 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 N₂. The solid was dissolved by adding 0.5 mL of CH₂Cl₂; 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 \( \eta^1(E) \)-bound ligand by the amine did not occur to an appreciable extent. 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\(_2\)Cl\(_2\) 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 \([\text{Cp(NO)(PPh}_3\text{)}\text{Re(\(\eta^1(E)-L\))}]^+\) Complexes (1-8).** The compounds \([\text{Cp(NO)(PPh}_3\text{)}\text{Re(\(\eta^1(S)-\text{Th}\))}]^+\)BF\(_4\), where Th = thiophene (T), 2,5-dimethylthiophene (2,5-Me\(_2\)T), benzothiophene (BT), and 2-methylbenzothiophene (2-MeBT), were recently\(^6\) synthesized utilizing a method similar to that used for the preparations of \([\text{Cp(NO)(PPh}_3\text{)}\text{Re(L’)}]^+\) 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 $[\text{Cp(NO)(PPh}_3\text{)Re(Cl-CH}_2\text{Cl)}]^+$. Changing the solvent from \(\text{CH}_2\text{Cl}_2\) 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 $\eta^1(E)$-complexes

$$\text{Cp(NO)(PPh}_3\text{)Re(ClPh)}^+ + L \rightarrow [\text{Cp(NO)(PPh}_3\text{)Re(\eta^1(E)-L)}]^+$$

$$\begin{align*}
E &= S & E &= \text{Se} \\
1, L &= \text{T} & 6, L &= \text{Sel} \\
2, L &= 2-\text{MeT} & 7, L &= 2-\text{MeSel} \\
3, L &= 2,5-\text{Me}_2\text{T} & 8, L &= 2,5-\text{Me}_2\text{Sel} \\
4, L &= \text{BT} & \\
5, L &= 3-\text{MeBT} & 
\end{align*}$$

as tan-yellow powders in yields of 94-85%. The compounds 1-8 were characterized by elemental analysis and IR, $^1\text{H}$ and $^{13}\text{C}$ NMR spectrometry; $^{77}\text{Se}$ NMR data were obtained for compounds 6-8. The slightly lower $\nu(\text{NO})$ 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 $\sigma$-donor ligand than thiophene; the same trend is observed in the $\nu(\text{CO})$ values of the sulfur-selenium pairs in the isoelectronic complexes $[\text{Cp(CO)(PPh}_3\text{)Ru(\eta^1(E)-L)}]^+$. The $^1\text{H}$ NMR resonances of Sel in 6 are not distinguishable in the spectrum because they overlap with those of the PPh$_3$. The 2-D $^1\text{H}/^{13}\text{C}$ HETCOR spectrum, however, clearly shows peaks for H(2)H(5) ($\delta$ 7.45) and H(3)H(4) ($\delta$ 7.21) which are upfield of the corresponding resonances for the free selenophene ligand (H(2)H(5) ($\delta$ 7.88), H(3)H(4) ($\delta$ 7.23)). $\eta^1(\text{S})$ coordination of thiophene in 1 and $\eta^1(\text{Se})$ coordination of selenophene in $[\text{Cp(CO)(PPh}_3\text{)Ru(\eta^1(E)-L)}]^+$ result in a similar upfield shift.$^7,^{18}$ The $^{13}\text{C}$ 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. A similar downfield shift upon η¹(E)-coordination has been reported in the complexes: [Cp(CO)(PPh₃)Ru(η¹(E)-L)]⁺,¹⁷ Cp(CO)₂Re(η¹(E)-L),¹⁹,²⁰ [Cp(CO)₂Fe(η¹(S)-T)]⁺,²¹ and [Cp(CO)₂Ru(η¹(S)-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-Me₂T) and 8 (2,5-Me₂Sel) occur as single resonances in their room temperature ¹H NMR spectra. At low temperature (283 K), the ¹H NMR spectra of 3 and 8 in CD₂Cl₂ 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 (Tc = 195 K) for 3 and 42(1) kJ/mol (Tc = 215 K) for 8 at their coalescence temperatures (Tc).²³ Coalescence of the methyl group signals has been observed in the related complexes [CpRu(CO)(PPh₃)(η¹(E)-L)]⁺; the 2,5-Me₂T complex has a free energy of activation of 40 kJ/mol (Tc = 213 K), while the value is 44 kJ/mol (Tc = 225 K) for the 2,5-Me₂Sel 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 such as Re(Cl)(CO)₃(EMe₂)₂ and Pt(Br)(Me)(EMe₂)₂, the inversion barrier is also lower in the S than the Se analog. The low temperature ¹H NMR spectra of 1 and 6 in CD₂Cl₂ show only a slight broadening of the proton resonances at the freezing point (178 K) of CD₂Cl₂; this indicates that the Tc values for 1 and 6 are lower than 178 K. The lower Tc
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)(PPh₃)Re(L-yl) Complexes (9-15).**

Abstraction of a proton from the \( \eta^1(S) \) complexes \([\text{Cp(NO)}(\text{PPh}_3)\text{Re}(\eta^1(S)-\text{Th})]\text{BF}_4\), where \( \text{Th} = \text{T}(1), 2,5-\text{Me}_2\text{T}(3), \text{or BT}(4) \), with KOH in methanol\(^6\) gives the neutral thienyl complexes \( \text{Cp(NO)}(\text{PPh}_3)\text{Re}(2-\text{Thyl})(9), \text{Cp(NO)}(\text{PPh}_3)\text{Re}(3-(2,5-\text{Me}_2\text{Thyl}))(11), \) and \( \text{Cp(NO)}(\text{PPh}_3)\text{Re}(2-\text{BTyl})(12) \) in moderate 28-60% yields. There is a side product in these reactions which is proposed to be \( \text{Cp(NO)}(\text{PPh}_3)\text{Re(OH)} \), based on its IR (\( \nu(\text{NO})\)(CH\(_2\)Cl\(_2\)): 1679 cm\(^{-1}\)) and \(^1\text{H} \) NMR ((CD\(_2\)Cl\(_2\)) \( \delta: 7.52-7.30 \) (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\(_2\)Cl\(_2\) rapidly gives (eq 3) the corresponding deprotonated \( \text{Cp(NO)}(\text{PPh}_3)\text{Re(2-L-yl)} \) complexes in greater than 90% yield. The cationic amine complex \([\text{Cp(NO)}(\text{PPh}_3)\text{Re(amine)})^+\), resulting from displacement of the thiophene or selenophene ligand, is not observed in IR spectra of the reaction mixtures. Only \([\text{Cp(NO)}(\text{PPh}_3)\text{Re(\eta^1(S)-2,5-\text{Me}_2\text{Thyl})})^+ (3) \) cannot be converted to its L-yl complex \( \text{Cp(NO)}(\text{PPh}_3)\text{Re}(3-(2,5-\text{Me}_2\text{Thyl}))(11) \) with Dabco; however, KOH/methanol does effect this conversion.\(^6\)
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 $\nu$(NO) values for the compounds 9-15 are ~70 cm$^{-1}$ lower than those of their starting cationic complexes. The $^{77}$Se NMR resonances for selenyl complexes 14 (2-Selyl: $\delta$ 705.1) and 15 (2-(5-MeSelyl): $\delta$ 719.2) are more than 300 ppm downfield of those of the cationic starting complexes 6(Sel: $\delta$ 368.2) and 7(2-MeSel: $\delta$ 386.5) and have chemical shift values similar to that of 2-cyanoselenophene ($\delta$ 709.3).
Deprotonation of 1, 4 and 6 with Bases of Varying pKₐ. 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 pKₐ values was used in this reaction. The reactions were monitored by changes in the v(NO) region of the IR spectrum of the solutions. The results are presented in Table 4. The pKₐ of the bases required for deprotonation of the η¹(S)-thiophene complex (1) lies between that of 2,6-dimethylpyridine (2,6-Me₂py) (pKₐ 6.99) and morpholine (pKₐ 8.33). The η¹(S)-benzothiophene complex (4) requires a stronger base with a pKₐ between Dabco (pKₐ 8.7) and (n-Pr₃)N (pKₐ 10.71). On the other hand, the η¹(Se)-selenophene complex (6) requires a base with a pKₐ between pyridine (py) (pKₐ 5.25) and 4-Mepy (pKₐ 6.02). Thus the required base ranges are as follows: 4 (Sel) (pKₐ 5.25-6.02) < 1 (T) (pKₐ 6.99-8.33) < 4 (BT) (pKₐ 8.7-10.71).

Synthesis and Characterization of L-yl carbene complexes 16, 17, and 18. The reactions of Cp(NO)(PPh₃)Re(2-Tyl) (9) and Cp(NO)(PPh₃)Re(2-BTyl) (12) with HO₃SCF₃ to form the cationic carbene complexes, [Cp(NO)(PPh₃)Re(2-Tylcarbene)]⁺ and [Cp(NO)(PPh₃)Re(2-BTylcarbene)]⁺, respectively, were recently reported.⁶ The L-yl complexes Cp(NO)(PPh₃)Re(2-Tyl) (9), Cp(NO)(PPh₃)Re(2-BTyl) (12), and Cp(NO)(PPh₃)Re(2-Selyl) (14) all react with one equivalent of HBF₄•Et₂O or HO₃SCF₃ to give the corresponding cationic carbene complexes [Cp(NO)(PPh₃)Re(2-Tylcarbene)]⁺ (16), [Cp(NO)(PPh₃)Re(2-BTylcarbene)]⁺ (17), and [Cp(NO)(PPh₃)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 Et₂O:CH₂Cl₂. The isolated bright yellow to bright orange solids are stable in
air for greater than 3 weeks. In CD$_2$Cl$_2$, 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 v(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 $^1$H and $^{13}$C NMR resonances were made using a combination of 2-D $^1$H/$^1$H COSY, $^1$H/$^1$H NOESY and $^1$H/$^{13}$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 \([\text{Cp(NO)(PPh}_3\text{)Re(=C(H)(Ph))}]+\) 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 \(^1\text{H}\) 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 \(^{13}\text{C}\) NMR spectra exhibit a carbene resonance (16, \(\delta 267.96,\) d, \(J_{C-P} = 7.4\) Hz; 17, \(\delta 277.71,\) d, \(J_{C-P} = 7.9\) Hz; 18, \(\delta 274.83,\) d, \(J_{C-P} = 6.8\) Hz) that is coupled to the phosphorus; these chemical shifts are similar to those of related carbenes: \([\text{Cp(NO)(PPh}_3\text{)Re(=C(H)(SCH}_3\text{))}]+\) (\(\delta 274.4,\) 27 [Cp(NO)(PPh3)Re(=C(H)(Ph))]+ (\(\delta 288.6,\) 26 The C(3) resonances of the starting material L-yl complexes (9, \(\delta 135.76;\) 12, \(\delta 131.71;\) 14, \(\delta 138.33\) all move upfield approximately 70 ppm upon protonation and formation of the carbene (16, \(\delta 55.93;\) 17, \(\delta 66.21;\) 18, \(\delta 49.59\) since this carbon becomes saturated in the reaction. At the same time, the C(4) and C(5) olefin carbons of 16 (\(\delta 145.83\) C(4), 149.24 C(5))and 18 (\(\delta 146.73\) C(4), 152.81 C(5)) shift slightly downfield of those (9, \(\delta 127.32\) C(4), 128.34 C(5); 14, \(\delta 130.21\) C(4), 132.42 C(5)) in the L-yl starting complexes.

**Molecular Structure of \([\text{Cp(NO)(PPh}_3\text{)Re(2-BTylcarbene)}](\text{O}_3\text{SCF}_3)\) (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: \([(\text{Cp(NO)(PPh}_3\text{)Re=C(H)(Ph)})^+\] (1.949(6)Å),26 \(\text{Cp}^*\text{(NO)(P(OPh)}_3\text{)Re(=CH}_2\text{)}\) (1.898(18)Å).28 The longer Re=C(11) bond is likely due to S-to-C(11) \(\pi\)-bonding which reduces the Re-to-C(11) \(\pi\)-
bonding, as has been observed in other thiocarbene complexes.\textsuperscript{29} In the closely related C-pyrrolyl complex, [CpRe(NO)(PPh\textsubscript{3})Re(C=NHCH\textsubscript{2}CH=CH)]\textsuperscript{+} (2.046(3)Å),\textsuperscript{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\textsubscript{3})Re-CH\textsubscript{2}-]\textsubscript{2}S+CH\textsubscript{3})I,\textsuperscript{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\textsubscript{3})Re\textsuperscript{+} 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\textsubscript{5}Me\textsubscript{5})Re(CO)\textsubscript{2}(η\textsuperscript{1}(S)-3-MeBT).\textsuperscript{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.\textsuperscript{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\textsubscript{3})Re(2-Tylcarbene)]\textsuperscript{+} (16) with Nucleophiles.**

Nucleophiles typically react with carbene,\textsuperscript{33} thiocarbene\textsuperscript{34,35} and dithiocarbene\textsuperscript{29} complexes by adding to the carbene carbon. Complex 16, [Cp(NO)(PPh\textsubscript{3})Re(2-Tylcarbene)]\textsuperscript{+}, in a 5 mm NMR tube with a wide variety of
nucleophiles either does not react (Me₂S, MeSH, (Co(CO)₄)⁻⁻⁻) or undergoes deprotonation (Me₃N, Me₂HN, H₂MeN, Me₃P, 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 Me₂S 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 PPh₃ 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 PPh₃, which is also unfavorable.

**Deprotonation Studies of 16, 17 and 18.** The hydrogens on C(3) of the carbene complex [Cp(NO)(PPh₃)Re(2-Tylcarbene)]⁺ (16) are acidic enough to protonate a variety of amines and phosphines to give the thienyl complex Cp(NO)(PPh₃)Re(2-Tyl) (9) in quantitative yield (eq 5). The deprotonation of 16 occurs immediately, the color of the solution turning from bright yellow to orange. The v(NO) of the carbene (1720 cm⁻¹) shifts by ~70 cm⁻¹ to the lower wavenumber of the thienyl complex (1654 cm⁻¹). The pKₐ 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 pKₐ between that of (p-FC₆H₄)₃P (pKₐ 1.97) and Ph₃P (pKₐ 2.73). The thienylcarbene (16) and the selenylcarbene (18) are less acidic than 17 and both have a pKₐ between (m-MeC₆H₄)₃P (pKₐ 3.30) and (p-MeC₆H₄)₃P (pKₐ 3.84).

Deuterated 16, 17 and 18 were prepared by reaction of 9, 12 and 14 with DO₃SCF₃; 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 CD₂Cl₂ 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 DO₃SCF₃ are dissolved in CD₂Cl₂, 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)(PPh₃)Re(2-(5-methylthienyl)) (10) and Cp(NO)(PPh₃)Re(2-(5-methylselenyl)) (15) in CD₂Cl₂ with triflic acid at -42° C in 5 mm NMR tubes gives the corresponding carbene compounds [Cp(NO)(PPh₃)Re(2-(5-methylthienyl)carbene)]⁺ (19) and [Cp(NO)(PPh₃)Re(2-(5-methylselenyl)carbene)]⁺ (20) in quantitative yield. The IR, ¹H and ¹³C NMR
spectra closely resemble those of the isolated 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 η¹(E) complexes 2 and 7 appear (eq 6). The reaction is complete within 1 h with no evidence in the ¹H or ¹³C NMR spectra for other products. Attempts to isolate 19 at low temperature (-78° C) gave only the rearranged η¹(S) isomer. The reaction of DO₃SCF₃ 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 PPh₃. 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 η¹(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)(PPh₃)Re(3-(2,5-Me₂Tyl)) (11) produces [Cp(NO)(PPh₃)Re(η¹(S)-2,5-Me₂T)]⁺ (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 stabilized 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 studies³⁶-⁴⁰ of the deuterium exchange of thiophene with D₂ 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 η⁵-thiophene complex CpRu(η⁵-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 η⁵-adsorbed thiophene.⁴¹ An alternative mechanism⁵,⁶ involves η¹(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 η¹(S)-bound thiophene(Scheme 1, path a); the formation of 2-deutero-benzothiophene in the reaction⁵ of Cp(CO)(PPh₃)Ru(2-BTyl) with DO₃SCF₃ serves as an organometallic model for
this step, which was originally proposed by Cowley.\textsuperscript{43} The thienyl species could also undergo D\textsuperscript{+} 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 $\eta^1(S)$-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.

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**References**


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Table 1. Crystal and Data Collection Parameters for [Cp(NO)(PPh3)Re(2-BTylcarbene)]O3SCF3 (17b)

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ᵃ Estimated standard deviations are given in parentheses.
Table 3. Atomic Coordinates (x10^4) and Equivalent Isotropic Displacement Coefficients (Å² x 10³) for [Cp(NO)(PPh₃)Re(2-BTylcarbene)]O₃SCF₃ (17b).

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<th>z</th>
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*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 pKₐ (eq 3)

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<th>1 (T)</th>
<th>4 (BT)</th>
<th>6 (Sel)</th>
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<td>no rxn</td>
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<td>Dabco</td>
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Table 5. Deprotonation of Carbene Complexes 16, 17 and 18 with Bases of Varying pKₐ (eq 5)

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<th>17</th>
<th>18</th>
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<td>1.03ᵃ</td>
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<td>(p-FC₆H₄)₃P</td>
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<td>no rxn</td>
<td>no rxn</td>
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<td>(o-MeC₆H₄)₃P</td>
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<td>(m-MeC₆H₄)₃P</td>
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<td>(p-MeOC₆H₄)₃P</td>
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Figure 1. ORTEP Drawing of the cation \([\text{Cp(NO)(PPh}_3\text{)Re(2-BTylcarbene)}]^+\) in 17b.
Figure 2. The HOMO (left) for the fragment \([\text{Cp(NO)}(\text{PPh}_3)\text{Re}]^+\) and its bonding with the carbene in 17 (right).
Scheme 1

\[
\text{2-thienyl intermediate}
\]

\[
\text{2,5-deuteration}
\]

\[
\text{carbene intermediate}
\]

\[
\text{3,4-deuteration}
\]

\[
\text{path a} \quad \text{path b}
\]

\[
+ D^+ \quad + D^+
\] at C(2) at C(3)
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 $\eta^5$- and the $\eta^1(\text{Se})$- 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 $^{77}\text{Se}$ 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 $\eta^5$-selenophene and the region for $\eta^1(\text{Se})$-selenophene is over 150 ppm when the charge of the complex is considered. The successful use of $^{77}\text{Se}$ NMR for studies of the hydrodesulfurization surface is highly dependent on the use of isotopic labeling of selenophene. Even though $^{77}\text{Se}$ is a more sensitive nucleus than $^{13}\text{C}$, 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 $\eta^1(\text{S})$-bound thiophenes, $\eta^1(\text{S})$-benzothiophene and $\eta^1(\text{Se})$-bound selenophenes has been demonstrated. The deprotonation and rearrangement of the $\eta^1(\text{E})$- 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 \([\text{Cp(NO)(PPh}_3\text{)Re(2-benxothienylcarbene)}]_3\text{SCF}_3\) 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 \(\eta^1(E)\)-bound complex. Based on these model reactions, a new mechanism for the H/D exchange of thiophene over the hydrodesulfurization catalyst has been proposed.