Synthesis, Equilibrium Binding, and ^{77}Se NMR Studies of η^1-Selenophene (Seln) Complexes: [CpRu(CO)(PPh$_3$)(η^1(*Se*)-Seln)]BF$_4$

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Reactions of Cp(CO)(PPh$_3$)RuCl (Cp = C$_5$H$_5$) with Ag$^+$ and selenophenes (Seln) produce the stable selenium-bound (η^1(*Se*)) selenophene complexes [Cp(CO)(PPh$_3$)Ru(η^1(*Se*)-Seln)]$^+$ (Seln = selenophene (Sel), 2-methylselenophene (2-MeSel), and 2,5-dimethylselenophene (2,5-MeSel)). The molecular structure of [Cp(CO)(PPh$_3$)Ru(η^1(*Se*)-2-MeSel)]$^+$ was determined, and ^{1}H and ^{13}C NMR and IR data for all of the Seln complexes are compared with those of their thiophene analogs. Equilibrium constants (*K'*) for the replacement of thiophene (T) by selenophenes, thiophenes, benzo[*b*]thiophene (BT), dibenzothiophene (DBT), 2,8-dimethyldibenzothiophene (2,8-Me$_2$DBT), and *p*-tolyl sulfide (PTS) increase in the following 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 × 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 η^1(*Se*), η^2, and η^5 modes of selenophene coordination to transition metals. Crystals of Cp(CO)(PPh$_3$)Ru(η^1(*Se*)-2-MeSel)]BF$_4$ are triclinic, space group $P\bar{1}$ (No. 2) with a = 10.594(2) Å, b = 14.276(2), c = 9.402(2) Å, α = 97.97(2)°, β = 91.63(2)°, γ = 87.47(1)°, and Z = 4.

Introduction

Adsorption of thiophene at an active metal site is a necessary first step in the mechanism of thiophene hydrodesulfurization (HDS) on heterogeneous catalysts.[2] On the basis of studies of model organometallic complexes, two modes for thiophene (T) binding, η^5 and η^1(*S*), are most common.[3,4] 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 following order: T < 2-MeT, 3-MeT < 2,5-Me$_2$T.[5,6] In the organometallic model complexes [CpRu(η^5-Th)]$^+$,[7] where Th is thiophene or its methyl-substituted derivatives, equilibrium constants for η^5 binding of Th increase in the same order, which is consistent with η^5 binding on the Co/Mo/Al$_2$O$_3$ catalyst. Support for this mode of adsorption can also be found in the results of reactivity studies conducted on η^5-thiophene complexes.[2,4,8-11]

The η^1(*S*)-thiophene coordination mode occurs in several complexes[3,4] including [CpRu(CO)(PPh$_3$)(η^1(*S*)-Th)]$^+$,[12] [CpRu(CO)$_2$(η^1(*S*)-Th)]$^+$,[13] and CpRe(CO)$_2$(η^1(*S*)-Th).[14] Equilibrium constants (*K'*) for thiophene ligand exchange in [CpRu(CO)$_2$(η^1(*S*)-Th)]$^+$ show that η^1(*S*)-thiophene binding increases as the number of methyl groups in the thiophene increases. Thus, *K'* increases in the following 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 η^5- and η^1(*S*)-thiophenes follow the same trend as that observed on the HDS catalyst. Kinetic studies of η^1(*S*)-thiophene dissociation from [CpRu(CO)$_2$(η^1(*S*)-Th)]$^+$ [13] and CpRe(CO)$_2$(η^1(*S*)-Th)[14] 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 η^1(*S*)-thiophene forms a stronger bond to the metal as a result of the increasing number of electron-releasing methyl groups, which makes the sulfur a better σ-donor to the metal.

Selenophene (Sel), the selenium analog of thiophene (Figure 1), has recently become of interest as a means of determining the mode of selenophene adsorption on HDS catalyst surfaces.[15] Recently we described[16] the

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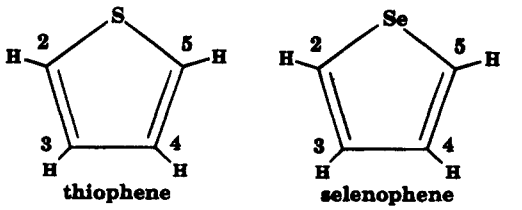
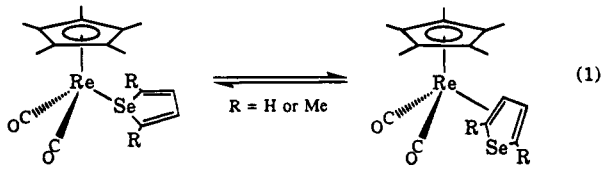


Figure 1. Structures and numbering of thiophene (T) and selenophene (Sel).

synthesis, reactions, and ^{77}Se NMR chemical shifts of a series of η^5-selenophene complexes: (η^5-Sel)Cr(CO)$_3$,[17,18] [(η^5-Sel)Mn(CO)$_3$]$^+$, [Cp*Ru(η^5-Sel)]$^+$, and [Cp*Ir(η^5-Sel)]$^{2+}$. The η^5-Sel complexes are structurally and chemically very similar to the analogous η^5-thiophene complexes. ^{77}Se NMR chemical shift values for η^5-coordinated Sel fall into the region between δ 370 and 150. Within this range the ^{77}Se chemical shift is sensitive to the ionic charge, other ligands in the complex, and the number of methyl groups in the selenophene.

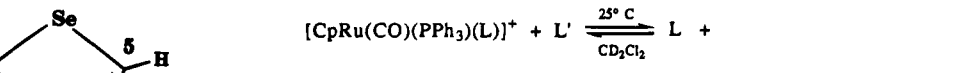
Our group has also previously reported on the coordination of selenophenes (Seln) in the complexes Cp'Re(CO)$_2$(Seln) (Cp' = Cp or Cp*).[15,19] In the electron-rich complex Cp*Re(CO)$_2$(Seln) (Cp * = η^5-C$_5$Me$_5$), selenophene (Sel) is η^2-coordinated through a C=C double bond. In the 2,5-dimethylselenophene (2,5-Me$_2$Sel) complex Cp*Re(CO)$_2$(2,5-Me$_2$Sel), the ligand is coordinated through the Se atom in an $\eta^1(Se)$ manner. When the selenophene ligand is 2-methylselenophene (2-MeSel), both the $\eta^1(Se)$ and η^2 isomers are observed and they are in equilibrium with each other (eq 1). Replace-



(1)

ment of the Cp* ligand with the less electron donating Cp (η^5-C$_5$H$_5$) ligand increases the equilibrium amount of the $\eta^1(Se)$ isomer and decreases the amount of the η^2 isomer. This shift in isomer distribution is reasonable since a decrease in the electron density on the metal would reduce π back-bonding to the olefin in the η^2 isomer but would strengthen selenium to rhenium donation in the $\eta^1(Se)$ isomer.[20,21]

In this paper, we present the synthesis and characterization of several new $\eta^1(Se)$-selenophene complexes [CpRu(CO)(PPh$_3$)($\eta^1(Se)$-Seln)]BF$_4$ (Seln = selenophene (Sel), 2-methylselenophene (2-MeSel), or 2,5-dimethylselenophene (2,5-Me$_2$Sel)). The X-ray-determined structure of [CpRu(CO)(PPh$_3$)($\eta^1(Se)$-2-MeSel)]BF$_4$ is described and compared with that of the analogous thiophene complex. Equilibrium constants for the ligand replacement reaction (eq 2) are reported and are compared with those of the analogous $\eta^1(S)$-thiophene complexes [CpRu(CO)(PPh$_3$)($\eta^1(S)$-Th)]$^+$.[12] Finally, ^{77}Se NMR chemical shift values for the new $\eta^1(Se)$-Seln



(2)

complexes are discussed in relation to those of selenophene in its η^5 and η^2 complexes.

Experimental Section

General Procedures. All reactions and manipulations were carried out under an atmosphere of dry N_2 using standard Schlenk techniques unless otherwise stated.[22,23] All solvents were reagent grade or better and were dried and distilled under N_2 by the following methods. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from Na/benzophenone. Hexanes and dichloromethane (CH_2Cl_2) were distilled from CaH_2. Acetone was dried with potassium carbonate (K_2CO_3) and distilled. The solvents were used immediately after distillation except for acetone, which was stored over K_2CO_3 under N_2. The neutral alumina (Brockman, activity I, ~150 mesh) used for chromatography was deoxygenated at room temperature in high vacuum for 16 h, then deactivated with 5% w/w N_2-saturated deionized distilled water, and stored under N_2.

The ^1H and ^{13}C NMR spectra were recorded on 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, δ = 0.00) or residual CH_2Cl_2 (δ = 5.33). The ^{77}Se NMR spectra were recorded on the Varian VXR-300 spectrometer at room temperature and referenced to selenophene (δ = 605.0 ppm). Fast atom bombardment (FAB) mass spectra were obtained using a Kratos MS-50 mass spectrometer. Infrared spectra were obtained on a Nicolet 710 FTIR spectrophotometer using a solution cell with NaCl salt plates. Elemental analyses were performed by either Galbraith Laboratories, Inc., Knoxville, TN, or Desert Analytics, Tucson, AZ.

The following compounds were prepared by literature methods: CpRu(CO)(PPh$_3$)Cl,[24] [CpRu(CO)(PPh$_3$)(Th)]BF$_4$ (Th = thiophene (T), 2-methylthiophene (2-MeT), 2,5-dimethylthiophene (2,5-Me$_2$T), benzothiophene (BT), and dibenzothiophene (DBT)),[12] selenophene (Sel),[25,26] 2-methylselenophene (2-MeSel),[27] 2,5-dimethylselenophene (2,5-Me$_2$Sel),[28] *p*-tolyl sulfide (PTS),[29] 2,8-dimethyldibenzothiophene(2,8-Me$_2$DBT).[30]

[Cp(CO)(PPh$_3$)Ru(η^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)(PPh$_3$)RuCl in 20 mL of CH_2Cl_2 was added 0.056 g (0.288 mmol) of $AgBF_4$. A white AgCl precipitate formed, and the solution turned from orange to yellow. After being stirred for 1 h at room temperature, the solution was filtered through Celite and the volatiles were removed under vacuum. The yellow oily residue was taken up into 2–3 mL of CH_2Cl_2; upon addition of 20 mL of Et_2O, product **1** precipitated as a yellow powder. The powder was filtered out and washed with 10 mL of Et_2O three times and dried under vacuum. Yield of **1**: 0.167 g, 86%. ^1H NMR (δ) (CD_2Cl_2): 7.79–7.77 (m, H(2), H(5)), 7.31–7.29 (m, H(3), H(4)), 4.92 (s, Cp), 7.59–7.35 (m, Ph). ^{13}C

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NMR (δ) (CD_2Cl_2): 200.74 (d, J_{C-P} = 18.3 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} = 1.3 Hz, Cp). ^{77}Se NMR (δ) (CD_2Cl_2): 411.6 (d, J_{Se-P} = 12 Hz). IR (cm^{-1}) (CH_2Cl_2): 1991. Anal. Calcd for $C_{28}H_{24}OPRuSeBF_4$: C, 49.88; H, 3.59. Found: C, 50.33; H, 3.72. If a more crystalline product was desired, the powder was recrystallized from a minimum of CH_2Cl_2 layered with a 5–7-fold excess of Et_2O at −20 °C overnight; this yielded bright yellow crystals.

[Cp(CO)(PPh$_3$)Ru(η^1(*Se*)-2-MeSel)](BF$_4$) (2). Compound **2** was synthesized in the same manner as **1** using 1.00 mL of 2-MeSel, 0.103 g (0.209 mmol) of Cp(CO)(PPh$_3$)RuCl, and 0.056 g (0.29 mmol) of $AgBF_4$. Yellow crystals of **2** were obtained (0.161 g, 81%). ^{1}H NMR (δ) (CD_2Cl_2): 7.35 (H(5)), 7.10 (m, H(4)), 6.89 (m, H(3)), 2.47 (s, CH_3), 4.87 (s, Cp), 7.65–7.30 (m, Ph). ^{13}C NMR (δ) (CD_2Cl_2): 200.6 (d, J_{C-P} = 17.4 Hz, CO), 157.93 (d, J_{C-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). ^{77}Se NMR (δ) (CD_2Cl_2): 427.4 (d, J_{Se-P} = 12 Hz). IR (cm^{-1}) (CH_2Cl_2): 1988. FAB mass spectrum (*m/e*): 601.0 (M^+), 456.9 (M^+ − 2-MeSel). Anal. Calcd for $C_{29}H_{26}OPRuSeBF_4$: C, 50.44; H, 3.81. Found: C, 49.97; H, 3.78.

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

[Cp(CO)(PPh$_3$)Ru(η^1(*Se*)-2,8-Me$_2$DBT)]BF$_4$ (4). Compound **4** was made using the same method previously published[12] for the synthesis of [Cp(CO)(PPh$_3$)Ru(η^1(*S*)-DBT)]SO_3CF_3 substituting 2,8-Me_2DBT for DBT. The reaction utilized 0.100 g (0.203 mmol) of CpRu(CO)(PPh$_3$)Cl, 0.129 g (0.609 mmol) of 2,8-Me_2DBT, and 0.400 g (0.205 mmol) of $AgBF_4$. The product **4** was isolated as a yellow solid. Yield: 0.126 g, 76%. ^{1}H NMR (CD_2Cl_2): 7.87 (s, DBT), 2.52 (s, CH_3), 7.59–7.35 (m, PPh_3), 4.72 (s, Cp). IR (cm^{-1}) (CH_2Cl_2): 1992. Anal. Calcd for $C_{38}H_{35}OPRuSBF_4{\cdot}0.2CH_2Cl_2$: C, 60.01; H, 4.16. Found: C, 60.21; H, 4.15.

[Cp(CO)(PPh$_3$)Ru(η^1(*S*)-(p-H$_3$CC$_6$H$_4$)$_2$S)]SO$_3$CF$_3$ (5). A solution of 0.100 g (0.203 mmol) of CpRu(CO)(PPh$_3$)Cl and 0.053 g (0.21 mmol) of AgOTf in 20 mL of CH_2Cl_2 was stirred in a foil-covered flask for 1 h. A white precipitate slowly formed, and the dark yellow solution lightened in color. After filtration through Celite, 0.15 g (0.708 mmol) of (p-$H_3CC_6H_4)_2S$ (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 × 10 mL) to remove the excess PTS. The yellow solid **5** was dissolved into 5 mL of CH_2Cl_2; the solution was filtered, and 30 mL of hexanes was added to precipitate a bright yellow powder. The product **5** was filtered out and dried under a stream of N_2 and finally under vacuum. Yield: 0.153 g (92%, based on Ru). ^{1}H NMR (δ) (CD_2Cl_2): 7.56–7.52 (m), 7.46–7.43 (m), 7.21–7.12 (m), 7.02–6.99 (m), 5.04 (s, Cp), 2.37 (s, CH_3). IR (cm^{-1}) (CH_2Cl_2): 1992. Anal. Calcd for $C_{39}H_{37}O_4PRuS_2F_3$: C, 57.14; H, 4.18. Found: C, 57.95; H, 4.52.

X-ray Structure Determination of [CpRu(CO)(PPh$_3$)-(η^1(*Se*)-2-MeSel)]BF$_4$ (2). A single crystal of **2** suitable for X-ray diffraction study was obtained by vapor diffusion of Et_2O into a saturated CH_2Cl_2 solution of **2** at −20 °C. The single crystal was mounted on the end of a glass fiber. Cell constants were determined from reflections found in a 2θ range of 25 to 30°. Pertinent data collection and reduction information is 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.

Table 1. Crystal and Data Collection Parameters for [CpRu(CO)(PPh$_3$)(η^1(*Se*)-2-MeSel)]BF$_4$ (2)

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

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

Table 2. Selected Bond Distances (Å) and Angles (deg) for [CpRu(CO)(PPh$_3$)(η^1(*Se*)-2-MeSel)]BF$_4$ (2)

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

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

[a] Estimated standard deviations are given in parentheses.

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 ^{1}H NMR signals of the reactants and products as previously described.[12,13]

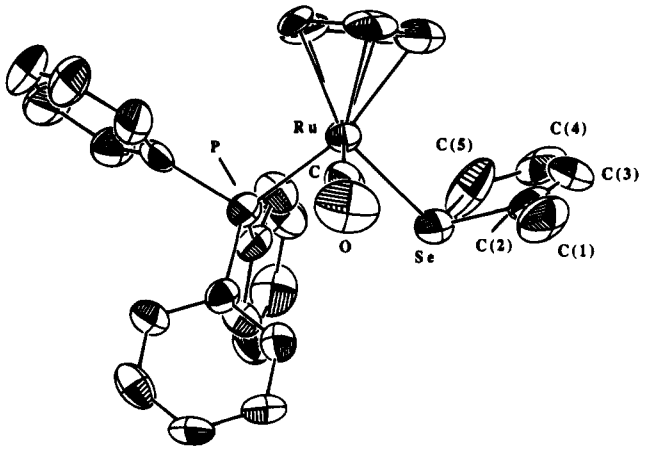


Figure 2. ORTEP drawing of $[CpRu(CO)(PPh_3)(\eta^1(Se)\text{-}2\text{-}Me_2Sel)]^+$ (**2**).

Table 3. Positional Parameters and *B*(eq) Values (Å²) for $[CpRu(CO)(PPh_3)(\eta^1(Se)\text{-}2\text{-}MeSel)]BF_4$ (2)

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

About 0.020 mmol of a $[Cp(CO)(PPh_3)Ru(L)]^+$ complex was placed in a 5 mm NMR tube and then dissolved in 0.5 mL of CD_2Cl_2, and an equimolar amount of the incoming ligand (L′) was added under N_2. The solution was frozen in liquid nitrogen and 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 precooled and thermostated at 25.0 °C; CD_2Cl_2 was the internal lock and reference (δ 5.32). A 38 s 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 eq 3, where I'_{Cp} and I_{Cp} are the Cp peak integrals of $Cp(CO)(PPh_3)$-

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

$Ru(L')^+$ and $Cp(CO)(PPh_3)Ru(L)^+$, respectively; I_{Me} is the integral of the Me peak of L′ and *x* is 3 (for L′ = 2-MeT, 2-MeSel) or 6 (for L′ = 2,5-Me_2T, 2,5-Me_2Sel, 2,8-Me_2DBT, PTS). The *K* values in Table 4 are averages of at least two independent determinations. The error limits in Table 4 are average deviations from the mean value. The solutions were stable for 6 weeks or longer.

Results and Discussion

Synthesis and Characterization of $[CpRu(CO)(PPh_3)(\eta^1(Se)\text{-Seln})]^+$ Complexes (1−3). The compounds $[CpRu(CO)(PPh_3)(\eta^1(Se)\text{-Seln})]BF_4$ (Seln = Sel (**1**), 2-MeSel (**2**), or 2,5-Me_2Sel (**3**)) were synthesized from $CpRu(CO)(PPh_3)Cl$, $AgBF_4$, and the appropriate ligand in CH_2Cl_2 (eq 4). The halide extraction method

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

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

has been used previously to make a variety of cationic ruthenium complexes $[CpRu(CO)(PPh_3)(L)]^+$ (L = PR_3, CO,[24] Th[12,13]). The complexes **1**−**3** are all bright yellow, air-stable solids and are soluble in most polar organic solvents.

The ^1H NMR spectra of **1**−**3** show selenophene proton resonances that are upfield (~0.1 ppm) of those in the free selenophenes. The ^1H chemical shifts of the Sel in **1** are approximately 0.5 ppm downfield of the corresponding protons in the analogous thiophene complex $[CpRu(CO)(PPh_3)(\eta^1(S)\text{-T})]BF_4$. These differences are approximately the same as those in the two free ligands. Despite the asymmetry at the Ru, the H(2) and H(5) protons in **1** and the methyl groups in **3** occur as single resonances in their room-temperature ^1H NMR spectra. At low temperature (198 K) the ^1H NMR spectrum of **3** in CD_2Cl_2 shows two broad resonances at 2.42 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).[31] Coalescence of the methyl groups in the 2,5-dimethylthiophene complex $[CpRu(CO)(PPh_3)(\eta^1(S)\text{-}2,5\text{-}Me_2T)]^+$ occurs at T_c = 213 K with a free energy of activation of 40 kJ/mol.[12] 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 organosulfur and -selenium complexes[32] such as $ReCl(CO)_3(EMe_2)_2$ and $PtBr(Me)(EMe_2)_2$ the inversion bar-

(31) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; p 96.
(32) Abel, E.; Bhargava, S. K.; Orrell, K. G. In *Progress in Inorganic Chemistry*; Wiley: New York, 1984; Vol. 32, pp 1−118.

rier is also lower in the S than the Se analog. A low-temperature ^1H NMR spectrum of **1** in CD_2Cl_2 shows only a slight broadening of the proton resonances at the freezing point (178 K) of CD_2Cl_2; this indicates that the T_c for **1** is lower than 178 K. The lower T_c for **1** as compared with that for **3** suggests that steric interactions between the substituents in the 2,5-positions of the selenophene and the bulky triphenylphosphine ligand reduce the rate of inversion at selenium. The assignment of a resonance to H(5) in **2** was done using the 2D $^1H/^{13}C$ HETCOR NMR spectrum. It was necessary to use this 2D technique because of overlapping ^1H resonances from the PPh_3 and the 2-MeSel ligands.

The ^{13}C NMR spectra of **1**–**3** were assigned using the 2D $^1H/^{13}C$ HETCOR NMR technique because resonances of both the SeIn and the PPh_3 ligands occurred in the same region. The ^{13}C chemical shift values of selenophene in **1**–**3** are downfield (~12 ppm, C(2), C(5); ~4 ppm, C(3), C(4)) compared to those of the free selenophene. The ^{13}C resonances of the SeIn ring carbons are consistently downfield (~4 ppm, C(2), C(5); ~2 ppm, C(3), C(4)) of those in the corresponding thiophene complex.[12] A similar downfield shift is also seen in the free SeIn 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.[12]

The ν(CO) band in the IR spectra of **1**–**3** is consistently 8–10 cm^{-1} smaller than in the corresponding thiophene complexes,[12] which suggests that selenophene is a better σ donor ligand than thiophene.

Molecular Structure of [CpRu(CO)(PPh_3)(η^1(*Se*)-2-MeSel)]BF_4 (2). The X-ray-determined molecular structure of the cation [CpRu(CO)(PPh_3)(η^1(*Se*)-2-MeSel)]$^+$ is shown in Figure 2. The selenophene ring is essentially planar with a dihedral angle between the least-squares planes of C(2)–Se–C(5) and C(2)–C(3)–C(4)–C(5) of only 0.89°. The selenium has pyramidal geometry as indicated by the angle (113.83(7)°) between the Ru–Se bond and the vector between Se and the midpoint between C(2) and C(5); also, the sum (304°) of the three angles around the Se is substantially less than the 360° required if the Se were planar. The Ru–Se bond distance (2.494(2) Å) is 0.102 Å longer than the corresponding Ru–S bond distance (2.392(1) Å) in [CpRu(CO)(PPh_3)(η^1(*S*)-2-MeT)]$^+$ due to the larger size of the selenium atom. The C(2)–Se (1.90(2) Å) and C(5)–Se (1.85(2) Å) bond distances are similar to those in free selenophene (1.855(7) Å)[33] and (η^5-2,5-Me_2Sel)-$Cr(CO)_3$ (1.910(1) Å),[18] although the error limits are rather large in **2**. The C–Se distances in **2** are approximately 0.15 Å longer than the C–S distances in the 2-MeT complex [CpRu(CO)(PPh_3)(η^1(*S*)-2-MeT)]$^+$ due to the larger size of the Se atom. The C(2)–Se–C(5) bond angle in **2** is 4.3° smaller than the corresponding C(2)–S–C(5) angle in [CpRu(CO)(PPh_3)(η^1(*S*)-2-MeT)]$^+$; this difference is probably also due to the larger size of Se. Overall, the combination of the longer Ru–Se and C–Se bonds and the smaller C(2)–Se–C(5) bond angle move the methyl groups in 2-MeSel further from the other ligands in the Ru coordination sphere than occurs with 2-MeT. For this reason, 2-MeSel is a less sterically demanding ligand than 2-MeT.

(33) Brown, R. D.; Burden, F. R.; Godfrey, P. D. *J. Mol. Spectrosc.* **1968**, *25*, 413.

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

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

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

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

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

[a] Reference 12.

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

Using K values previously determined for Th[12] and the values in Table 4, relative equilibrium constants (K') were calculated (Table 5) for the displacement of thiophene by the other ligands (eq 5). In a previous

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

study[12] of this equilibrium using substituted thiophenes as L′ ligands, it was noted that K' increases (Table 5) in the following order: T (1.00) < 2,5-Me_2T (2.76) < 2-MeT (4.11) < 3-MeT (6.30) < BT (29.9) < Me_4T (57.4) < DBT (74.1) ≪ THT ($>7.1 \times 10^6$). By comparison with tetrahydrothiophene (THT), all the thiophene ligands are weakly coordinating, thiophene (T) being the most weakly binding. The addition of a methyl group as in 2-MeT or 3-MeT increases the coordinating ability of the thiophene; the electron-releasing methyl group presumably makes the sulfur a stronger σ-donor to the Ru. However, two methyl groups in the 2- and 5-positions reduce the coordinating ability of 2,5-Me_2T, as compared

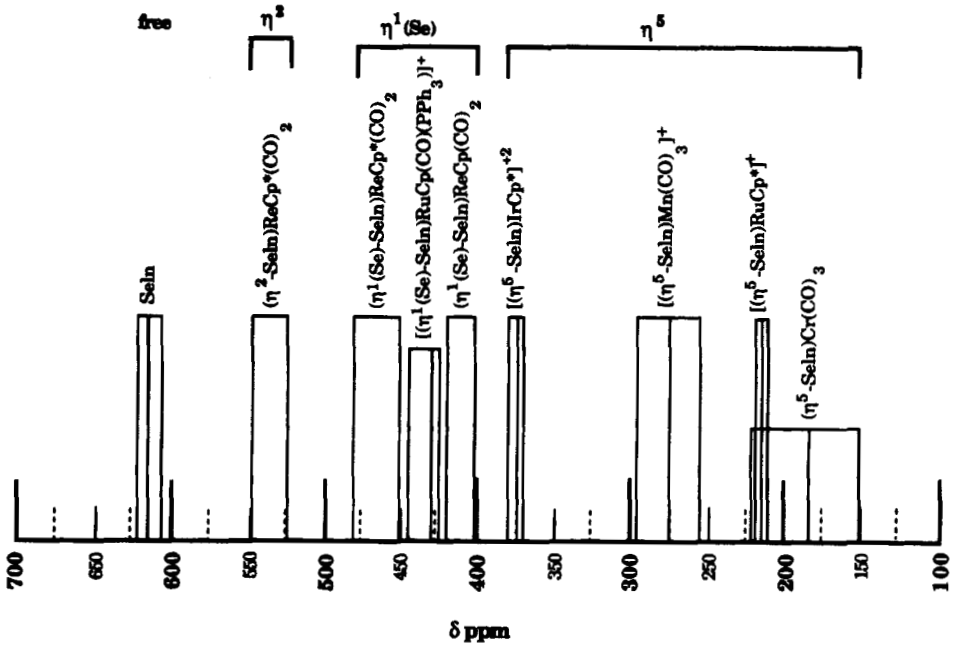
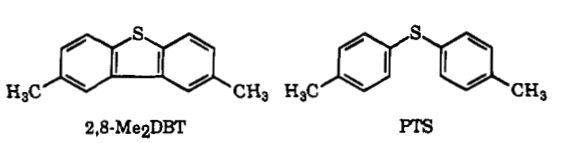


Figure 3. ^{77}Se NMR chemical shifts of selenophene complexes.

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

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

For the dibenzothiophene-related ligands, the K' values increase in the following order: DBT (74.1) < 2,8-Me_2DBT (358) < PTS (7.11×10^3). The larger K' for 2,8-Me_2DBT as compared with that for DBT undoubtedly results from the electron-donating methyl groups which make the sulfur a better σ-donor to Ru. The p-tolyl sulfide (PTS) ligand binds about 96 times more strongly than DBT and about 20 times more strongly than 2,8-Me_2DBT. The DBT and 2,8-Me_2DBT



ligands are structurally similar except for the C—C bond between the tolyl rings which creates the thiophene ring. Delocalization within the thiophene may be responsible for the lower coordinating ability of 2,8-Me_2-DBT as compared with PTS. It is also possible that PTS is a less bulky ligand than 2,8-Me_2DBT because of its ability to rotate around the S—tolyl bonds.

^{77}Se NMR Studies of Coordinated Selenophenes. As part of an investigation of ^{77}Se chemical shifts of selenophenes and their complexes, we determined the ^{77}Se chemical shifts of the $\eta^1(Se)$-selenophene complexes [CpRu(CO)(PPh_3)($\eta^1(Se)$-Seln)]$^+$; these values are reported in the Experimental Section. They are also plotted in Figure 3 with those of the free selenophenes and their η^2, $\eta^1(Se)$, and η^5 complexes. In general, the various modes of selenophene coordination define certain ^{77}Se chemical shift regions. The free selenophenes[16,34] are furthest downfield with a chemical shift range from δ 621 for 2,5-Me_2Sel to δ 605 for Sel. Somewhat upfield are the η^2 complexes in which the Seln is coordinated only through two carbon atoms; at this time only two compounds, Cp*Re(CO)$_2$(η^2-Sel) (δ 524) and Cp*Re(CO)$_2$(η^2-2-MeSel) (δ 549),[19] are known with the η^2 structure. Upfield from the η^2 compounds are those with $\eta^1(Se)$-Seln ligands, which have chemical shifts in the range δ 480–402. Finally, the most upfield selenophenes are those that are η^5-coordinated to transition metals. These chemical shifts[16] cover a broad range and increase in the following order: [(η^5-Seln)IrCp*]$^{2+}$ < [(η^5-Seln)Mn(CO)$_3$]$^+$ < [(η^5-Seln)RuCp*]$^+$ < (η^5-Seln)Cr(CO)$_3$. In general, the ^{77}Se chemical shifts of the η^5-Seln complexes move to higher field as the positive charge on the complex decreases, but it is evident from the Mn and Ru complexes that the metal and its other ligands also influence the ^{77}Se chemical shift values.

Figure 3 shows that there are rather well-defined regions for the different modes of Seln binding. This suggests that ^{77}Se NMR chemical shifts can be used to distinguish Seln binding modes in metal complexes. It also suggests that solid state ^{77}Se NMR studies of

(34) McFarlane, H. C. E.; McFarlane, W. In *NMR of Newly Accessible Nuclei*; Academic Press: New York, 1983; Vol. 2, pp 275–299.

selenophene adsorbed on HDS catalysts may be able to establish mode(s) of selenophene binding to the catalyst surface.

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

Supplementary Material Available: A fully labeled structure and tables of hydrogen atom coordinates, thermal parameters, bond distances and angles, and least-squares planes (7 pages). Ordering information is given on any current masthead page.

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