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Synthesis, Reactivity, and ^{77}Se NMR Studies of the η^2- and $\eta^1(Se)$-Selenophene Complexes $Cp'(CO)_2Re(Sel)$

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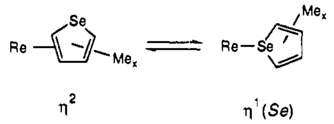
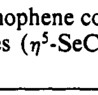
Abstract: Selenophenes coordinate in $Cp'(CO)_2Re(Sel)$ ($Cp' = C_5H_5$ or C_5Me_5; Sel = selenophenes) as a rapidly equilibrating mixture of $\eta^1(Se)$ and η^2 isomers. Increasing the electron density on the Re by replacing Cp with Cp* favors η^2-coordination,



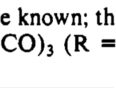
while addition of methyl groups to the selenophene favors the η^1(Se) isomer. These shifts in the $\eta^2 \rightleftarrows \eta^1(Se)$ equilibrium can be readily explained by noting that electron-donating methyl groups in the selenophene enhance the donor ability of the Se and reduce the π-acceptor ability of the olefin which favors Se-coordination, while increasing the electron density on the Re strengthens π-back-bonding to the η^2 ligand. The uncoordinated selenophene Se atom in $Cp^*(CO)_2Re(\eta^2\text{-Sel})$ (**1**) is capable of binding to $M(CO)_4(L)(THF)$ (M = Cr, Mo, W; L = CO or PPh_3) to give dinuclear selenophene-bridged complexes $Cp^*(CO)_2Re(\mu_2\text{-}\eta^2(Se)\text{-Sel})[M(CO)_4(L)]$ in which the selenophene is η^2 bonded to the Re and Se-bonded to a second metal (M). The reaction of **1** with $Fe_2(CO)_9$ gives three different types of compounds. One of them (**11**) results from $Fe(CO)_4$ addition to the Se of the η^2 isomer; another presumably results from coordination of $Fe(CO)_3$ to the diene portion of the $\eta^1(Se)$ isomer. The third product has a thiaferrole-type structure in which a C–Se bond has been cleaved. ^{77}Se NMR studies of these different types of selenophene complexes are also reported.

Introduction

One aspect of our studies of the mechanism(s) of thiophene hydrodesulfurization (HDS) on heterogenous catalysts[2] involves examining various modes of thiophene (T) coordination[3] on transition-metal catalysts. It would be desirable to probe thiophene bonding on heterogeneous catalysts by comparing spectroscopic properties of adsorbed thiophene with those of thiophene in its fully characterized complexes. Solid-state NMR would be a useful spectroscopy for making such comparisons; however sulfur isotopes are not generally suitable for NMR studies. On the other hand, ^{77}Se with a 7.6% natural abundance and a nuclear spin of $^1/_2$ has a receptivity that is 2.98 times greater[4] than that of ^{13}C and a chemical shift range that is much greater than that of ^{13}C.[5] Selenophene has structural, bonding, and reactivity properties that are very similar to those of thiophene.[6] Therefore, we have begun studies of selenophene (Sel) as a model for thiophene adsorbed on HDS catalysts and coordinated in transition-metal complexes. In the present paper, we report a study of three different modes of selenophene coordination in its complexes.

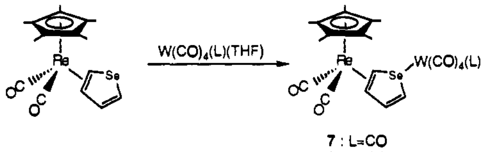


T



Sel

Very few selenophene complexes are known; the first were the η^5-Sel derivatives $(\eta^5\text{-}SeC_4R_2H_2)Cr(CO)_3$ (R = H or Me)[7] in which the selenophene is π-coordinated through all five atoms in the ring. The other was the η^2-Sel complex (eq 1) communicated[8] by us in 1990; this bonding mode was especially interesting because the analogous thiophene complex $Cp^*(CO)_2Re(T)$ contained an S-bound thiophene. Complex **1** reacted with $W(CO)_4(L)(THF)$ to give complexes in which the Sel is η^2-coordinated to the Re and Se bound to the W.[8] In the present paper, we describe further details of selenophene coordination and reactivity in the $Cp'(CO)_2Re$ system; ^{77}Se NMR studies of these complexes are also presented.



(1)

1

7 : L=CO
10 : L=PPh$_3$

Experimental Section

General Procedures. All reactions were performed under an N_2 atmosphere in reagent grade solvents, using standard Schlenk techniques.[9] Diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled from Na/benzophenone, CH_2Cl_2 and hexanes from CaH_2. The solvents were stored over 4-Å molecular sieves under N_2. The neutral alumina (~150 mesh, Brockman I, Aldrich) used for chromatography was deoxygenated at room temperature under high vacuum for 16 h, deactivated with 5% (w/w) N_2-saturated water, shaken, and stored under N_2. The ^{1}H and ^{13}C NMR spectra were obtained on both Nicolet NT-300 and Varian VXR-300 spectrometers with $CDCl_3$ as the internal lock. The ^{77}Se NMR spectra were recorded on the Varian VXR-300 spectrometer and referenced to selenophene (605 ppm) at room temperature. Electron-ionization mass spectra (EIMS) were run on a Finnigan 4000 spectrometer. Fast atom bombardment (FAB) spectra were obtained with use of a Kratos MS-50 mass spectrometer. Infrared spectra were obtained on either a Perkin-Elmer 681 or Digilab FTS-7 FT-IR spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Photochemical reactions (using a 450W mercury UV lamp) were carried out in a quartz tube which was maintained at −20 °C with

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use of a Lauda RK 20 constant temperature circulator.

The following compounds were prepared by literature methods: $Cp^*Re(CO)_3$,[10] $CpRe(CO)_3$,[11] $W(CO)_5(PPh_3)$,[12] Sel,[13] 2-MeSel,[14] 2,5-Me_2Sel.[15]

$Cp^*(CO)_2Re(\eta^2\text{-Sel})$ (1). A solution of $Cp^*(CO)_2Re(THF)$, prepared by UV irradiation[16] of a THF solution (30 mL) of $Cp^*Re(CO)_3$ (0.20 g, 0.49 mmol) at -20 °C, was stirred with selenophene (2.0 mL, 24.5 mmol) at room temperature for 7 h. Following removal of the solvent in vacuo, the residue was chromatographed on a neutral alumina column (1 × 15 cm). First, unreacted $Cp^*Re(CO)_3$ was eluted with hexanes and then a yellow band was obtained with hexanes–CH_2Cl_2 (4:1). The yellow eluent was concentrated and cooled to -20 °C to give moderately air-stable light yellow crystals of 1 (0.11 g, 44%). IR (hexanes) ν(CO): 1962 (s), 1898 (s) cm^{-1}. EIMS (70 eV) *m/e* 510 (M^+, based on ^{187}Re and ^{80}Se), 454 ($M^+ - 2CO$), 378 (M^+ - Sel), 350 (M^+ - (Sel + CO)). Anal. Calcd for $C_{16}H_{19}O_2ReSe$: C, 37.79; H, 3.77. Found: 37.96; H, 3.75.

$Cp^*(CO)_2Re(\eta^2\text{-2-MeSel})$ (2a) and $Cp^*(CO)_2Re(\eta^1(Se)\text{-2-MeSel})$ (2b). This compound was prepared in a similar manner as described for 1 starting with $Cp^*Re(CO)_3$ (0.20 g, 0.49 mmol) and 2-MeSel (0.50 mL, 0.80 g, 5.6 mmol). After chromatography, the product 2 was isolated as moderately air-stable light-yellow crystals (0.13 g, 48%). IR (hexanes) ν(CO): (**2a**) 1962 (s), 1898 (s) cm^{-1}; (**2b**) 1927 (s), 1865 (s) cm^{-1}. EIMS (16 eV) *m/e* 524 (M^+, based on ^{187}Re and ^{80}Se), 468 ($M^+ - 2CO$), 378 (M^+ - MeSel), 350 (M^+ - (MeSel + CO)). Anal. Calcd for $C_{17}H_{21}O_2ReSe$: C, 39.08; H, 4.05. Found: C, 39.09; H, 4.05.

$Cp^*(CO)_2Re(\eta^1(Se)\text{-2,5-}Me_2Sel)$ (3). Complex 3 was synthesized in the same manner as described for 1 starting with $Cp^*Re(CO)_3$ (0.20 g, 0.49 mmol) and 2,5-Me_2Sel (0.40 mL, 4.0 mmol). The product 3 was obtained as yellow, moderately air-stable crystals (0.12 g, 46%). IR (hexanes) ν(CO): 1925 (s), 1866 (s) cm^{-1}. EIMS (70 eV) *m/e* 538 (M^+, based on ^{187}Re and ^{80}Se), 482 ($M^+ -2CO$), 378 ($M^+ - Me_2Sel$), 350 ($M^+ - (Me_2Sel + CO)$). Anal. Calcd for $C_{18}H_{23}O_2ReSe$: C, 40.29; H, 4.32. Found: C, 40.20; H, 4.35.

$Cp(CO)_2Re(\eta^2\text{-Sel})$ (4a) and $Cp(CO)_2Re(\eta^1(Se)\text{-Sel})$ (4b). The synthesis of 4a and 4b follows that used for 1 starting with $CpRe(CO)_3$ (0.10 g, 0.30 mmol) and Sel (1.0 mL, 12.2 mmol). After workup as described for 1, the mixture of 4a and 4b was obtained as moderately air-stable yellow crystals (51 mg, 39% yield). IR (hexanes) ν(CO): (**4a**) 1973 (s), 1906 (s) cm^{-1}; (**4b**) 1943 (m), 1883 (m) cm^{-1}. EIMS (70 eV) *m/e* 440 (M^+, based on ^{187}Re and ^{80}Se), 384 ($M^+ - 2CO$), 308 (M^+ - Sel), 280 (M^+ - (Sel + CO)). Anal. Calcd for $C_{11}H_9O_2ReSe$: C, 30.14; H, 2.07. Found: C, 30.66; H, 2.13.

$Cp(CO)_2Re(\eta^1(Se)\text{-2-MeSel})$ (5). Compound 5 was prepared by the same method as described for 1 starting with $CpRe(CO)_3$ (0.10 g, 0.30 mmol) and 2-MeSel (0.50 mL, 0.80 g, 5.6 mmol). Moderately air-stable yellow crystals (58 mg, 43%) were obtained. IR (hexanes) ν(CO): 1942 (s), 1880 (s) cm^{-1}, EIMS (70 eV) *m/e* 454 (M^+, based on ^{187}Re and ^{80}Se), 398 ($M^+ - 2CO$), 308 (M^+ - MeSel), 280 (M^+ - (MeSel + CO)).

Reaction of 1 with $Me_3O(BF_4)$ To Give $[Cp^*(CO)_2Re(\eta^2\text{-Sel}\cdot CH_3)](BF_4)$ (6). To a solution of 1 (35 mg, 0.069 mmol) in CH_2Cl_2 (5 mL) was added $(Me_3O)BF_4$ (12 mg, 0.081 mmol). After being stirred at room temperature for 1 h, the solution was filtered through Celite. Following evaporation of the solvent, the light yellow residue was recrystallized from CH_2Cl_2–Et_2O (1:10) at -20 °C to yield pale yellow crystals of 5 (11 mg, 26%). IR (CH_2Cl_2) ν(CO): 1980 (s), 1905 (s) cm^{-1}. FAB MS (CH_2Cl_2–3-nitrobenzyl alcohol matrix): *m/e* 525 (M^+, based on ^{187}Re and ^{80}Se). Anal. Calcd for $C_{17}H_{22}BF_4O_2ReSe$: C, 33.46; H, 3.63. Found: C, 33.17; H, 3.60.

Reaction of 1 with $W(CO)_5(THF)$ To Give $Cp^*(CO)_2Re(\mu_2\text{-}\eta^2(Se)\text{-Sel})W(CO)_5$ (7). A solution of $W(CO)_5(THF)$[17] was generated by UV irradiation of a THF solution (25 mL) of $W(CO)_6$ (60 mg, 0.17 mmol). To the stirred solution of $W(CO)_5(THF)$ was added 1 (50 mg, 0.098 mmol) at room temperature. The resulting solution was stirred for 7 h. After evaporation of the solution to dryness in vacuo, the residue was chromatographed on neutral alumina (1 × 10 cm) with hexanes–CH_2Cl_2 (2:1) as the eluent. The yellow band was collected and reduced in volume under vacuum. Slow cooling of the concentrated solution to -70 °C gave air-stable, pale-yellow crystals (57 mg, 70%). IR (hexanes) ν(CO): 2076 (w), 1980 (w), 1940 (s), 1932 (s), 1924 (s), 1912 (m) cm^{-1}. EIMS (70 eV) *m/e* 778 ($M^+ - 2CO$, based on ^{187}Re and ^{80}Se), 750 ($M^+ - 3CO$), 722 ($M^+ - 4CO$), 694 ($M^+ - 5CO$), 510 ($M^+ - W(CO)_5$). Anal. Calcd for $C_{21}H_{19}O_7ReSeW$: C, 30.30; H, 2.30. Found: C, 30.58; H, 2.34.

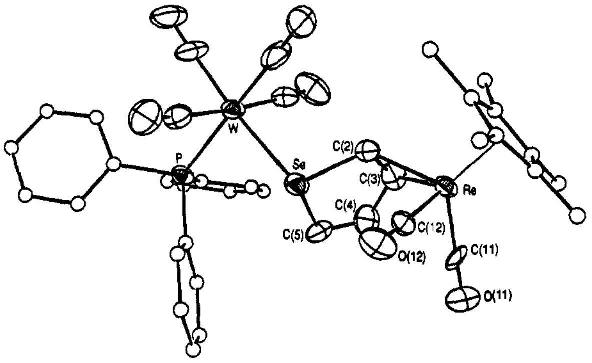

Figure 1. ORTEP drawing of $Cp^*(CO)_2Re(\mu_2\text{-}\eta^2(Se)\text{-Sel})[W(CO)_4(PPh_3)]$ (**10**).

Reaction of 1 with $Mo(CO)_5(THF)$ To Give $Cp^*(CO)_2Re(\mu_2\text{-}\eta^2(Se)\text{-Sel})Mo(CO)_5$ (8). Compound 1 was reacted with $Mo(CO)_5(THF)$ in a similar manner as described for 7 starting with $Mo(CO)_6$ (51 mg, 0.19 mmol) and 1 (65 mg, 0.13 mmol). Air-stable, tan-yellow crystals of 8 (63 mg, 66%) were obtained. IR (hexanes) ν(CO): 2071 (w), 1978 (m), 1949 (s), 1941 (s), 1927 (s), 1912 (m) cm^{-1}. FAB MS (CH_2Cl_2–3-nitrobenzyl alcohol matrix): *m/e* 510 ($M^+ - Mo(CO)_5$, based on ^{187}Re and ^{80}Se).

Reaction of 1 with $Cr(CO)_5(THF)$ To Give $Cp^*(CO)_2Re(\mu_2\text{-}\eta^2(Se)\text{-Sel})Cr(CO)_5$ (9). Compound 1 was reacted with $Cr(CO)_5(THF)$ in a similar manner as described for 7 starting with $Cr(CO)_6$ (45 mg, 0.20 mmol) and 1 (60 mg, 0.12 mmol). Pale yellow, air-stable crystals of 9 (59 mg, 71%) were obtained. IR (hexanes) ν(CO): 2061 (w), 1978 (m), 1943 (s), 1934 (s), 1926 (s), 1913 (m) cm^{-1}. FAB MS (CH_2Cl_2-3-nitrobenzyl alcohol matrix): *m/e* 702 (M^+, based on ^{187}Re and ^{80}Se), 510 ($M^+ - Cr(CO)_5$). Anal. Calcd for $C_{21}H_{19}CrO_7ReSe$: C, 36.01; H, 2.73. Found: C, 36.07; H, 2.73.

Reaction of 1 with $W(CO)_4(PPh_3)(THF)$ To Give $Cp^*(CO)_2Re(\mu_2\text{-}\eta^2(Se)\text{-Sel})[W(CO)_4(PPh_3)]$ (10). To a solution of $W(CO)_4(PPh_3)(THF)$,[18] prepared by UV photolysis of $W(CO)_5(PPh_3)$ (90 mg, 0.015 mmol) in 25 mL of THF, was added 1 (60 mg, 0.12 mmol). After the solution was stirred for 7 h, the product 10 was isolated as air-stable, pale-yellow crystals (92 mg, 73%) following the workup used for 7. IR (hexanes) ν(CO): 2014 (m), 1955 (m), 1908 (m), 1873 (s), 1852 (s) cm^{-1}. FAB MS (CH_2Cl_2-3-nitrobenzyl alcohol matrix): *m/e* 1068 (M^+, based on ^{187}Re and ^{80}Se), 510 ($M^+ - W(CO)_4(PPh_3)$).

Reaction of 1 with $Fe_2(CO)_9$ To Give 11, 12, and 13. To a THF (20 mL) solution of 1 (70 mg, 0.14 mmol) was added $Fe_2(CO)_9$ (100 mg, 0.27 mmol) at room temperature. With 24 h of stirring, the solution color changed from pale yellow to red orange. After the solvent was evaporated in vacuo, the residue was chromatographed on neutral alumina (1 × 15 cm). The first band, eluted with hexanes, was concentrated under vacuum and slowly cooled to -20 °C to give air-stable, needle-shaped red crystals of $Cp^*(CO)_2Re(\mu_2\text{-}\eta^6\text{-}SeC_4H_4Fe(CO)_3)Fe(CO)_3$ (**13**) (15 mg, 14%). The second and third yellow bands were eluted with CH_2Cl_2–hexanes (1:4). Slow cooling of solutions from these bands to -20 °C gave moderately air-stable yellow crystals of $Cp^*(CO)_2Re(\mu_2\text{-}\eta^2\text{-(Se)-Sel})Fe(CO)_4$ (**11**) (22 mg, 25%) and $Cp^*(CO)_2Re(\mu_2\text{-}\eta^4\text{(Se)-Sel})Fe(CO)_3$ (**12**) (26 mg, 28%), respectively. **11**: IR (hexanes) ν(CO) 2062 (s), 2002 (s), 1990 (s), 1900 (s), 1862 (s) cm^{-1}; CIMS (ammonia), *m/e* 651 (M^+ + H, based on ^{187}Re and ^{80}Se). Anal. Calcd for $C_{19}H_{19}O_5FeReSe$: C, 35.20; H, 2.95. Found: C, 35.28; H, 2.97. **12**: IR (hexanes) ν(CO) 2060 (s), 2000 (s), 1989 (s), 1920 (s), 1900 (s), 1862 (s) cm^{-1}; CIMS (ammonia), *m/e* 679 (M^+ + H, based on ^{187}Re and ^{80}Se). Anal. Calcd for $C_{20}H_{19}O_6FeReSe$: C, 35.52; H, 2.83. Found: C, 34.87; H, 2.54. **13**: IR (hexanes) ν(CO) 2064 (m), 2034 (s), 2018 (m), 1995 (s), 1974 (m), 1938 (w), 1921 (w), 1906 (m) cm^{-1}; CIMS (ammonia) *m/e* 790 (M^+ + H, based on ^{187}Re and ^{80}Se). Anal. Calcd

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Table I. ^{1}H NMR Data (δ) for the Complexes in CDCl$_3$

compd	H2	H3	H4	H5	Cp or Cp*	Me on Sel
1	4.52 (d)[a]	3.64 (br m)	7.02 (br m)	6.68 (d)[b]	1.98 (s)	
2a		6.57 (m)	3.58 (m)	4.45 (d)[c]	1.97 (s)	2.29 (s)
2b		6.82 (m)	7.03 (m)	7.64 (d)[d]	1.97 (s)	2.35 (s)
3		6.59 (s)	6.59 (s)		1.97 (s)	2.26 (s)
4a[e]	5.62 (d)[f]	4.70 (br m)	6.98 (br m)	6.86 (d)[g]	5.11 (s)	
4b[e]	7.97 (d)[h]	7.15 (d)	7.15 (d)	7.97 (d)	4.80 (s)	
5		6.73 (br m)	6.93 (dd)[i]	7.70 (d)	4.82 (s)	2.42 (s)
6	4.46 (d)	3.17 (dd)[j]	7.64 (dd)	6.10 (d)	2.07 (s)	3.06 (s)
7	4.16 (d)[k]	3.18 (br m)	7.01 (br m)	6.29 (d)[l]	2.01 (s)	
8	4.14 (d)[m]	3.21 (m)	7.04 (m)	6.35 (d)[n]	2.01 (s)	
9	4.06 (br s)	3.19 (br s)	7.07 (br s)	6.28 (br s)	2.00 (s)	
10	4.32 (d)	3.19 (dd)[o]	6.82 (dd)	5.29 (d)	1.97 (s)	7.53–7.38 (m)
11	4.02 (d)	3.20 (dd)[p]	7.09 (dd)	6.12 (d)	2.01 (s)	
12	5.85 (m)	3.54 (m)	3.54 (m)	5.85 (m)	1.99 (s)	
13	1.94 (m)	2.88 (m)[q]	5.87 (dd)[r]	8.54 (dd)	1.94 (s)	
Sel	8.05 (m)	7.37 (m)	7.37 (m)	8.05 (m)		
2-MeSel		6.92 (m)	7.11 (m)	7.64 (m)		2.35 (s)
2,5-Me$_2$Sel		6.65 (s)	6.65 (s)			2.50 (s)

[a] $J = 5.4$ Hz. [b] $J = 5.1$ Hz. [c] $J = 6.3$ Hz. [d] $J = 4.8$ Hz. [e] 0 °C. [f] $J = 5.7$ Hz. [g] $J = 5.4$ Hz. [h] $J = 6.0$ Hz. [i] $J = 5.7, 5.4$ Hz. [j] $J = 5.1, 5.4$ Hz. [k] $J = 6.0$ Hz. [l] $J = 5.4$ Hz. [m] $J = 6.0$ Hz. [n] $J = 5.7$ Hz. [o] $J = 5.7, 6.3$ Hz. [p] $J = 6.0, 5.4$ Hz. [q] $J_{H2,3} = 5.5$ Hz, $J_{H3,4} = 2.5$ Hz. [r] $J_{H3,5} = 1.0$ Hz, $J_{H4,5} = 8.8$ Hz.

Table II. ^{13}C{^{1}H} NMR Data (δ) for the Complexes in CDCl$_3$

compd	selenophene	Cp* or Cp	Me on Cp*	CO	Me on Sel
1	134.3 (C4), 119.8 (C5), 52.4 (C3), 46.4 (C2)	97.4	10.3	205.4, 205.0	
2	140.6, 132.4, 130.1, 128.3, 53.5, 47.3	97.3, 94.8	10.2, 10.6	206.1, 206.0, 205.3	15.8, 18.1
3	129.4, 128.2	94.5	10.5	*b*	16.2
4[a]	147.8, 134.2, 131.1, 121.7, 49.4, 43.4	88.1, 82.0		202.9, 202.5, 202.3	
5	144.2, 131.4, 127.2			202.1	15.9
6	156.8, 111.7, 45.7, 37.7	101.0	10.0	204.4, 201.7	27.5
7	140.9, 119.1, 51.1, 44.0	99.0	10.1	204.9, 200.9, 198.1	
8	139.8, 119.5, 50.1, 44.9	98.8		205.3, 201.0	
9	140.9, 119.0, 49.0, 44.7	98.9		216.2, 204.9, 203.3	
11	143.2, 118.6, 51.1, 43.7	99.2	10.1	214.7, 204.8, 203.0	
12	87.0, 46.2	94.9	10.7	207.4, 208.8	
13	173.8 (C5), 111.0 (C4), 45.1 (C2), 23.2 (C3)	98.3	10.0	211.1, 207.0	
Sel	130.3, 129.3				
2-MeSel	146.4, 129.3, 128.4, 127.6				17.9
2,5-Me$_2$Sel	144.3, 127.1				18.1

[a] At 0 °C. [b] Not observed due to low intensity.

for $C_{22}H_{19}O_8Fe_2ReSe$: C, 33.57; H, 2.43. Found: C, 33.56; H, 2.42.

X-ray Structure Determination of 13. A single crystal of complex **13** suitable for X-ray diffraction study was obtained by recrystallization from hexanes solution at −20 °C. A single crystal was carefully mounted on the tip of a glass fiber. The X-ray diffraction intensity data were collected on an Enraf-Nonius CAD4 diffractometer and the cell constants were determined from a list of reflections found by an automated search routine. The empirical absorption correction was made on the basis of a series of ψ scans. No decay corrections were necessary. Relevant crystal data and parameters associated with the data and parameters associated with the data collection for **13** are given in Table IV.

The positions of the Re, Se, and Fe atoms were obtained by direct methods.[19] The remainder of the non-hydrogen atoms were located in a difference Fourier map. In the final cycles of refinement, all of the non-hydrogen atoms were given anisotropic temperature factors.

Hydrogen atoms were not included in the model. Refinement of the structure was carried out with the CAD4-SDP package[20] with use of scattering factors from the usual sources.[21] Selected bond distances and angles for **13**, together with some for **10**,[8] are presented in Tables V and VI; ORTEP drawings of **10** and **13** are given in Figures 1 and 2, respectively.

Results and Discussion

Synthesis of Cp′(CO)$_2$Re(Sel) Complexes and Interconversion of the η^2- and η^1(*Se*) Isomers. The reaction of Cp*(CO)$_2$Re(THF) with selenophene in THF solution results in the formation of 2,3-η^2-selenophene complex **1** (Scheme I). The ^{1}H NMR spectrum (Table I) of **1** [δ 4.52 (H2), 3.64 (H3), 7.02 (H4), 6.72 (H5)] in CDCl$_3$ shows that the two selenophene protons on the coordinated C(2)–C(3) bond are shifted substantially upfield compared to those in free selenophene [δ 8.05 (m, H2,5), 7.37 (m, H3,4) in CDCl$_3$].[22] In the ^{13}C NMR spectrum (Table II) of **1**, two of the four carbon resonances [δ 46.4 (C2), 52.4 (C3), 134.3 (C4), 119.8 (C5)] lie considerably upfield (75–85 ppm) of those in free selenophene [δ 130.3 (C2,5), 129.3 (C3,4) in CDCl$_3$],

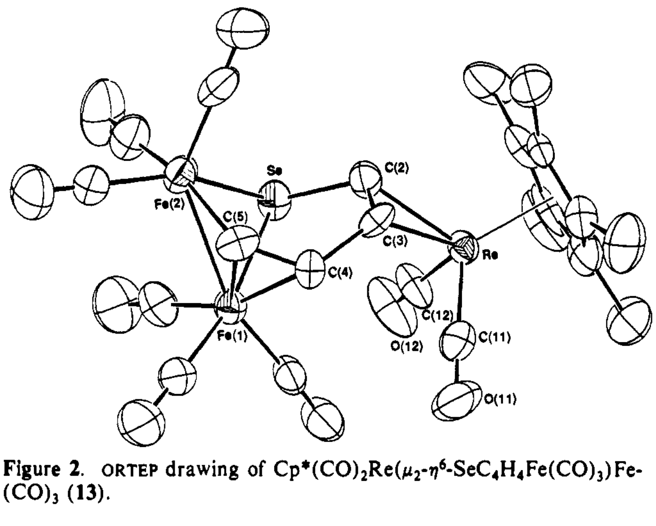

Figure 2. ORTEP drawing of Cp*(CO)$_2$Re(μ_2-η^6-SeC$_4$H$_4$Fe(CO)$_3$)Fe(CO)$_3$ (**13**).

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(19) SHELXS-86, G. M. Sheldrick, Institut für Anorganische Chemie der Universitat, Göttingen, F.R.G.

(20) Enraf-Nonius Structure Determination Package; Enraf-Nonius: Delft, Holland.

(21) *International Table for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV.

(22) Fringuelli, F.; Gronowitz, S.; Hörnfeldt, A.-B.; Johnson, I.; Taticchi, A. *Acta Chem. Scand. Ser. B* **1974**, *28*, 175.

Table III. ^{77}Se NMR Data (δ) for the Complexes in $CDCl_3$

compd	δ
$Cp^*(CO)_2Re(\eta^2\text{-SeI})$ (**1**)	524
$Cp^*(CO)_2Re(\eta^2\text{-2-MeSeI})$ (**2a**)	549
$Cp^*(CO)_2Re(\eta^1(Se)\text{-2-MeSeI})$ (**2b**)	452
$Cp^*(CO)_2Re(\eta^1(Se)\text{-2,5-Me}_2\text{SeI})$ (**3**)	480
$Cp(CO)_2Re(\eta^2\text{-SeI})$ (**4a**)	546
$Cp(CO)_2Re(\eta^1(Se)\text{-SeI})$ (**4b**)	402
$Cp(CO)_2Re(\eta^1(Se)\text{-2-MeSeI})$ (**5**)	420
$[Cp^*(CO)_2Re(\eta^2\text{-SeI}\cdot CH_3)](BF_4)$ (**6**)	506
$Cp^*(CO)_2Re(\mu_2\text{-}\eta^2(Se)\text{-SeI})W(CO)_5$ (**7**)	380
$Cp^*(CO)_2Re(\mu_2\text{-}\eta^2(Se)\text{-SeI})Mo(CO)_5$ (**8**)	426
$Cp^*(CO)_2Re(\mu_2\text{-}\eta^2(Se)\text{-SeI})Cr(CO)_5$ (**9**)	461
$Cp^*(CO)_2Re(\mu_2\text{-}\eta^2(Se)\text{-SeI})[W(CO)_4(PPh_3)]$ (**10**)	425[a]
$Cp^*(CO)_2Re(\mu_2\text{-}\eta^2(Se)\text{-SeI})Fe(CO)_4$ (**11**)	475
$Cp^*(CO)_2Re(\mu_2\text{-}\eta^4(Se)\text{-SeI})Fe(CO)_3$ (**12**)	892
$Cp^*(CO)_2Re(\mu_2\text{-}\eta^6\text{-SeC}_4H_4Fe(CO)_3)Fe(CO)_3$ (**13**)	557
SeI	605
2-MeSeI	612
$2,5\text{-Me}_2\text{SeI}$	621

[a] Doublet, $J_{Se-P} = 15$ Hz.

Table IV. Crystal Data and Experimental Details for the Structure Determination of $Cp^*(CO)_2Re(\mu_2\text{-}\eta^6\text{-SeC}_4H_4Fe(CO)_3)Fe(CO)_3$ (**13**)

formula	$C_{22}H_{19}O_8Fe_2SeRe$
formula wt	788.24
space group	$P2_1/n$
a, Å	8.076 (2)
b, Å	25.890 (2)
c, Å	12.153 (3)
β, deg	94.65 (1)
V, Å^3	2532.7 (8)
Z	4
d_{calcd}, g/cm^3	2.071
cryst size, mm	0.31 × 0.11 × 0.12
μ(Mo Kα), cm^{-1}	74.549
data collection instrument	Enraf-Nonius CAD4
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)
no. of orientation reflcns, range (2θ)	25, 16.4–32.2°
temp, °C.	22 (1)
scan method	θ–2θ
data collection range, 2θ, deg	4.0–45.0
total unique reflcns	3281
no. of unique reflcns obs ($F_o^2 > 3\sigma(F_o^2)$)	2244
no. of parameters refined	307
trans. factors: max, min (ψ scans)	0.9996, 0.8132
R[a]	0.0309
R_w[b]	0.0387
quality-of-fit indicator[c]	1.29
largest shift/esd, final cycle	<0.01
largest peak, e/Å^3	0.6 (1)

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

Table V. Selected Bond Distances (Å)[a] for **10** and **13**

	10	**13**
Re–C(2)	2.23 (1)	2.190 (9)
Re–C(3)	2.28 (2)	2.254 (8)
Se–W	2.681 (2)	
Se–C(2)	1.95 (1)	1.934 (9)
Se–C(5)	1.92 (1)	
C(2)–C(3)	1.44 (2)	1.43 (1)
C(3)–C(4)	1.44 (2)	1.52 (1)
C(4)–C(5)	1.34 (2)	1.31 (1)
Se–Fe(1)		2.367 (2)
Se–Fe(2)		2.357 (2)
Fe(1)–C(4)		2.189 (8)
Fe(1)–C(5)		2.069 (9)
Fe(2)–C(5)		1.974 (9)
Fe(1)–Fe(2)		2.558 (2)

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

Scheme I

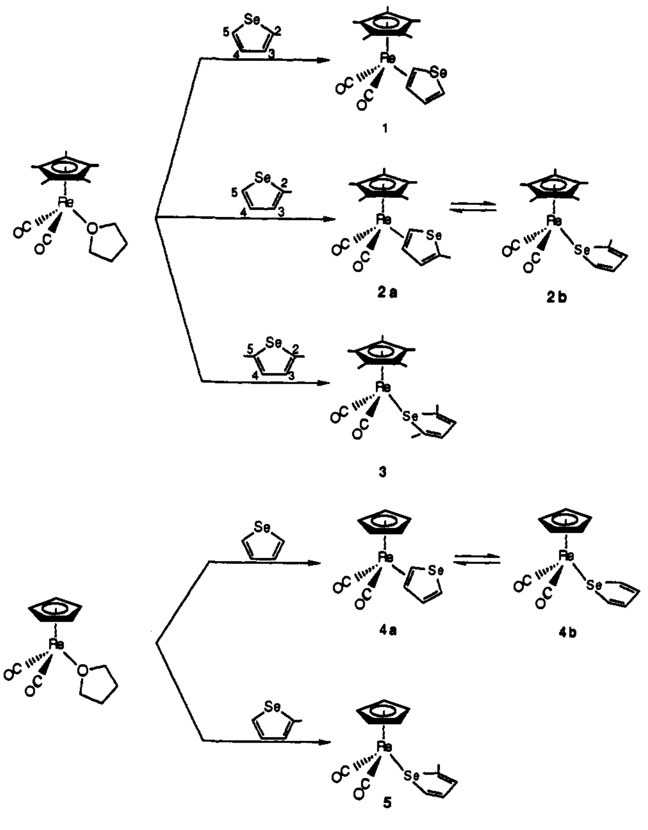

Table VI. Selected Bond Angles (deg)[a] for **10** and **13**

	10	**13**		**13**
C(2)–Re–C(3)	37.1 (5)	37.4 (3)	Fe(1)–Se–Fe(2)	65.58 (5)
C(2)–Re–C(11)	110.1 (5)	88.7 (4)	Fe(1)–Se–C(2)	101.9 (3)
C(2)–Re–C(12)	87.8 (6)	110.6 (4)	Fe(2)–Se–C(2)	102.6 (3)
C(3)–Re–C(11)	81.7 (6)	108.0 (4)	Se–Fe(1)–Fe(2)	57.03 (5)
C(3)–Re–C(12)	110.1 (5)	78.6 (4)	Se–Fe(1)–C(4)	81.6 (2)
C(11)–Re–C(12)	87.0 (6)	89.9 (5)	Se–Fe(1)–C(5)	84.7 (2)
W–Se–C(2)	100.8 (5)		Fe(2)–Fe(1)–C(4)	76.6 (2)
W–Se–C(5)	111.3 (5)		Fe(2)–Fe(1)–C(5)	49.1 (2)
C(2)–Se–C(5)	86.3 (5)		C(4)–Fe(1)–C(5)	35.6 (3)
Re–C(2)–Se	122.0 (8)	123.0 (4)	Se–Fe(2)–Fe(1)	57.39 (5)
Re–C(2)–C(3)	73.3 (8)	73.7 (5)	Se–Fe(2)–C(5)	87.1 (3)
Se–C(2)–C(3)	109.0 (9)	113.0 (7)	Fe–C(4)–C(3)	116.2 (5)
Re–C(3)–C(2)	69.6 (9)	68.8 (5)	Fe–C(4)–C(5)	67.2 (5)
Re–C(3)–C(4)	120 (1)	130.3 (6)	C(3)–C(4)–C(5)	124.7 (8)
C(2)–C(3)–C(4)	115 (1)	119.8 (8)	Fe(1)–C(5)–Fe(2)	78.5 (3)
C(3)–C(4)–C(5)	117 (1)	124.7 (8)	Fe(1)–C(5)–C(4)	77.2 (5)
Se–C(5)–C(4)	113 (1)		Fe(2)–C(5)–C(4)	127.3 (7)

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

also indicating characteristic η^2-coordination via the C2,3 atoms. These chemical shifts are unequivocally assigned on the basis of selective ^{1}H decoupled ^{13}C NMR experiments and a comparison of coupling constants. In free selenophene, the α-carbons (C2 and C5) appear at lower field than the β-carbons (C3 and C4) (131.0, C_α; 129.8, C_β in acetone-d_6).[22] However, in the η^2-coordinated selenophene complex **1**, the α-carbons occur at higher field than the β-carbons. Although the chemical shifts of α-carbons in five-membered rings containing one heteroatom vary irregularly, it is a unique feature that the coupling constants $J_{C\alpha-H\alpha}$ are larger than $J_{C\beta-H\beta}$ (in free selenophene $^1J_{C\alpha-H\alpha} = 189$; $^1J_{C\beta-H\beta} = 166$ Hz).[22] This feature is often used for the assignment of chemical shifts.[23] In complex **1**, the coupling constants show the same trends, and the coupling constants of the coordinated carbons are smaller than those of the uncoordinated carbons: $J_{C2-H2} = 178$ Hz, $J_{C3-H3} = 163$ Hz, $J_{C4-H4} = 165$ Hz, $J_{C5-H5} = 183$ Hz. It is also well-known that the NMR signals of η^2-coordinated olefins and arenes are far upfield of the corresponding free ligands.[24] In the η^2-coordinated benzene complex [Cp*Re-

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(23) Bird, C. W.; Cheeseman, G. W. H. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W. Eds.; Pergamon Press: Oxford, 1984; Vol. 4, p 940.

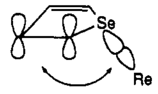
(CO)$_2$](μ_2-η^4-C$_6$H$_6$)[Cp*Re(CO)$_2$],[25] there are upfield shifts in both the ^{1}H and ^{13}C NMR spectra (δ 2.85, 4.14; δ 40.9, 50.6) with respect to free benzene (δ 7.15 in ^{1}H; δ 128.0 in ^{13}C).[26] Thus, all of the NMR results are consistent with a 2,3-η^2-selenophene in **1**. A partially successful X-ray diffraction study of **1** also supports this mode of Sel coordination, but disorder in the Sel ring prevented complete refinement.

While Sel is η^2-bound in **1**, 2,5-Me$_2$Sel is coordinated through the Se atom in complex **3** (Scheme I). In the ^{1}H NMR spectrum of **3**, the equivalent H3 and H4 protons (δ 6.59) and equivalent CH$_3$ groups (δ 2.26) are slightly upfield of those (δ 6.65 and 2.50) in free 2,5-Me$_2$Sel, which establishes the ligand as being Se-coordinated. A similar small upfield shift was observed for the S-bound thiophenes in Cp′(CO)$_2$Re(Th),[28] where Cp′ = C$_5$H$_5$ or C$_5$Me$_5$ and Th = T, 2-MeT, 3-MeT, 2,5-Me$_2$T, and Me$_4$T. There is no evidence for an η^2 isomer of **3** in either the IR or NMR spectra. Although no Se-coordinated selenophenes have been reported previously, the Se atom in **3** is presumably pyramidal and the Re therefore does not lie in the 2,5-Me$_2$Sel plane; this structural type is characteristic of S-bound thiophene complexes.[3,28b,29]

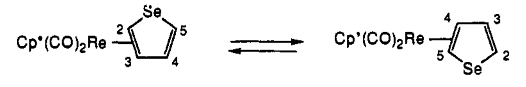
When 2-MeSel reacts (Scheme I) with Cp*(CO)$_2$Re(THF), a complex is formed which analyzes as Cp*(CO)$_2$Re(2-MeSel). However, it is evident from the number of absorptions in the solution IR and ^{13}C NMR spectra that it consists of two isomers, the η^2- (**2a**) and Se-coordinated (**2b**) isomers, which are present in a 1.1:1 ratio in CDCl$_3$ solution at room temperature. The ^{1}H NMR signals assignable to the 2-MeSel ligand in the minor isomer (**2b**) [δ 7.64 (d, H5), 7.03 (m, H4), 6.82 (m, H3), 2.35 (s, CH$_3$)] are slightly upfield of those [δ 7.77 (m, H5), 7.11 (m, H4), 6.92 (m, H3), 2.29 (s, CH$_3$)] in free 2-MeSel in CDCl$_3$; a similar small upfield shift was observed for the Se-bound 2,5-Me$_2$Sel in **3**. In contrast, the major isomer (**2a**) [δ 4.45 (d, H5), 3.58 (m, H4), 6.57 (m, H3), 2.29 (s, CH$_3$)] shows two resonances (H4 and H5) which are substantially upfield from those in free 2-MeSel: this indicates that η^2-coordination occurs at C4 and C5. Two high-field resonances (δ 53.5 and 47.3) in the ^{13}C NMR spectrum (Table II) of **2** also support 4,5-η^2-coordination of 2-MeSel in the η^2 isomer (**2a**).

It is interesting to compare ν(CO) values of the Se and η^2 isomers of complex **2**. An IR spectrum of **2** shows four ν(CO) bands at 1962, 1898 and 1927, 1865 cm^{-1} in hexanes. Two (1962, 1898 cm^{-1}) are the same as those in Cp*(CO)$_2$Re(η^2-Sel) (1962, 1898 cm^{-1}), and the other two (1927, 1865 cm^{-1}) are very similar to those of Cp*(CO)$_2$Re(η^1(Se)-2,5-Me$_2$Sel) (1925, 1866 cm^{-1}). Thus, η^2-Sel coordination gives ν(CO) values that are about 35 cm^{-1} higher than those with Se-coordination, indicating that the Se-coordinated selenophene donates more electron density to Re than the η^2-coordinated ligand.

Variable-temperature ^{1}H NMR studies of **2** in CDCl$_3$ show that the methyl peaks of the two isomers (**2a** and **2b**) coalesce at 42 °C, which indicates that they are in rapid equilibrium. The mechanism of Se $\rightleftarrows$ η^2 isomerization is intramolecular since 2-MeSel does not dissociate on the isomerization time scale ($t_{1/2}$ = ~0.03 s, which was estimated by variable-temperature NMR studies and computer simulation of the NMR spectra). This is established by a study of the methyl coalescence in the presence of free 2-MeSel; in this experiment the free 2-MeSel methyl peak does not coalesce with the complexed ligand methyl groups. Supporting intramolecular isomerization of the Se and η^2 isomers is a measurement of the rate of 2-MeSel substitution by PPh$_3$ to form Cp*(CO)$_2$Re(PPh$_3$); this substitution in CDCl$_3$ at 45 °C occurs with a half-life of ~20 min which is much longer than the half-life (~0.03 s) for isomerization. A reasonable mechanism for this intramolecular isomerization involves simple Re migration from its position on the Se out of the plane of the selenophene ring to the C4–C5 π-bond above the ring plane.



Considering the rapid interconversion of the η^1(*Se*) and η^2 isomers of **2**, it seemed possible that **1**, which appeared to exist in only the η^2 form, might be in rapid equilibrium with its other equivalent isomer (eq 2). The interconversion of these isomers, **A** and **B**, would presumably occur via an Se-coordinated isomer



(2)

A **B**

of the type observed for compounds **2** and **3**. To test for this type of fluxionality a spin saturation transfer ^{1}H NMR experiment[27] was performed. When the signal for H5 (as labeled in **A**) was irradiated, the intensity of the H2 signal decreased. Likewise when the signal for H2 (as labeled in **A**) was irradiated, the intensity of the H5 signal decreased. This observation of spin saturation transfer establishes that **1** is fluxional as shown in eq 2. The interconversion of **A** and **B** probably occurs via a Se-coordinated intermediate as observed in **2** and **3**; this is supported by the detection of a very low concentration of the η^1(Se) isomer in the ν(CO) [1908 (w), 1838 (w) cm^{-1}] region of the IR spectrum of **1** in CH$_2$Cl$_2$. However, there is no unequivocal evidence that rules out a process involving migration of the Re around only the unsaturated hydrocarbon portion of the selenophene.

On the basis of our studies of the Cp*(CO)$_2$Re(Sel) complexes, we know that selenophenes may coordinate to the Re either through the Se or η^2 through two carbons depending upon the number of methyl groups on the selenophene ring. Electron-donating methyl groups in the selenophene enhance the donor ability of the Se which favors the Se-bonded isomers; methyl groups probably also inhibit η^2-coordination. Therefore, with 2,5-Me$_2$Sel, only the Se-coordinated isomer is observed; whereas Sel is η^2-bound and 2-MeSel gives a mixture of Se and η^2 isomers which are in rapid equilibrium with each other. In contrast to Cp*(CO)$_2$Re(Sel) where Sel is η^2-coordinated (except for a trace of the η^1(*Se*) isomer as noted above), the Cp analogue Cp(CO)$_2$Re(Sel) exists as a mixture of η^2 (**4a**) and η^1(*Se*) (**4b**) isomers (Scheme I). It is the number of absorptions in the solution IR and ^{1}H and ^{13}C NMR spectra of **4**, as for **2**, that indicates the presence of two isomers. Broad signals in the ^{1}H NMR spectrum of **4** in CDCl$_3$ at room temperature demonstrate that the two isomers are in rapid equilibrium. The ratio of η^2 (**4a**) and η^1(*Se*) (**4b**) isomers is 1:3 in CDCl$_3$ solution at room temperature. At 0 °C, the ^{1}H NMR peaks are much sharper, and it is observed that the Sel signals of the Se-bound major isomer (**4b**) [δ 7.97 (d, H2,5), 7.15 (d, H3,4), $J_{H2,3}$ = 6 Hz] are slightly upfield of those [δ 8.05 (m, H2,5), 7.37 (m, H3,4)] in free Sel in CDCl$_3$. A similar small upfield shift was noted previously for the Se-bound 2,5-Me$_2$Sel in **3** and S-bound thiophene complexes, Cp′(CO)$_2$Re(Th).[28] In this ^{1}H NMR spectrum, the η^2 minor isomer (**4a**) shows two upfield signals for H2 and H3 [δ 6.86 (d, H5, $J_{H4,5}$ = 5.4 Hz), 6.98 (br m, H4), 5.62 (d, H2, $J_{H2,3}$ = 5.1 Hz), 4.70 (br, m, H3)] characteristic of η^2-coordination. Two high-field resonances (δ 49.4 and 43.4) in the ^{13}C NMR spectrum (Table II) also support η^2-coordination of Sel in **4a**. Whereas Cp*(CO)$_2$Re(2-MeSel) exists as a mixture of the η^2 and Se

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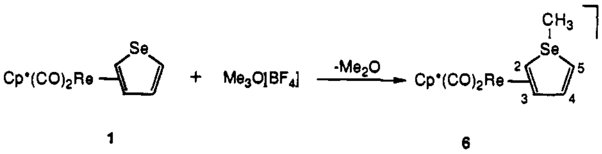
isomers, the Cp analogue Cp(CO)$_2$Re(2-MeSel) (**5**) exists mainly as the Se isomer (Scheme I). The Se-coordination is shown by a small upfield shift of the selenophene protons in **5** [δ 7.70 (d, H5, $J_{H4,5}$ = 5.7 Hz), 6.93 (d of d, H3, $J_{H3,4}$ = 6.0 Hz), 6.73 (br m, H4), 2.42 (s, CH$_3$)] as compared to those in free 2-MeSel [δ 7.77 (m, H5), 7.11 (m, H4), 6.92 (m, H3), 2.59 (s, CH$_3$)]. It is interesting that there is only one ^{13}CO signal in the room temperature ^{13}C NMR spectrum of **5** (Table II) since this indicates that there is rapid inversion at the Se.

The preference for η^2 versus Se binding appears to depend upon a delicate balance of electronic and possibly steric effects. As compared with the Cp compounds, the Cp* analogues favor η^2-coordination. The additional electron density provided by the Cp* ligand to the Re increases π-back-bonding to the η^2-olefinic bond of Sel favoring the η^2 isomer. Also the higher electron density on the Re in the Cp* complexes reduces the Lewis acid character of the Re, weakening the bond with the electron-donating selenium in the Se-bounded isomer, again promoting η^2-coordination.

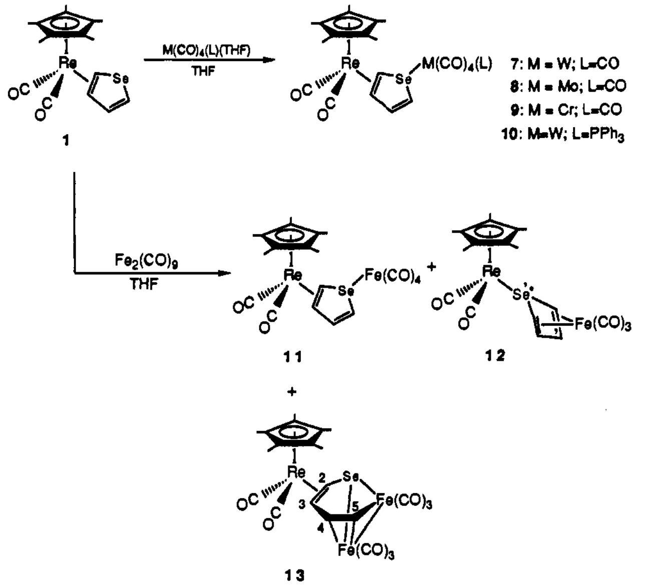
Reaction of Cp*(CO)$_2$Re(η^2-Sel) (1) with (Me$_3$O)BF$_4$. Complex **1** reacts with Me$_3$O[BF$_4$] to give the Se-methylated selenophene complex **6** in 26% yield (eq 3). In the ^{1}H NMR spectrum of **6**, the chemical shifts of the selenophene protons are 4.46 (H2), 3.17 (H3), 7.64 (H4), and 6.10 (H5) ppm. The H2, H3, H5 protons are slightly upfield of the same groups [δ 4.52 (H2), 3.64 (H3), 6.68 (H5)] in **1**. However, the chemical shift of H4 (δ 7.64) is downfield of that (δ 7.02) in **1**. The Se·CH$_3$ signal occurs at δ 3.06, which is very similar to that in Me$_3$Se$^+$ (δ 2.96)[30] but downfield of typical sulfonium methyl groups, as in CpRe(NO)(PPh$_3$)(CH$_2$SMe$_2$)$^+$ (δ 2.60)[31] and Cp*Ir(η^4-2,5-Me$_2$T·CH$_3$)$^+$ (δ 2.80).[32] The observation of only two ^{13}CO resonances in **6** suggests that inversion at Se is occurring rapidly.



(3)

Reaction of Cp*(CO)$_2$Re(η^2-Sel) (1) with M(CO)$_4$(L)(THF) (M = W, Mo, Cr; L = CO or PPh$_3$). As in its reaction (eq 3) with Me$_3$O$^+$, the uncoordinated selenophene Se atom in **1** reacts with M(CO)$_4$(L) (M = W, Mo, Cr; L = CO or PPh$_3$) to give the selenophene-bridged bimetallic complexes **7**, **8**, **9**, and **10** (Scheme II) in 65–75% yield. In the ^{1}H and ^{13}C NMR spectra of each of these complexes (Tables I and II), there are two upfield protons and two upfield carbon resonances that indicate the selenophene is still η^2-coordinated. The X-ray structure determined[8] for **10** confirms the selenophene is η^2-bonded to the Re and Se-bonded to the W (Figure 1). While the selenophene ring is planar, the distance (1.44 (2) Å) between the C(2) and C(3) atoms which are coordinated to the Re is substantially longer than that (1.369 (1) Å) in free Sel.[33] The uncoordinated C(3)–C(4) and C(4)–C(5) distances (1.44 (2) and 1.34 (2) Å, respectively) are nearly the same as those (1.433 (3) and 1.369 (1) Å, respectively) in free Sel. Although the C(2)–Se–C(5) angle of 86.3 (5)° is essentially the same as that (87.46 (4)°) in free Sel,[33] the C(2)–Se and C(5)–Se distances (1.95 (1) and 1.92 (1) Å) are considerably longer than that in Sel (1.855 (1) Å).[33] As in S-coordinated thiophene complexes, the Se in **10** is pyramidal as indicated by the angle (112.1 (6)°) between the W–Se vector and the vector from Se to the midpoint of the line from C(2) to C(5). The corresponding angle in Cp*(CO)$_2$Re(T) is 140°.[28b] From the above data, it is clear that the structure of the selenophene has been changed significantly as a result of its coordination to the two metals. The lengthening of the C–Se bond is especially interesting because it is the analogous C–S bonds in thiophene which must be cleaved on HDS catalysts.

Scheme II



Reaction of Cp*(CO)$_2$Re(η^2-Sel) (1) with Fe$_2$(CO)$_9$. When complex **1** reacts with Fe$_2$(CO)$_9$ in THF solution, three products (**11**, **12**, and **13**) are isolated (Scheme II). Even though the η^2 isomer of **1** is by far the predominant isomer, its rapid interconversion with the η^1(*Se*) isomer (vide supra) suggests that the reaction of **1** with Fe$_2$(CO)$_9$ could occur through either the Se or η^2 isomer. The diene portion of the Se-bound selenophene might be expected to react with "Fe(CO)$_3$" to give **12** since the analogous thiophene product was obtained from the reaction of Cp*(CO)$_2$Re(η^1(*S*)-T) with Fe$_2$(CO)$_9$.[28] On the other hand, the Se atom of the η^2-bound Sel might react with "Fe(CO)$_4$" to form **11**. Compound **12** is formulated as Cp*(CO)$_2$Re(μ_2-η^4(*Se*)-Sel)Fe(CO)$_3$, in which selenophene is Se-bound to the Re and η^4-bound through the diene to the Fe. This structure is based on the very similar spectroscopic properties of **12** compared to those of the thiophene analogue Cp*(CO)$_2$Re(μ_2-η^4(*S*)-T)Fe(CO)$_3$,[28a] whose structure was established by X-ray diffraction studies. Compound **11** is assigned the same basic structure as that of Cp*(CO)$_2$Re(μ_2-η^2(*Se*)-Sel)M(CO)$_5$ (**7**, **8**, and **9**) based on their ^{1}H and ^{13}C NMR spectra (Tables I and II).

The third product **13** isolated (Scheme II) from the reaction of **1** with Fe$_2$(CO)$_9$ has a thiaferrole-type structure.[34] This product is obtained by the formal insertion of Fe(CO)$_3$ into the Se–C(5) bond, which is presumably activated by coordination of the C2–C3 bond to rhenium; this gives a six-membered ring. Another "Fe(CO)$_3$" then coordinates to the selenium and the C(4)–C(5) bond. The 18-electron configuration of both Fe atoms is completed by formation of an Fe–Fe bond. Complex **13** is not formed from **12** since the room temperature reaction of **12** with Fe$_2$(CO)$_9$ in THF for 24 h does not give **13**. Complex **13** was characterized by its elemental analyses, IR, MS, ^{1}H, and ^{13}C NMR spectra (Tables I and II), as well as by an X-ray structure determination (vide infra). The ^{1}H NMR spectrum of **13** was assigned on the basis of its coupling constants, COSY 2D ^{1}H NMR and gated-decoupled ^{13}C NMR spectroscopy, and comparison with ^{1}H NMR spectra of 2-methylthiaferrole,[34a] 3-methylthiaferrole,[34a] and 2,5-dimethylthiaferrole.[34b] The signal for H2 overlaps with the Cp* signal; the other three selenophene protons occur as multiplets as 2.88 (d of d of d, H3), 5.87 (d of d, H4), and 8.54 (d of d, H5) with $J_{H2,3}$ = 5.5 Hz, $J_{H3,4}$ = 2.5 Hz, $J_{H3,5}$ = 1.0 Hz, and $J_{H4,5}$ = 8.8 Hz. The proton-coupled ^{13}C

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NMR spectrum shows all four carbon signals of the selenophene split into doublets, clearly indicating that all four carbon atoms bear one proton each. The four ^{13}C chemical shifts [δ 173.8 (C5, J_{C5-H5} = 150 Hz), 111.0 (C4, J_{C4-H4} = 156 Hz), 23.2 (C3, J_{C3-H3} = 152 Hz), 45.1 (C2, J_{C2-H2} = 175 Hz)] are assigned by comparison with those of 3-methylthiaferrole.[34a]

Structure of Cp*(CO)$_2$Re(μ_2-η^6-SeC$_4$H$_4$Fe(CO)$_3$)Fe(CO)$_3$ (13). The structure of **13** (Figure 2) shows a six-membered ring consisting of the five selenophene atoms and a Fe(CO)$_3$ group. This ring bridges Cp*Re(CO)$_2$ and Fe(CO)$_3$ groups. The C(2)–C(3) distance (1.43 (1) Å) is very similar to that (1.44 (2) Å) in complex **10**, but it is substantially longer than that (1.369 (1) Å) in free Sel.[33] The Fe–Se (2.367 (2), 2.357 (2) Å), and Fe–Fe distances (2.558 (2) Å) are normal, but the Fe-coordinated C(4)–C(5) distance (1.31 (1) Å) is unusually short. A similar short distance was observed for the corresponding, coordinated olefinic C–C distance (1.29 (5) Å) in benzothiaferrole.[34b] The other general features of the core structure of **13** are very similar to those in 2-methylthiaferrole[34a] and benzothiaferrole,[34b] except that the Cp*(CO)$_2$Re group is coordinated to the C(2)–C(3) olefinic bond in **13**. The geometry of the opened selenophene ring in **13** is also very similar to that in Os$_3$(CO)$_{10}$(C$_4$H$_4$Se), in which the ring bridges two of the three Os atoms.[35]

^{77}Se NMR Studies of the Complexes. The ^{77}Se NMR results described in this section are the first to be reported for selenophene transition-metal complexes. The chemical shifts in all of the selenophene complexes (except **12**) are upfield of that in free selenophene (Table III). In contrast, ^{77}Se chemical shifts of Me$_2$Se transition-metal complexes are downfield with respect to free Me$_2$Se (0 ppm): *cis*-[(Me$_2$Se)$_2$PtCl$_2$] (120 ppm),[36a] *trans*-[(Me$_2$Se)$_2$PtCl$_2$] (135 ppm),[36a] *trans*-[(Me$_2$Se)$_2$Pt(SCN)$_2$] (134 ppm),[36b] *cis*-[(Me$_2$Se)$_2$Pt(NCO)$_2$] (92 ppm),[36b] *cis*-[(Me$_2$Se)$_2$Pt(NCO)Cl] (118, 92 ppm),[36b] *trans*-[(Me$_2$Se)$_2$Pt(NCO)Cl] (134 ppm).[36b] In free selenophenes, the ^{77}Se chemical shifts move downfield upon adding electron-donating methyl groups to the ring (Table III). The chemical shifts of selenophene complexes also move downfield, approximately 20–30 ppm for each methyl group added to the selenophene ring (Table III). As the Cp* ligand is replaced by Cp in the η^2 isomer of **1**, the selenium chemical shift moves downfield from 524 ppm to 546 ppm. However, the opposite trend is observed in the η^1(Se) isomers: Cp*(CO)$_2$Re(η^1(*Se*)-2-MeSel) (**2b**) (452 ppm) and Cp(CO)$_2$Re(η^1(*Se*)-2-MeSel) (**5**) (420 ppm).

The ^{77}Se chemical shifts of the η^1(*Se*) isomers **2b** (452 ppm) and **4b** (402 ppm) are 100–150-ppm upfield of those in the η^2 isomers **2a** (549 ppm) and **4a** (546 ppm). This large difference should be very useful in distinguishing η^2 and η^1(*Se*) modes of selenophene adsorption on HDS catalysts by solid-state ^{77}Se NMR spectrometry. In the selenophene-bridged complexes Cp*(CO)$_2$Re[μ_2-η^2(*Se*)-Sel]M(CO)$_5$ (**7–10**), the ^{77}Se chemical shift moves upfield as the group VI metal M becomes heavier: M = Cr, 461 ppm; M = Mo, 426 ppm; M = W, 380 ppm. In general, the ^{77}Se chemical shifts of these complexes encompass a broad range (402–892 ppm) and are sensitive to the nature of the selenophene binding mode to the Re as well as to the other ligands coordinated to the metal. These results suggest that ^{77}Se NMR can be applied to studies of selenophene adsorption on catalyst surfaces.

Acknowledgment. We are grateful to Dr. Lee M. Daniels of the Iowa State University Molecular Structure Lab for determining the structure of **13**.

Supplementary Material Available: ORTEP drawing and tables of positional and thermal parameters and complete bond distances and angles for **13** (6 pages); a listing of calculated and observed structure factors of **13** (13 pages). Ordering information is given on any current masthead page.

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