Carbon−Selenium Bond Cleavage by a Rhodium Complex

David A. Vicic, Andrew W. Myers, and William D. Jones*

Department of Chemistry, University of Rochester, Rochester, New York 14627

Received March 13, 1997[⊗]

*Summary: The complex Cp*Rh(PMe$_3$)PhH (Cp* = C$_5$Me$_5$) reacts thermally with selenophene to give a C−Se insertion product. X-ray structural characterization shows a planar 6-membered ring containing a localized butadiene structure. ^{77}Se NMR studies display an upfield resonance consistent with a non-aromatic metallaselenabenzene ring.*

Introduction

There has been a great deal of activity recently using homogeneous transition metal complexes as models for the hydrodesulfurization (HDS) of sulfur compounds found in crude oil.[1] Thiophenes, which are the most difficult of the organosulfur compounds to desulfurize, have become the substrates of choice in modeling studies for the HDS process. Important contributions in homogeneous modeling studies include the identification of various binding modes of thiophene and the documentation of the reactivity of these bound thienyl fragments.[2]

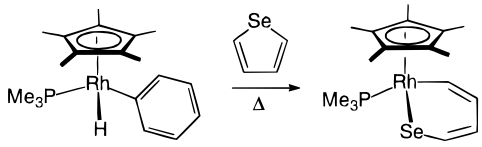
While there is a better understanding of the reactivity of bound thienyl fragments, many of the salient features of the HDS process remain unknown. The lack of conclusive mechanistic evidence, coupled with the great importance of developing more efficient catalysts, has spawned some novel approaches to obtaining new mechanistic information. One such approach is the use of aromatic chalcogen complexes as substitutes for thiophenic molecules. There have been limited reports of the use of selenophenes as thiophene substitutes in HDS modeling studies,[3] and even fewer with tellophene.[4,5] As Angelici has pointed out,[3] selenium is an attractive sulfur analog because of its spectroscopic properties. ^{77}Se has a 7.6% natural abundance and a nuclear spin of $^1/_2$. Its receptivity is 2.98 times greater than ^{13}C, and it also has a chemical shift range much greater than ^{13}C. Consequently, spectroscopic studies of selenophene might be valuable in obtaining information concerning modes of binding on the catalyst surface.

Angelici has studied the reactions of selenophene with various organometallic complexes as well as identified the ^{77}Se chemical shifts of the metal−selenophene species formed. ^{77}Se NMR data for intact selenophene complexes of rhenium, manganese, iridium, ruthenium, chromium, molybdenum, and tungsten have been reported.[3] The authors cited a general trend whereby the η^5-complexes all fell within 225 ppm of each other (δ 375−150). However, they noted that the C−Se inserted complex **1** showed a very different ^{77}Se chemical shift at δ 905.4.[3d] Only two other complexes have been reported in which the C−Se bond in selenophene has been cleaved (Chart 1).[3b,5]

In this paper we present a reaction of selenophene with Cp*Rh(PMe$_3$)(H)(Ph) which yields a C−Se inserted product with ^{77}Se spectroscopic properties quite different than known inserted complexes.

Results and Discussion

Cp*Rh(PMe$_3$)(H)(Ph) **2** has been shown to thermally eliminate benzene to produce the very reactive 16-electron fragment [Cp*Rh(PMe$_3$)].[6] This fragment is capable of inserting into the C−S bonds of various thiophenes, benzothiophenes, and dibenzothiophenes.[1e,7] We found that when **2** is heated at 60 °C for 13 h in the presence of selenophene, complex **3** is obtained in 83% yield (eq 1). The ^{1}H NMR spectrum of **3** displays four



2 **3** (1)

multiplets at δ 6.70, 6.45, 6.21, and 5.99 for the vinylic hydrogens in the complex. These values are substantially upfield of the resonances of Angelici's iridaselenabenzene **1** ($\sim\delta$ 7.5) and suggest little aromatic character in the 6-membered ring of **3**.

Complex **3** was also characterized by X-ray crystallography and crystallizes in the orthorhombic space group $Pca2_1$ with $Z = 8$, which requires that there be

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1997.

(1) See, for example: (a) Selnau, H. E.; Merola, J. S. *Organometallics* **1993**, *12*, 1583. (b) Garcia, J. J.; Mann, B. E.; Adams, H.; Bailey, N. A.; Maitlis, P. M. *J. Am. Chem. Soc.* **1995**, *117*, 2179. (c) Buys, I. E.; Field, L. D.; Hambley, R. W.; McQueen, A. E. D. *J. Chem. Soc., Chem. Commun.* **1994**, 557. (d) Paneque, M.; Taboada, S.; Carmona, E. *Organometallics* **1996**, *15*, 2678. (e) Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1991**, *113*, 559. (f) Chen, J.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 199. (g) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Herrer, V.; Sanchez-Delgado, R. *J. Am. Chem. Soc.* **1993**, *115*, 2731. (h) Curtis, M. D.; Druker, S. H. *J. Am. Chem. Soc.* **1997**, *119*, 1027. (i) Luo, S.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1992**, *114*, 8515.

(2) For recent reviews, see: (a) Jones, W. D.; Vicic, D. A.; Chin, R. M.; Roache, J. H.; Myers, A. W. *Polyhedron*, in press. (b) Bianchini, C.; Meli, A. *J. Chem. Soc., Dalton Trans.* **1996** 801. (c) Rauchfuss, T. B. *Prog. Inorg. Chem.* **1991**, *39*, 259. (d) Sánchez-Delgado, R. A. *J. Mol. Catal.* **1994**, *86*, 287. (e) Angelici, R. J. *Coord. Chem. Rev.* **1990**, *105*, 61.

(3) (a) Choi, M. G.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 7811. (b) Choi, M. G.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 5651. (c) White, C. J.; Angelici, R. J. *Organometallics* **1994**, *13*, 5132. (d) White, C. J.; Angelici, R. J.; Choi, M. G. *Organometallics* **1995**, *14*, 332.

(4) Singh, K.; McWhinnie, W. R. *Coal Sci.* **1995**, 1725.

(5) (a) Arce, A. J.; Deeming, A. J.; De Sanctis, Y.; Machado, R.; Manzur, J.; Rivas, C. *J. Chem. Soc., Chem. Commun.* **1990**, 1568. (b) Arce, A. J.; Machado, R.; Rivas, C.; De Sanctis, Y.; Deeming, A. J. *J. Organomet. Chem.* **1991**, *419*, 63.

(6) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91.

(7) (a) Dong, L.; Duckett, S. B.; Ohman, K. F.; Jones, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 151. (b) Myers, A. W.; Jones, W. D. *J. Am. Chem. Soc.* **1995**, *117*, 11704. (c) Myers, A. W., Jones, W. D., *Organometallics* **1996**, *15*, 2905.

S0276-7333(97)00209-4 CCC: $14.00

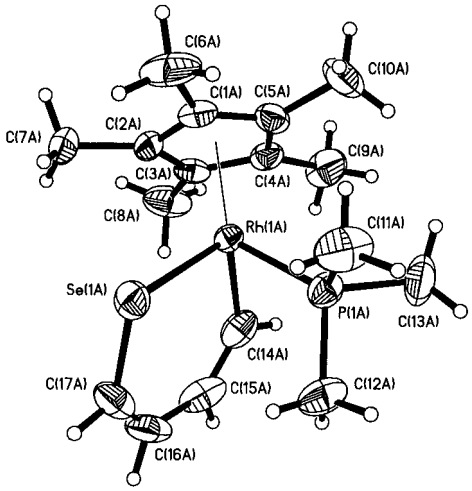


Figure 1. ORTEP drawing of **3**. Ellipsoids are shown at the 50% probability level.

Chart 1

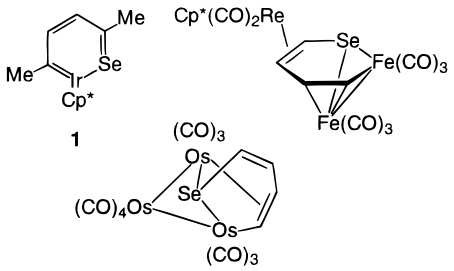


Table 1. Crystallographic Data for 3

chem formula	$C_{17}H_{28}PRhSe$
cryst syst	orthorhombic
space group (No.)	*Pca*2$_1$ (29)
Z	8
a, Å	19.817(3)
b, Å	9.4203(12)
c, Å	19.888(3)
vol., Å^3	3712.7(8)
ρ_{calc}, g cm^{-3}	1.593
temp, °C	−80
radiation; λ, Å	Mo; 0.710 73
2θ range, deg	4.1−56.0
data collcd	$-25 \le h \le 26$, $-12 \le k \le 9$, $-26 \le l \le 22$
no. of data collcd	21030
no. of unique data	7893
no. of obs data ($F_o > 4\sigma(F_o)$)	6392
agreement between equiv data (R_{int})	0.0468
no. of params varied	469
μ, mm^{-1}	2.957
abs cor	empirical (SADABS)
range of transm factors	0.67−0.93
R1(F_o), wR2(F_o^2), ($F_o > 4\sigma(F_o)$)	0.0509, 0.0661
R1(F_o), wR2(F_o^2) (all data)	0.0698, 0.0708
goodness of fit	1.116

two independent molecules within the asymmetric unit. The ORTEP drawing of **3** can be seen in Figure 1 and the corresponding crystallographic data in Table 1. An interesting disorder arose in each of the independent metallaselenabenzene rings where two different orientations of the ring (refined as 54/46% and 81/19% occupancy for the two molecules) can be seen. Successful anisotropic refinement of each molecule was possible using the SHELX SAME instruction to keep the distances within the rings similar. Figure 2 shows the disorder in one of the molecules of the asymmetric unit.

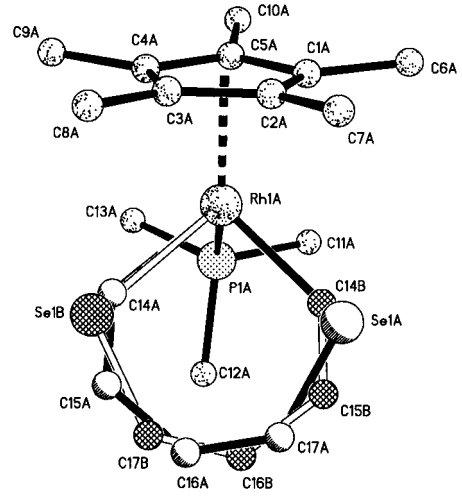
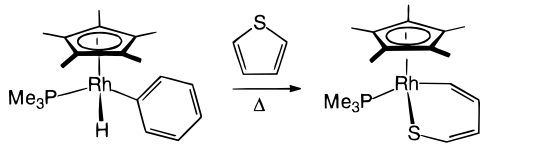


Figure 2. Ball and stick figure showing the disorder found in the metallaselenabenzene ring. Hydrogens are omitted for clarity.

The structure of **3** contains a metallaselenabenzene ring which is nearly planar. The average pucker between the C14−Rh1−Se1 and Se1−C17−C16−C15−C14 planes of all the molecules in the asymmetric unit is only 3.5° which is very similar to the analogous metallathiabenzene ring (4° pucker) which is formed when **2** is reacted with thiophene to form complex **4** (eq 2).[8] The carbon−carbon bond distances of C14−C15,



(2)

C15−C16, and C16−C17 in **3** are 1.37(2), 1.45(1), and 1.31(1) Å, showing the bond alteration for a localized diene structure, analogous to that seen in complex **4**. The average rhodium−selenium bond distance in **3** is 2.456(3) Å which is expectedly longer than the average rhodium−sulfur bond distance in **4** (2.323(3) Å).[8]

The rhodium insertion into the carbon−selenium bond is not reversible. When a solution of **3** in C_6D_{12} is heated at temperatures up to 120 °C in the presence of excess thiophene, none of complex **4** is seen in the ^{1}H or ^{31}P NMR spectrum. After heating at these elevated temperatures for 24 h, decomposition is observed (a black solid is formed) rather than a reversible reaction producing free selenophene. Similar thermal stability has been seen with the sulfur analog **4**, although reversible C−S insertion has been seen with 2-methylbenzothiophene.[7c]

^{77}Se NMR of 3. The ^{77}Se{^{1}H} spectrum of **3** consists of a doublet of doublets (J_{Rh-Se} = 56.3 Hz, J_{P-Se} = 6.2 Hz) at δ 31.9, which is referenced to free selenophene at δ 605.[3b] No other rhodium−selenophene complexes have been studied by ^{77}Se NMR spectroscopy. The chemical shift of the C−Se inserted product is very different from that of complex **1**, which appears at δ 905.4,[3d] and is also much more upfield than that of Cp*-(CO)$_2$Re(μ_2-η^6-SeC$_4$H$_4$Fe(CO)$_3$)Fe(CO)$_3$, which appears

(8) Blonski, C.; Myers, A. W.; Palmer, M.; Harris, S.; Jones, W. D. *Organometallics*, submitted for publication.

at δ 557.[3b] The chemical shifts of transition-metal selenophene complexes therefore appear to be very sensitive to the metal used as well as to the binding mode of the coordinated selenophene.

Experimental Section

General Procedures. All operations were performed under a nitrogen atmosphere unless otherwise stated. Hexanes and cyclohexane were distilled from dark purple solutions of sodium benzophenone ketyl/diglyme. Selenophene (97%) was purchased from Aldrich Chemical Co. and used without further purification. Cp*Rh(PMe_3)PhH was synthesized as previously reported.[9] A Siemens-SMART three-circle CCD diffractometer was used for X-ray crystal structure determination. Elemental analyses were obtained from Desert Analytics. All ^{1}H, ^{13}C, ^{31}P, and ^{77}Se NMR spectra were recorded on a Bruker AMX400 spectrometer.

Synthesis of 3. **2** (75 mg, 0.19 mmol) was dissolved in 4 mL of cyclohexane and 1 mL of selenophene. The solution was heated for 13 h in a resealable Teflon ampule. The solvents were then removed under vacuum and the residue was dissolved in the minimum amount of hexanes and cooled at −30 °C for 2 days. The red crystals which had formed were collected and dried under vacuum. Yield: 71.5 mg (83%). ^{1}H NMR (C_6D_{12}): δ 1.30 (d, J = 10.1 Hz, PMe_3), 1.65 (d, J = 2.6 Hz, Cp*), 5.99 (dt, J = 9.9, 3.2 Hz, CH), 6.21 (dd, J = 10.0, 7.0 Hz, CH), 6.45 (ddd, J = 9.5, 7.1, 2.9 Hz, CH), 6.70 (tdd, J = 9.0, 3.9, 1.1 Hz, CH). ^{13}C{^{1}H} NMR (C_6D_{12}, 25 °C, 100 MHz): δ 139.4 (dd, J = 31.7, 23.5 Hz, Rh-CH), 128.3 (s, CH), 127.8 (t, J = 2.7 Hz, SeCH), 114.0 (s, CH), 99.2 (t, J = 4.2 Hz, C_5Me_5) 15.8 (d, J = 35.5 Hz, PMe_3) 9.18 (s, C_5Me_5). ^{31}P{^{1}H} (C_6D_{12}, 25 °C, 162 MHz): δ 8.0 (d, J = 158.7 Hz). ^{77}Se (C_6D_6, 25 °C, 76 MHz) 31.9 (dd, J_{Rh-Se} = 56.3, J_{P-Se} = 6.2 Hz) Anal. Calcd (found) for $RhPSeC_{17}H_{28}$: C, 45.86 (45.59); H, 6.34 (6.44).

X-ray Structural Determination of (C_5Me_5)Rh(PMe_3)-(η^2-C,Se-C_4H_4Se), 3. Slow evaporation of a hexanes solution of **3** produced red prisms. A single crystal of dimensions 0.25 × 0.36 × 0.34 mm^3 was mounted on a glass fiber with epoxy. Data were collected at −80 °C on a Siemens SMART CCD area detector system employing a 3 kW sealed tube X-ray source operating at 2 kW. A total of 1.3 hemispheres of data were collected over 6 h, yielding 21 030 data after integration using SAINT (see Table 1). Laue symmetry revealed an orthorhombic crystal system, and cell parameters were determined from 8192 unique reflections.[10] The space group was assigned as $Pca2_1$ on the basis of systematic absences using XPREP, and the structure was solved and refined using the SHELX95 package. For a Z value of 8 there are two independent molecules of **3** within the asymmetric unit. Examination of a difference map following isotropic refinement of the (C_5Me_5)-Rh(PMe_3) fragment showed evidence for an orientation disorder of the rhodaselenabenzene group for each of the two independent molecules. In the refinement model, the two different orientations were allowed to refine independently while restraining intra-ring distances to be similar using the SHELX SAME instruction. The occupancies of the two orientations were also refined. In the final model, non-hydrogen atoms were refined anisotropically (on F^2), with hydrogens included in idealized locations. The Flack parameter of 0.03 indicated the correct choice of enantiomorph, with the structure refining with R_1 = 0.0509 and wR_2 = 0.0661.[11] Fractional coordinates and thermal parameters are given in the Supporting Information.

Acknowledgment is made to the National Science Foundation (Grant CHE-9421727) for their support of this work.

Supporting Information Available: Tables of bond distances and angles, atomic coordinates, thermal parameters, and least squares planes (13 pages). Ordering information is given on any current masthead page.

OM970209U

(9) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650.

(10) It has been noted that the integration program SAINT produces cell constant errors that are unreasonably small, since systematic error is not included. More reasonable errors might be estimated at 10× the listed values.

(11) Using the SHELX95 package, $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$, w$R_2$ = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [f(\text{Maximum of 0 or } F_o^2) + (1 - f)F_c^2]$.