Synthetically, this condensation forms a new C–C bond and rearranges the oxidation pattern with formation of a versatile carbonyl group with high chemo- and regioselectivity.

Acknowledgment. We thank the National Science Foundation for their generous support of our programs. G.D. thanks NATO and R.J.K. NIH for fellowships in partial support of their postdoctoral studies in these laboratories.

Supplementary Material Available: IR and ^{1}H and ^{13}C NMR data for various enones (3 pages). Ordering information is given on any current masthead page.

η^2- and $\eta^2(Se)$-μ_2-Selenophene (Sel) Coordination in $Cp^*(CO)_2Re(2,3\text{-}\eta^2\text{-}Sel)$ and $Cp^*(CO)_2Re(\eta^2(Se)\text{-}\mu_2\text{-}Sel)[W(CO)_4(PPh_3)]$

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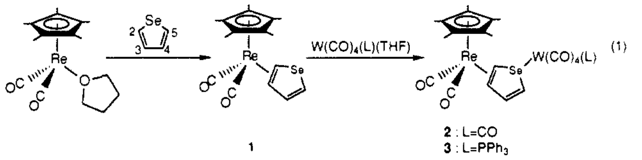
Received June 21, 1990

In connection with our interest in the mechanism(s) of the hydrodesulfurization (HDS) of thiophenes on heterogeneous catalysts,[2] we have explored various modes of thiophene (T) coordination in transition-metal complexes. Those that are known are shown in Chart I. Complexes with η^5-,[3] S-,[4] η^4-,[5] $\eta^4(S)$-μ_2-,[6] and $\eta^4(S)$-μ_3-bound[7] and ring-opened[8] thiophene coordination have been characterized by X-ray crystallography. The complex $(NH_3)_5Os(2,3\text{-}\eta^2\text{-}T)^{2+}$ was proposed[9] to contain a 2,3-η^2-thiophene ligand on the basis of ^{1}H NMR spectroscopic evidence. In a previous report,[6] we described the synthesis of the complex $Cp^*(CO)_2Re(T)$ in which the thiophene (T) was S-coordinated to the rhenium. In this communication, we report the analogous selenophene (Sel) complex $Cp^*(CO)_2Re(Sel)$ in which the selenophene is 2,3-η^2-coordinated to the metal (eq 1). Moreover,



$Cp^*(CO)_2Re(2,3\text{-}\eta^2\text{-}Sel)$ (**1**) reacts with $W(CO)_4(L)(THF)$, where L = CO or PPh_3 and THF = tetrahydrofuran, to give $Cp^*(CO)_2Re(\eta^2(Se)\text{-}\mu_2\text{-}Sel)[W(CO)_4(L)]$ (**2**, L = CO; **3**, L = PPh_3) in which the selenophene is η^2-bonded to the Re and Se-bonded to the W, a bonding mode not previously observed for either thiophene or selenophene.

A solution of $Cp^*(CO)_2Re(THF)$, prepared by UV irradiation[10] of a THF solution (30 mL) of $Cp^*Re(CO)_3$ (0.20 g, 0.49 mmol) at −20 °C, was stirred with selenophene[11] (2.0 mL, 24.5 mmol) at room temperature for 7 h. After removal of the solvent in vacuo, the residue was chromatographed in CH_2Cl_2/hexane (1:4) on neutral alumina. Slow evaporation of the solvent from the yellow band gave moderately air-stable light yellow crystals of $Cp^*(CO)_2Re(2,3\text{-}\eta^2\text{-}Sel)$ (**1**)[12] (45% yield). As compared with the ^{1}H NMR spectrum of free selenophene (δ 8.05 m, H2,5; 7.37 m, H3,4 in $CDCl_3$),[13] two of the selenophene protons in **1** move substantially upfield (δ 4.52 d, H2; 3.64 m br, H3; 7.02 m br, H4; 6.72 d, H5), characteristic of η^2-olefin ligands.[14] In addition, the expected splitting patterns of the four individual protons for 2,3-η^2-Sel coordination are observed. In the ^{13}C NMR spectrum of **1**, two of the four carbon resonances (δ 46.4, 52.4, 119.8, 134.3) lie considerably upfield of those in free selenophene (δ 129.3, 130.3 in $CDCl_3$), also indicating η^2-coordination[14] via two carbon atoms.

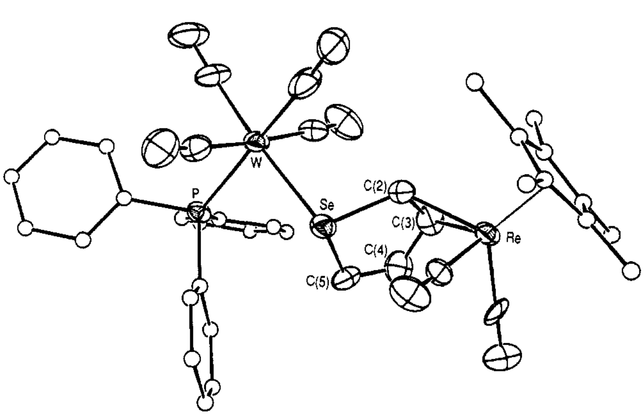
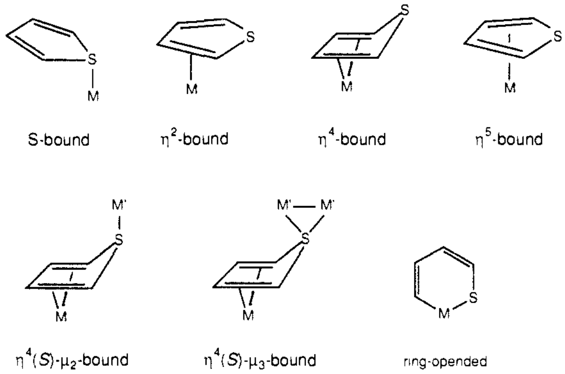


Figure 1. ORTEP drawing of $Cp^*(CO)_2Re(\eta^2(Se)\text{-}\mu_2\text{-}Sel)[W(CO)_4(PPh_3)]$ (**3**). Selected bond distances (Å) and angles (deg) are Re–C(2) = 2.23 (1). Re–C(3) = 2.28 (2), W–Se = 2.681 (2), Se–C(2) = 1.95 (1), Se–C(5) = 1.92 (1), C(2)–C(3) = 1.44 (2), C(3)–C(4) = 1.44 (2), C(4)–C(5) = 1.34 (2), C(2)–Se–C(5) = 86.3 (5). The dihedral angle between the C(2)–Re–C(3) and Se–C(2)–C(3)–C(4)–C(5) planes is 117 (1)°.

Chart I



The uncoordinated selenophene Se atom in **1** is capable of binding to a $W(CO)_5$ group to give **2** (eq 1). Thus, $Cp^*(CO)_2Re(\eta^2\text{-}Sel)$ (**1**; 50 mg, 0.098 mmol) reacts with a solution of $W(CO)_5(THF)$,[15] prepared by UV irradiation of a THF solution (25 mL) of $W(CO)_6$ (60 mg, 0.17 mmol), at room tem-

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[1] Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Chemical Sciences Division.

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[12] **1**: IR (hexanes) ν(CO) 1962 (s), 1898 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.02 (br, m, 1 H, Sel), 6.72 (d, 1 H, Sel), 4.52 (d, 1 H, Sel), 3.64 (br, m, 1 H, Sel), 1.98 (s, 15 H, Cp*); ^{13}C NMR ($CDCl_3$) δ 205.4 and 205.0 (CO), 134.3, 119.8, 52.4 and 46.4 (Sel), 97.4 (C of Cp*), 10.3 (Me of Cp*); 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: C, 37.96; H, 3.75. An X-ray study of **1** clearly shows 2,3-η^2 coordination of Sel, but final refinement was not successful due to disorder of the Sel ring.

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perature for 7 h. After evaporation of the solution to dryness in vacuo, the residue was chromatographed on neutral alumina with hexanes/CH_2Cl_2 (2:1) as the eluent. The yellow band was collected and reduced in volume under vacuum. Cooling the concentrated solution to −70 °C gave air-stable, pale yellow crystals (70% yield) of **2**.[16] As in **1**, the ^1H and ^{13}C NMR spectra of **2** show two upfield protons (δ 4.16 d, H2; 3.18 d of d, H3; 7.01 d of d, H4; 6.29 d, H_5) and two upfield carbons (δ 44.0, 51.1, 119.1, 140.9), which indicate the presence of the η^2-selenophene.

The PPh_3 derivative of **2** was prepared in the same manner from $Cp^*(CO)_2Re(\eta^2\text{-Sel})$ (60 mg, 0.12 mmol) and $W(CO)_4(PPh_3)(THF)$, generated by UV photolysis of $W(CO)_5(PPh_3)$ (90 mg, 0.15 mmol) in THF. Crystals of air-stable, pale yellow **3**[17] (73% yield) were obtained from hexanes/CH_2Cl_2 (2:1) at −70 °C. An X-ray diffraction study[18] of **3** shows (Figure 1) the selenophene ring to be planar. The Re-coordinated C(2)–C(3) distance (1.44 (2) Å) is substantially longer than that (1.369 (1) Å) in free Sel,[19] while 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 (86.3 (5)°) is essentially the same as that (87.46 (4)°) in free Sel,[19] the C(2)–Se and C(5)–Se distances (1.95 (1) and 1.92 (1) Å) are considerably longer than in Sel (1.855 (1) Å).[19] As in S-coordinated thiophene complexes, the Se in **3** 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 $Cp^*(CO)_2Re(T)$ is 140°.[20] 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 bonds is especially interesting because it is the analogous C–S bonds in thiophenes that must be cleaved on HDS catalysts.

A question that arises in this work is why selenophene is 2,3-η^2-bonded to $Cp^*(CO)_2Re$ and thiophene is S-bonded. A possible explanation is that the π-system of selenophene, which has been suggested to be more electron rich than that of thiophene,[21] would form a stronger π-donor bond to the Re than would thiophene. On the other hand, the relative π-accepting properties of Sel and T, as well as the coordinating abilities of the Se and S atoms, are also involved; thus it is not clear at this time what factors determine the coordination modes of these ligands.

Acknowledgment. We are grateful to Dr. Lee M. Daniels of the Iowa State University Molecular Structure Lab for determining the structure of **3**.

Supplementary Material Available: Description of the data collection and structure solution, ORTEP drawing of **3**, tables of crystal data, positional and thermal parameters, complete bond distances and angles, and least-squares planes (15 pages); listing of calculated and observed structure factors for **3** (23 pages). Ordering information is given on any current masthead page.

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[16] **2**: IR (hexanes) ν(CO) 2076 (w), 1980 (m), 1940 (s), 1932 (s), 1924 (s), 1912 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.01 (d of d, 1 H, Sel), 6.29 (d, 1 H, Sel), 4.16 (d, 1 H, Sel), 3.18 (d of d, 1 H, Sel), 2.01 (s, 15 H, Cp*); ^{13}C NMR ($CDCl_3$) δ 204.9, 200.9, 198.1 (CO), 140.9, 119.1, 51.1, and 44.0 (Sel), 99.0 (C of Cp*), 10.1 (Me of Cp*); 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.

[17] **3**: IR (hexanes) ν(CO) 2014 (m), 1955 (m), 1908 (m), 1873 (s), 1852 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.53–7.38 (m, 15 H, PPh_3), 6.82 (d of d, 1 H, Sel), 5.29 (d, 1 H, Sel), 4.32 (d, 1 H, Sel), 3.19 (d of d, 1 H, Sel), 1.97 (s, 15 H, Cp*).

[18] Crystallographic data for **3**: Pale yellow crystals of $3\cdot1.5CH_2Cl_2$ were grown from CH_2Cl_2/hexanes at −70 °C; triclinic, space group $P\bar{1}$ (No. 2); $a = 13.390$ (5) Å, $b = 13.812$ (6) Å, $c = 12.559$ (3) Å; $\alpha = 116.89$ (2)°, $\beta = 95.89$ (2)°, $\gamma = 86.66$ (2)°; $V = 2060$ (1) $Å^3$; $d_{calcd} = 1.915$ g/cm^3; $Z = 2$; $\mu = 69.77$ cm^{-1} (Mo Kα). Diffraction data were collected at −75 ± 1 °C by using an Enraf-Nonius CAD4 automated diffractometer. A total of 6723 reflections were collected. Of the 4980 unique data, 4085 reflections having $I > 3\sigma(I)$ were used to solve the structure. The positions of the Re, W, Se, and P atoms were given by direct methods. The remainder of the non-hydrogen atoms were located in difference Fourier maps following least-squares refinement of the known atoms. $R = 4.8\%$ and $R_w = 6.4\%$ ($w = 1/\sigma^2(|F_o|)$). Details of data collection and refinement are given in the supplementary material.

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Synthesis of the First Metal-Complexed Benzannulene. An Estimate of the Aromaticity of Tricarbonylchromium-Complexed Benzene Relative to the Aromaticity of Benzene Itself

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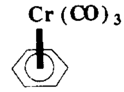
Received June 4, 1990

The upfield shift of about 2 ppm of the protons in tricarbonylchromium-complexed benzene (**1**) has prompted much investigation of its origin.[1] Such shifts have been interpreted as a combination of effects including quenching of the ring current, withdrawal of electron density from the ring by the $Cr(CO)_3$ moiety, the magnetic anisotropy of the chromium–ligand bond, and partial rehydbridization of the ring carbon atoms. The synthesis of **2**, the first annuleno-fused tricarbonylchromium-complexed benzene, permits a definitive statement to be made on the bond delocalization present in **1**, as well as an estimate of its effective resonance energy, relative to that of benzene.



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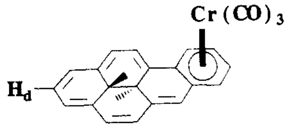

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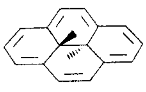

3

The bridged 14π annulene **3** (DMDHP, dimethyldihydropyrene) is an excellent probe for delocalization in fused aromatic systems such as **2** because the chemical shifts of the methyl protons are sensitive to the delocalization in the macrocyclic ring, yet are almost *invariant* to external substituents, even those with substantial anisotropic effects, because of the long distance involved (>5 Å) and the fact that the protons are three bonds separated from the π-periphery.[2,3] These protons do however respond linearly to the amount of bond fixation in the macrocyclic ring, with δ ranging from +1 (100% bond fixation) to −4.2 (0% bond fixation) ppm. Fusion of an aromatic annelating ring to **3**, as in **2**, causes bond fixation of the macrocyclic ring, the degree depending on the relative aromaticities of **3** and the annelating ring (in this case **1**). The aromaticity (as measured by bond-fixing ability) of **1** relative to that of benzene can thus be estimated by comparison of the methyl proton chemical shifts of **2** with those of its uncomplexed derivative **4**.[4] The synthesis of **2** (or an isomer) was thus undertaken.

No metal complexes of benzannulenes have been reported, perhaps in part because of the limited stability of most benzannulenes. Indeed heating **4** with $Cr(CO)_6$ or $Cr(CO)_3(CH_3CN)_3$ gave no complexed annulene, only decomposition. Since the

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