Notes

Osmium-Mediated Electrophilic Addition Reactions with Selenophene and Activation of the Se−C Bond

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*Summary: The complex [Os(NH$_3$)$_5$(η^2-selenophene)](OTf)$_2$ (**1**) has been prepared and treated with several electrophilic reagents to afford Se-alkyl and 2H-selenophenium complexes in high yield. In many aspects, the reactivity observed for **1** directly parallels that seen for the thiophene analogue. Protonation (HOTf/MeCN) and alkylation (acetal/TBSOTf) occur at C2, affording (1,5-η^2)-2H-selenophenium complexes (**2** and **3**, respectively). Methylation (MeOTf/MeCN) occurs at the heteroatom, affording the 1-methylselenophenium complex **4,** which, when treated with a nucleophile, undergoes C−Se cleavage to form an η^2-4-(alkylseleno)-1,3-butadiene complex (**5**).*

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Introduction

Over the past two decades, synthetic chemists have witnessed explosive growth in the use of selenium-based reagents in organic synthesis.[1] Although these compounds possess a reactivity similar to that of their sulfur congeners, organoselenium compounds are considerably more reactive with both oxidizing and reducing conditions. Our interest in the development of a general methodology for the dearomatization and activation of aromatic heterocycles[2] has prompted a comprehensive exploration into the chemistry of η^2-coordinated pyrroles,[3,4] furans,[5,6] and thiophenes[7] with electrophiles. Given the versatility of organoselenium compounds, we set out to explore whether this dearomatization methodology could be applied to selenophene as well. Angelici et al. prepared the first example of an η^2-selenophene complex (Cp*Re(CO)$_2$(η^2-selenophene)) and documented its reaction with [Me$_3$O]BF$_4$ to afford a Se-methylated η^2-selenophenium complex.[8] Aside from this report, little is known regarding the chemistry of transition-metal selenophene complexes with electrophiles. The following account summarizes our findings with the pentaammineosmium(II) complex [Os(NH$_3$)$_5$(η^2-selenophene)](OTf)$_2$ (**1**).

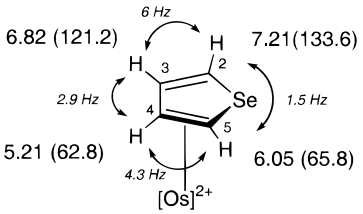

Figure 1. ^{1}H and ^{13}C NMR data for the complex [Os(NH$_3$)$_5$(η^2-selenophene)]$^{2+}$. [Os]$^{2+}$ = the cation [Os(NH$_3$)$_5$]$^{2+}$. Triflate counterions are omitted for clarity.

Results and Discussion

Synthesis of the η^2-Selenophene Complex. The η^2-selenophene complex **1** was prepared in 83% yield by reducing the precursor [Os(NH$_3$)$_5$(OTf)](OTf)$_2$ with Zn/Hg in MeOH in the presence of an excess (∼10 equiv) of selenophene. ^{1}H and ^{13}C NMR data clearly indicate an η^2-coordinated ligand. Two proton resonances at 7.21 and 6.82 ppm correspond to the protons on the uncoordinated double bond (i.e., H2 and H3), while the other two signals (6.05 and 5.21 ppm), shifted 1−2 ppm upfield relative to those of uncoordinated selenophene, correspond to the coordinated olefin protons. The ^{13}C NMR (CD$_3$CN) spectrum parallels the proton spectrum, showing two methine signals at 65.8 and 62.8 ppm shifted significantly upfield of the two uncoordinated methine carbons (Figure 1). These data are in agreement with those observed for the analogous η^2-thiophene complex[7] as well as for the complex Cp*Re(CO)$_2$(η^2-selenophene).[8] Whereas the pyrrole complex [Os(NH$_3$)$_5$(η^2-pyrrole)]$^{2+}$ undergoes a rapid ($t_{1/2}$ ≈ 1−100 s^{-1}) linkage isomerization at 22 °C,[3] all of the chalcogen heterocycle complexes appear static, even at elevated temperatures (e.g. for **1** at 80 °C in CD$_3$CN).

Electrophilic Additions. Upon coordination to pentaammineosmium(II), arenes, heterocycles, and dienes undergo facile addition reactions with a variety of carbon electrophiles.[2] Whereas η^2-pyrrole[3] and η^2-furan[9] complexes undergo electrophilic addition primarily at the β-carbon, affording 3*H*-pyrrolium and furanium complexes, thiophenes bound to osmium undergo electrophilic addition mainly at the uncoordinated α-carbon or the heteroatom.[10,11] Treatment of **1** with stoichiomet-

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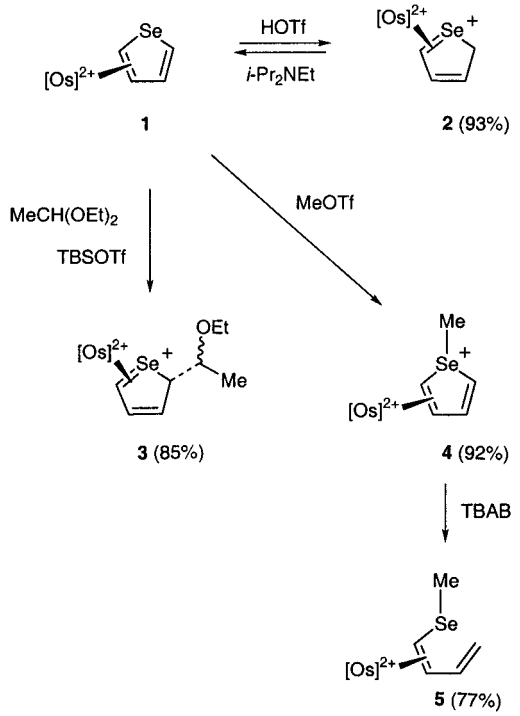

Figure 2. Reactivity of η^2-selenophene complex **1** and its selenophenium derivatives. TBAB = *n*-Bu_4NBH_4.

ric triflic acid (HOTf) in CH_3CN affords the (1,5-η^2)-2*H*-selenophenium complex **2** in 93% yield (Figure 2), analogous to the thiophenium complex obtained by protonation of the η^2-thiophene complex. The ^{1}H NMR (CD_3CN) spectrum shows a downfield singlet (9.24 ppm), two olefinic signals (7.03 and 6.76 ppm), *cis*-/*trans*-ammine resonances at 3.94 and 5.36 ppm, and two diastereotopic methylene signals at 3.31 and 2.44 ppm (J = 19.7 Hz). While the ^{1}H NMR spectrum does not provide conclusive evidence to differentiate between C2 or C3 protonation, comparison of the ^{13}C NMR spectrum with that of the 2*H*-thiophenium analog[7] unambiguously confirms a protonation at C2. ^{13}C NMR spectral features include two uncoordinated methine resonances (139.1 and 132.8 ppm), an upfield methine signal (84.0 ppm), and a methylene signal (39.0 ppm), a pattern identical with that observed for the 2*H*-thiophenium species.[10] The selenophenium complex is readily deprotonated by amine bases (i.e., *i*-Pr_2NEt, pyridine) to regenerate **1**.

Acetaldehyde diethyl acetal reacts with the selenophene complex **1** in the presence of the Lewis acid *tert*-butyldimethylsilyl triflate (TBSOTf) to afford the 2-substituted 2*H*-selenophenium complex **3** in 85% yield as a 3:2 mixture of diastereomers. This complex has spectroscopic features for the heterocycle that are very similar to those of the protonated selenophene complex **2**. ^{13}C NMR (CD_3CN) data include an upfield resonance for C5 (82.80 ppm) and olefinic resonances (140 and 133 ppm) corresponding to C3 and C4.

The selenophene complex **1** also reacts with methyl triflate in MeCN; however, in this case an irreversible addition occurs at the heteroatom, affording the 1-methyl selenophenium complex **4** in 92% yield. The resulting complex shows spectroscopic and electrochemical features that are practically identical with those of the 1-methylthiophenium analogue of osmium(II). [11] In addition, the ring resonances are positioned similarly to those reported for the {Cp*Re$(CO)_2$} analogue.[8] The facile β-acylation reactions observed for osmium thiophene complexes with anhydrides[10] appear to fail for **1**, affording instead the α-protonated selenophenium complex **2**.

Reactions of Selenophenium Complexes with Nucleophiles. The 2*H*-selenophenium complexes **2** and **3** either fail to react with or undergo deprotonation with common hydride or carbon nucleophiles such as CN^-, silyl ketene acetals, diethyl malonate, and borohydride salts. Their deprotonation results in the formation of (4,5-η)-selenophene complexes such as **1**. However, when complex **4** is treated with *n*-Bu_4NBH_4, carbon−heteroatom cleavage occurs to generate the selenium-substituted diene complex **5** in 77% yield (Figure 2). Carbon and proton NMR data along with electrochemical and combustion analysis data unambiguously confirm the formation of the diene product.[11] An upfield chemical shift in the ^{1}H NMR spectrum is observed for the selenium-bound methyl resonance from 3.07 ppm in the selenophenium complex **4** to 2.16 ppm in the diene **5**. Once again, this reaction is analogous to that observed for the thiophene analogue of **4**. In a recent report by Jones et al.,[12] the complex Cp*Rh(PMe_3)PhH was shown to react thermally with selenophene to give a six-membered-ring C−Se insertion product, but to our knowledge, an electrophile-promoted C−Se bond cleavage has not previously been demonstrated for a selenophene complex.

Concluding Remarks. Selenophene forms a thermally stable complex with the dearomatization agent pentaammineosmium(II), and its reactivity with electrophiles is profoundly altered relative to the uncoordinated ligand. While it is not surprising to find that the chemical reactivity of **1** is similar to that of its thiophene counterpart, several new reaction classes for selenophene have been demonstrated.

Experimental Section

General Considerations. All ^{1}H NMR spectra were recorded at 300 MHz and are referenced versus TMS. All ^{13}C NMR spectra were recorded at 75 MHz. The ^{13}C NMR (CD_3CN) resonance for the triflate anion (~122 ppm, q, J = 316 Hz) is not always observed. due to its low intensity, and is not reported. All cyclic voltammograms were recorded in CH_3CN using tetra-*n*-butylammonium hexafluorophosphate as electrolyte with a scan rate of 100 mV/s and are referenced to the normal hydrogen electrode (NHE) using ferrocene ($E_{1/2}$ = 0.55 V) as an internal standard. Selenophene was purchased from Acros Organics and deoxygenated prior to use. [Os$(NH_3)_5$(OTf)]-$(OTf)_2$ was synthesized as described by Lay et al.[13] All reactions were performed under nitrogen in a glovebox (Vacuum Atmospheres Co.).

{(4,5-η)-[Os$(NH_3)_5$]-selenophene}$(OTf)_2$ (1). Zinc amalgam (699 mg) was added to a solution of selenophene (595 mg, 4.61 mmol) in methanol (3.3 g), and the resulting slurry was stirred vigorously while solid [Os$(NH_3)_5$(OTf)]$(OTf)_2$ (326 mg, 0.452 mmol) was slowly added over a period of 5 min. Stirring was continued for 30 min, after which time the resulting golden brown slurry was filtered into 75 mL of stirred diethyl ether. The yellow precipitate was filtered, washed with diethyl

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ether (2 × 10 mL), and dried in vacuo, affording 263 mg (0.375 mmol) of a yellow solid (yield 83%). ^{1}H NMR (CD_3CN): δ 7.21 (dd, J = 6.0, 1.5 Hz, 1H), 6.82 (dd, J = 6.0, 2.9 Hz, 1H), 6.05 (dd, J = 4.3, 1.5 Hz, 1H), 5.21 (dd, J = 4.3, 2.9 Hz, 1H), 4.18 (br s, 3H), 2.91 (br s, 12H). ^{13}C NMR (CD_3CN): δ 133.6 (C), 121.2 (C), 65.8 (CH), 62.8 (CH). CV: $E_{p,a}$ = 0.65 V (NHE); $E_{p,c}$ = 0.09 V (NHE). Anal. Calcd for $C_6H_{19}N_5O_6F_6S_2SeOs$: C, 10.23; H, 2.72; N, 9.94. Found: C, 10.60; H, 3.03; N, 9.72.

{(1,5-η)-[Os(NH$_3$)$_5$]-2*H*-selenophenium}(OTf)$_3$ (2). Neat HOTf (43 mg, 0.287 mmol) was added to a solution of **1** (108 mg, 0.154 mmol) in 1.01 g of MeCN. After 5 min the resulting deep red solution was added to 50 mL of stirred diethyl ether. The precipitate was filtered, washed with diethyl ether (2 × 10 mL), and dried in vacuo, affording 122 mg (0.143 mmol) of a rose powder (yield 93%). ^{1}H NMR (CD_3CN): δ 9.24 (s, 1H), 7.03 (d, J = 5.6 Hz, 1H), 6.76 (dd, J = 5.6, 2.9 Hz, 1H), 5.36 (br s, 3H), 3.94 (br s, 12H), 3.31 (d, J = 19.7 Hz, 1H), 2.44 (d, J = 19.7 Hz, 1H). ^{13}C NMR (CD_3CN): δ 139.1 (CH), 132.8 (CH), 84.0 (CH), 39.0 (CH_2). Anal. Calcd for $C_7H_{20}N_5O_9F_9S_3SeOs$: C, 9.84; H, 2.36; N, 8.19. Found: C, 9.87; H, 2.32; N, 8.20.

{(1,5-η)-[Os(NH$_3$)$_5$]-2-(2-ethoxyethyl)selenophenium}(OTf)$_3$ (3). Dry acetaldehyde diethyl acetal (34 mg, 0.288 mmol) was added to a solution of **1** (117 mg, 0.167 mmol) in 1.19 g of MeCN. TBSOTf (53 mg, 0.200 mmol) was added, and the resulting deep red solution was allowed to stand for 5 min and then added to 50 mL of stirred diethyl ether. The precipitate was filtered, washed with diethyl ether (2 × 10 mL), and dried in vacuo, affording 131 mg (0.142 mmol) of a rose powder (yield 85%). ^{1}H NMR (CD_3CN): partial characterization of major isomer, δ 9.27 (s, 1H), 7.08 (m, 1H), 6.63 (overlapping m, 1H), 5.43 (br s, 3H), 4.04 (br s, 12H), 3.39 (q, J = 3.9 Hz, 1H), 1.40 (d, J = 5.9 Hz, 3H), 1.10 (t, J = 7.3 Hz, 3H). ^{13}C NMR (CD_3CN): major isomer, δ 140.2 (CH), 133.0 (CH), 82.8 (CH), 72.9 (CH), 66.6 (CH), 20.1 (CH_3), 15.5 (CH_3). ^{1}H NMR (CD_3CN): minor isomer, δ 9.17 (s, 1H), 7.03 (m), 6.63 (overlapping m, 1H), 5.43 (br s, 3H), 4.04 (br s, 12H), 3.29 (buried q, 1H), 1.25 (d, J = 5.9 Hz, 1H), 1.19 (t, J = 7.3 Hz, 1H). Anal. Calcd for $C_{11}H_{27}N_5O_{10}F_9S_3SeOs$: C, 14.27; H, 2.94; N, 7.57. Found: C, 14.01; H, 2.62; N, 7.79.

{(4,5-η)-[Os(NH$_3$)$_5$]-1-methylselenophenium}(OTf)$_3$ (4). A solution of CH_3OTf (89 mg, 0.568 mmol) was added to a solution of **1** (368 mg, 0.524 mmol) in 989 mg of CH_3CN. After 1 h, the solution was precipitated into 50 mL of stirred diethyl ether, and the precipitate was filtered, washed with diethyl ether (2 × 10 mL), and dried in vacuo, affording 418 mg (0.482 mmol) of yellow-orange solid (yield 92%). ^{1}H NMR (CD_3CN): δ 7.51 (dd, J = 5.1, 2.9 Hz, 1H), 6.91 (d, J = 5.1 Hz, 1H), 6.44 (d, J = 5.1 Hz, 1H), 5.55 (dd, J = 5.1 Hz, 2.9 Hz, 1H), 4.63 (br s, 3H), 3.40 (br s, 12H), 3.07 (s, 3H). ^{13}C NMR (CD_3CN): δ 154.4 (CH), 123.6 (CH), 66.9 (CH), 53.5 (CH_3), 24.7 (CH). CV: $E_{p,a}$ = 1.39 V (NHE). Anal. Calcd for $C_8H_{22}N_5O_9F_9S_3SeOs$: C, 11.06; H, 2.55; N, 8.06. Found: C, 11.27; H, 2.56; N, 8.00.

{(1,2-η)-[Os(NH$_3$)$_5$]-(*Z*)-4-(methylthio)-1,3-butadiene}(OTf)$_2$ (5). A solution of tetra-*n*-butylammonium borohydride (87 mg, 0.338 mmol) in 190 mg of acetonitrile was added to a solution of **4** (244 mg, 0.282 mmol) in 802 mg of acetonitrile. After 5 min, the reaction mixture was added to stirred CH_2Cl_2, and the precipitate was filtered, washed with CH_2Cl_2 (2 × 5 mL), and dried in vacuo, affording 146 mg (0.217 mmol) of a yellow powder (yield 77%). ^{1}H NMR (CD_3CN): δ 6.34 (d, J = 8.8 Hz, 1H), 5.47 (dd, J = 10.3 Hz, 8.8 Hz, 1H), 4.32 (overlapping m, 1H), 4.21 (br s, 3H), 3.25 (overlapping m, 1H), 3.09 (br s, 12H), 2.16 (s, 3H). ^{13}C NMR (CD_3CN): δ 138.5 (CH), 117.5 (CH), 52.8 (CH_2), 43.4 (CH), 19.3 (CH_3). CV: $E_{1/2}$ = 0.67 V (NHE). Anal. Calcd for $C_7H_{22}N_5O_6F_6S_2SeOs$: C, 11.68; H, 3.08; N, 9.73. Found: C, 11.95; H, 3.16; N, 8.00.

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