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Small Organoselenium Molecules. 1. Dimethyl Selenoxide: Structure, Complexation, and Gas-Phase Transformation

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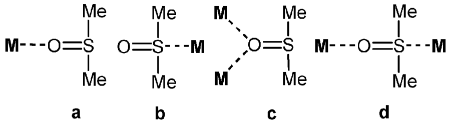
For the first time the structural characterization of dimethyl selenoxide coordinated to metal complexes has been performed confirming the Me_2SeO arrangement assigned by spectroscopic techniques for the molecule in solution and solid state. The structure of Me_2SeO is trigonal pyramidal with Se–O and Se–C bond lengths of 1.70 and 1.92 Å, respectively, and $\Sigma_{X-Se-Y} = 301°$. As a ligand, dimethyl selenoxide was found to bind to the rhodium centers of various Lewis acidity strengths by using only its oxo functionality in both terminal and bridging fashions. This O-directed coordination preference contrasts with an ambidentate (–S and –O) binding character revealed by dimethyl sulfoxide upon formation of analogous donor–acceptor complexes. The study of dimethyl selenoxide in the gas phase at 135–140 °C resulted in a thermal degradation of this molecule. The major decomposition product has been entrapped by a metal complex and identified as dimethyl selenide. The isolation of the coordinated Me_2Se fragment clearly demonstrates that the Me_2SeO molecule is less thermally stable than Me_2SO, which under similar reaction conditions shows no sign of decomposition at temperatures up to 160 °C.

Introduction

It is well established that dimethyl sulfoxide (Me_2SO, DMSO), widely known and used as a polar aprotic solvent, demonstrates an ambidentate character in reactions with transition metal complexes.[1] Depending on the nature of the metal center and other ligands, as well as the metal:ligand ratio, dimethyl sulfoxide can exhibit four different binding modes: very common terminal η^1-*O* (**a**) and η^1-*S* (**b**) as well as rare bridging μ^2-*O* (**c**)[2] and μ^2-*O*,*S* (**d**).[2f,3] Moreover, the linkage isomerism in the metal−DMSO complexes, both photochemical M−S → M−O and thermal M−O → M−S, has recently attracted much attention.[4]



In contrast to sulfur-containing ligands, the reactivity and coordination of analogous organoselenium molecules toward transition metal centers is not well researched. Geometrical characteristics of complexes as well as of some simple Se-containing molecules are still missing. For instance, the structure of biologically important dimethyl selenoxide, which is known as a good substrate for the bis(molybdopterin) enzyme dimethyl sulfoxide reductase[5] and is of interest as a cancer chemopreventive agent,[6] has remained unknown. Complexes of Me_2SeO with tin(IV) halides and some d- and f-transition

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metal perchlorates have been studied only by IR and Raman methods.[7]

This work is a part of a broader study aimed at investigations of structural characteristics and ligating properties of small organoselenium molecules, such as dimethyl selenoxide. We report here our results on Me_2SeO complexation by transition metal centers using both solution reactions and a gas-phase complexation approach. This study provides comparative reactivity data for two similar ligands, namely Me_2SO and Me_2SeO, in complexation reactions under the same experimental conditions. This work is based upon the observed fact[8] that the selected bidentate Lewis acids, dirhodium(II) carboxylates, do not significantly alter structural parameters of coordinated donors and that important feature was used to get the first geometric information on the dimethyl selenoxide molecule.

Experimental Section

General Data. All of the manipulations were carried out in a dry, oxygen-free, dinitrogen atmosphere by employing standard Schlenk techniques. The unligated form of $[Rh_2(O_2CCF_3)_4]$ (**1**) was prepared according to the literature procedures.[9] $[Rh_2(O_2CCH_3)_4]$ was purchased from Strem and used as received. Elemental analyses were performed by Canadian Microanalytical Services, Ltd. IR spectra were recorded on a Nicolet Magna 550 FTIR Spectrometer using KBr pellets. NMR spectra were obtained using Varian Gemini or XL-300 spectrometers at 300 MHz for ^1H, 57.3 MHz for ^{77}Se, and 75.1 MHz for ^{13}C. Chemical shifts are reported in ppm relative to TMS or $CHCl_3$ (7.24 ppm) for ^1H, $CDCl_3$ (77.0 ppm) for ^{13}C, and MeSeSeMe (275 ppm) or MeSeMe (0 ppm) in $CDCl_3$ for ^{77}Se. All ^{13}C and ^{77}Se NMR spectra were acquired in the proton-decoupled mode. MS data were determined on a Hewlett-Packard HP 5989 GC-LC-MS (70 eV for EI). Relative % peak abundance is given in parentheses following the *m*/*z* value for each ion.

Synthesis of Me_2SeO. Dimethyl selenoxide was prepared according to the literature procedures.[10]

Method I. Hydrogen peroxide (13 g, 30%, 0.12 mol) was placed in a 50 mL round-bottomed flask, and dimethyl selenide (10 g, 0.09 mol) was slowly added by syringe at -10 °C. The reaction mixture was stirred for 30 min and then warmed to room temperature during 1 h. Dioxane (25 mL) was added to the reaction mixture, and the reaction flask was put into a freezer at -78 °C for 2 h. The resulting frozen solid was kept under vacuum until the weight of solid no longer decreased. The residue was recrystallized from benzene to afford the title compound. Yield: 8.8 g, 75%. ^1H NMR ($CDCl_3$): δ 2.66 (s). ^{13}C NMR ($CDCl_3$): δ 33.78. ^{77}Se ($CDCl_3$): δ 945. GC-MS: *m*/*z* 126 (M^+, ^{80}Se, 100%), 110 (10), 97 (82), 80 (40). IR (KBr, cm^{-1}): 3033 w, 3017 w, 2940 w, 2930 w, 1395 w, 1375 w, 1119 s, 1109 s, 1065 s, 1009 s, 969 m, 890 s, 747 s, 723 m.

Method II. Dimethyl selenide (5.0 g, 0.045 mol) in $CHCl_3$ (100 mL) was placed in a 250 mL round-bottomed flask, and *m*-chloroperbenzoic acid (14 g, 70%, 0.05 mol) was added all at once at -10 °C. The mixture was warmed to room temperature and stirred for 30 min, and then it was quenched by addition of saturated $NaHCO_3$, filtered, dried, and concentrated. The resulting residue was purified by flash column chromatography using methanol ($R_f = 0.6$) affording the title compound. Yield: 4.0 g, 78%. The spectroscopic data are the same as for samples prepared by method I.

Coordination of Me_2SeO in Solutions. Synthesis of $[Rh_2(O_2CCF_3)_4]\cdot Me_2SeO$ (2). The solution containing Me_2SeO (0.012 g, 0.1 mmol) in 15 mL of benzene was carefully layered on a top of the CH_2Cl_2 solution containing **1** (0.060 g, 0.1 mmol, 20 mL of CH_2Cl_2). The mixing of layers resulted in the formation of green block-shaped crystals of **2** in a few days. They were collected, washed with hexanes, and dried in a vacuum. Yield: 0.043 g, 55%. Anal. Calcd for **2**, $Rh_2SeO_8F_{12}C_{12}H_6$: C, 18.40; H, 0.77. Found: C, 19.51; H, 1.10. IR (KBr, cm^{-1}): 3125 w, 3046 w, 2967 w, 2934 w, 1682 s, 1660 s, 1197 s, 1165 s, 859 m, 793 m, 741 s, 703 w.

Synthesis of $[Rh_2(O_2CCF_3)_4]\cdot 2Me_2SeO$ (3). The solution containing Me_2SeO (0.035 g, 0.3 mmol) in 20 mL of benzene was carefully layered on a top of the CH_2Cl_2 solution containing **1** (0.062 g, 0.1 mmol, 15 mL of CH_2Cl_2). After 1 week violet plate-shaped crystals of **3** started to grow at the bottom of the tube. They were collected, washed with hexanes, and dried in a vacuum. Yield: 0.059 g, 70%. Anal. Calcd for **3**, $Rh_2Se_2O_{10}F_{12}C_{12}H_{12}$: C, 15.87; H, 1.33. Found: C, 15.98; H, 1.40. IR (KBr, cm^{-1}): 3050 w, 3034 w, 3006 w, 2939 w, 2921 w, 2903 w, 1667 s, 1460 w, 1416 w, 1227 s, 1197 s, 1172 s, 1158 s, 969 m, 915 w, 894 w, 863 m, 786 m, 779 m, 741 s.

Synthesis of $[Rh_2(O_2CCH_3)_4]\cdot 2Me_2SeO$ (4). Dichloromethane (10 mL) was added to a mixture of two solids, Me_2SeO (0.042 g, 0.34 mmol) and $[Rh_2(O_2CCH_3)_4]$ (0.038 g, 0.09 mmol). The suspension was stirred for 1 h at room temperature to yield a clear blue-green solution. Hexanes (10 mL) were layered on a top of the CH_2Cl_2 solution to afford blue-violet crystals of **4** in 2−3 days. Yield: 0.060 g, 86%.

Gas-Phase Complexation Studies. Synthesis of $[Rh_2(O_2CCF_3)_4]\cdot Me_2Se$ (5). A mixture of **1** (0.066 g, 0.1 mmol) and Me_2SeO (0.011 g, 0.1 mmol) was sealed in an evacuated (10^{-2} atm) 10×60 mm Pyrex tube. The ampule was then placed in an electric furnace having a small temperature gradient along the length of the tube. The ampule was kept at 140 °C for 3 days to give red-brown needles deposited in the cold end of the tube where the temperature was at ca. 135 °C. Some unidentified powder residue was left in the hot end of the tube. Crystals of volatile product **5** were collected manually. Yield: 0.027 g, 35%. Anal. Calcd for **5**, $Rh_2SeO_8F_{12}C_{10}H_6$: C, 15.66; H, 0.79. Found: C, 16.14; H, 0.90.

X-ray Crystallographic Procedures. Single crystals of compounds **2**−**5** were obtained as described above. X-ray diffraction experiments were carried out on a Nonius FAST diffractometer with an area detector using Mo Kα radiation. Details concerning data collection have been fully described elsewhere.[11] Fifty reflections were used in cell indexing, and about 240 reflections, in cell refinement. Data were collected in a range $4° < 2\theta < 50°$ ($4° < 2\theta < 45°$ for **5**). Axial images were used to confirm the Laue group and all dimensions. The data were corrected for Lorentz and polarization effects by the MADNES program.[12] The intensities were also corrected for anisotropy effects using a local adaptation of the program SORTAV.[13] Reflection profiles were fitted, and

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Table 1. Crystallographic Data for $\{[Rh_2(O_2CCF_3)_4]\cdot Me_2SeO\}_\infty^1\cdot 1/2C_6H_6$ (**2**$\cdot 1/2C_6H_6$), $[Rh_2(O_2CCF_3)_4]\cdot 2Me_2SeO$ (**3**), $[Rh_2(O_2CCH_3)_4]\cdot 2Me_2SeO\cdot 2CH_2Cl_2$ (**4**$\cdot 2CH_2Cl_2$), and $\{[Rh_2(O_2CCF_3)_4]\cdot Me_2Se\}_\infty^1$ (**5**)

	2$\cdot 1/2C_6H_6$	**3**	**4**$\cdot 2CH_2Cl_2$	**5**
formula	$Rh_2SeO_9F_{12}C_{13}H_9$	$Rh_2Se_2O_{10}F_{12}C_{12}H_{12}$	$Rh_2Se_2Cl_4O_{10}C_{14}H_{28}$	$Rh_2SeO_8F_{12}C_{10}H_6$
fw	821.98	907.96	861.90	766.93
cryst system	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1$	$P2_1/c$
a (Å)	11.2884(10)	8.5443(9)	8.1902(9)	13.736(5)
b (Å)	11.8657(9)	9.761(3)	18.0206(19)	8.522(5)
c (Å)	20.0400(11)	14.603(3)	9.8268(11)	18.085(2)
α (deg)	74.657(6)	84.477(3)		
β (deg)	81.996(6)	88.517(18)	107.116(2)	91.09(2)
γ (deg)	64.516(4)	87.519(19)		
V (Å^3)	2335.7(3)	1210.8(5)	1386.1(3)	2117(2)
Z	4	2	2	4
ρ_{calcd} (g$\cdot$cm^{-3})	2.338	2.490	2.065	2.407
μ (mm^{-1})	3.109	4.507	4.244	3.418
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
transm factors	0.311−0.629	0.496−0.915	0.442−0.959	0.490−0.845
temp (K)	213(2)	213(2)	173(2)	213(2)
data/obsd/params	7832/6967/609	4031/3552/335	6067/5718/297	2635/2358/274
R1[a], wR2[b] [$I > 2\sigma(I)$]	0.0600, 0.1662	0.0497, 0.1246	0.0373, 0.0931	0.095, 0.2273
R1[a], wR2[b] (all data)	0.0676, 0.1779	0.0600, 0.1398	0.0401, 0.0946	0.1045, 0.2350
quality-of-fit[c]	1.074	1.065	1.044	1.120

[a] $R1 = \sum||F_o| - |F_c||/\simeq|F_o|$. [b] $wR2 = [\simeq[w(F_o^2 - F_c^2)^2]/\simeq[w(F_o^2)^2]]^{1/2}$. [c] Quality-of-fit $= [\simeq[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{params})]^{1/2}$, based on all data.

values of F^2 and $\sigma(F^2)$ for each reflection were obtained by the program PROCOR.[14] The coordinates of rhodium atoms for the structures were found in direct method E maps using the structure solution program SHELXTL.[15] The remaining atoms were located after an alternating series of least-squares cycles and difference Fourier maps.[16] The fluorine atoms of all CF_3 groups were disordered over two or three different rotational orientations. Anisotropic displacement parameters were assigned to all atoms, except the disordered fluorine atoms and disordered carbon atoms of solvent molecules. Relevant crystallographic data for complexes **2**$\cdot$1/2 C_6H_6, **3**, **4**$\cdot 2CH_2Cl_2$, and **5** are summarized in Table 1. Selected bond lengths and angles for **2**−**5** are given in Table 2.

Table 2. Selected Distances (Å) and Angles (deg) in Complexes $\{[Rh_2(O_2CCF_3)_4]\cdot(Me_2SeO)\}_\infty^1$ (**2**), $[Rh_2(O_2CCF_3)_4]\cdot(Me_2SeO)_2$ (**3**), $[Rh_2(O_2CCH_3)_4]\cdot(Me_2SeO)_2$ (**4**), and $\{[Rh_2(O_2CCF_3)_4]\cdot(Me_2Se)\}_\infty^1$ (**5**)

	2[a]	**3**[a]	**4**	**5**
Rh−Rh	2.4176(11)	2.4225(12)	2.3942(5)	2.428(3)
Rh−O_{TFA}	2.038(6)	2.036(6)	2.041(4)	2.04(2)
Rh−O_{Se}	2.295(5)	2.244(6)	2.290(5)	
Rh−Se				2.590(3)
Rh−Rh−O	174.3(2)	176.2(2)	178.01(11)	
Rh−Rh−Se				178.49(12)
Rh−O−Rh	118.1(2)			
Se−O	1.704(6)	1.687(6)	1.696(4)	
Se−C	1.917(10)	1.929(9)	1.921(7)	1.93(2)
O−Se−C	102.0(4)	101.3(5)	101.8(3)	
C−Se−C	98.0(5)	98.4(6)	96.1(3)	98.3(13)

[a] Average for two crystallographically independent molecules.

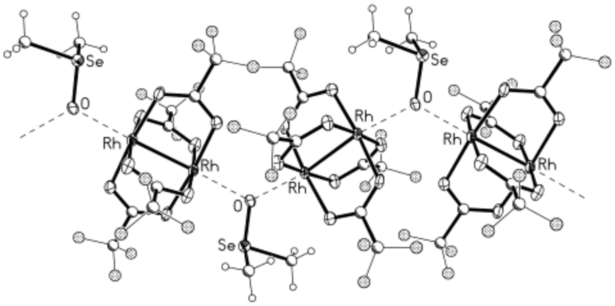

Figure 1. Fragment of the polymeric complex $\{[Rh_2(O_2CCF_3)_4]\cdot(CH_3)_2SeO\}_\infty^1$ (**2**) showing the alternating arrangement of $[Rh_2(O_2CCF_3)_4]$ and dimethyl selenoxide units. Atoms are represented by thermal ellipsoids at the 40% probability level. Fluorine, carbon, and hydrogen atoms are shown as spheres of arbitrary radii. Dashed lines indicate axial coordination to rhodium atoms.

Results

Solution interaction of dimethyl selenoxide, Me_2SeO, with **1** at room temperature afforded two types of crystalline adducts depending on the reagent concentrations, namely $\{[Rh_2(O_2CCF_3)_4]_n\cdot mMe_2SeO\}$, where n:m = 1:1 (**2**) and 1:2 (**3**). The monoadduct **2** and the bis-adduct **3** show distinctly different colors: green and violet, respectively. Both **2** and **3** are stable at room temperature, but **2** slowly loses crystallization solvent. Identities of products **2** and **3** were confirmed by chemical analysis and by X-ray crystallography. Two types of structures have been identified: an extended 1D coordination polymer in **2** (Figure 1); a discrete bis-adduct type in **3** (Figure 2a). The first one is built on the μ-O-coordination of dimethyl selenoxide ligands that bridge dirhodium complexes to form an infinite structural motif with an average Rh−O axial distance of 2.295(5) Å. In **3** two ligands are terminally coordinated to the axial positions of one dirhodium molecule. As expected, the average axial Rh−O distance for the terminally bound Me_2SeO ligand in **3** is a bit shorter (2.244(6) Å) than that in **2**, while average

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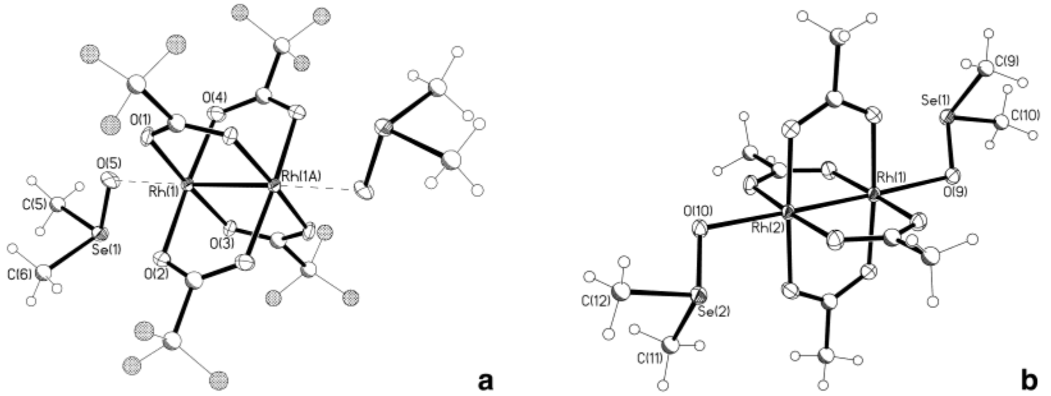

Figure 2. Perspective drawings of the $[Rh_2(O_2CR)_4]\cdot 2(CH_3)_2SeO$ molecules: (a) R = CF_3 (**3**); (b) R = CH_3 (**4**). Atoms are represented by thermal ellipsoids at the 40% probability level. Fluorine, carbon, and hydrogen atoms are shown as spheres of arbitrary radii. Dashed lines show axial coordination to rhodium atoms.

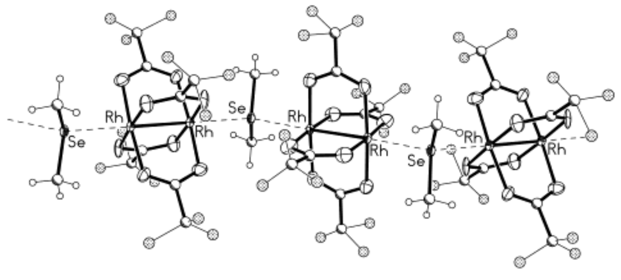

Figure 3. Fragment of 1D structure of **5**, $\{[Rh_2(O_2CCF_3)_4]\cdot(CH_3)_2Se\}^1_\infty$. Atoms are represented by thermal ellipsoids at the 40% probability level. Fluorine, carbon, and hydrogen atoms are shown as spheres of arbitrary radii. Dashed lines show axial coordination to rhodium atoms.

characteristics of the dirhodium cores are very similar for **2** and **3** (Table 2).

Solution interaction of Me_2SeO with $[Rh_2(O_2CCH_3)_4]$ resulted in the isolation of the only product, $[Rh_2(O_2CCH_3)_4]\cdot 2Me_2SeO$ (**4**), that crystallizes as a dichloromethane solvate. Crystals loose solvent very quickly, and that prevented obtaining accurate chemical analysis data for **4**. A bis-adduct type of structure has been confirmed for **4** by X-ray diffraction study (Figure 2b).[17] It is built on the terminal O-coordination of dimethyl selenoxide to the axial positions of the dirhodium unit. The Rh−O distance to the terminally bound Me_2SeO of 2.290(5) Å in **4** is a bit longer than that in **3** in accord with a decrease in Lewis acidity on going from **1** to dirhodium tetraacetate.

As a result of gas-phase reaction of Me_2SeO with **1** at 135−140 °C, novel product **5** has been isolated in the form of well-defined red-brown crystals that are stable at room temperature in air. Its chemical analysis characterization was consistent with the composition $[Rh_2(O_2CCF_3)_4]:(Me_2Se) = 1:1$. An X-ray structural investigation revealed the polymeric structure of the product **5** $\{[Rh_2(O_2CCF_3)_4]\cdot Me_2Se\}^1_\infty$ (Figure 3). It is built on the Me_2Se fragments bridging two rhodium centers to form an infinite 1D motif with the axial Rh−Se distances of 2.579(3) and 2.601(3) Å.

Discussion

This work tests an adduct formation approach for getting geometrical characteristics of molecules with unknown structures when direct crystallographic studies are not available. We decided to use the exceptional coordination ability of a bidentate coordinatively unsaturated inorganic complex, $[Rh_2(O_2CCF)_4]$ (**1**), for preparation of crystalline adducts with Me_2SeO followed by their X-ray crystallographic study.

The previous structural studies of adduct complexes of **1** with various donor molecules revealed an interesting and important feature: the geometrical characteristics of coordinated ligands do not significantly differ from those of the noncoordinated molecules. Some examples with sulfur molecules illustrating this observation are shown in Table 3. Therefore, the dimensional parameters of the coordinated ligand in this case can be regarded as a very close approximation for the geometry of a “free” molecule. In addition, acidic properties of the rhodium centers can be readily tuned by changing substituents on the carboxylates and that was used to demonstrate the ambidentate character of DMSO in solution.[22] Recently, flexibility in coordination of DMSO has been remarkably demonstrated by performing gas-phase complexation reactions using the significant volatility of complex **1**.[2f] For the system **1**−DMSO, novel adducts built on μ-O and μ-O,S coordination with new and varied stoichiometries have been discovered, namely $[Rh_2(O_2CCF_3)_4]_n\cdot m$DMSO with m:n = 7:8, 1:1, and 2:1. That variety along with a possibility for linkage isomerism[4] prompted us to examine the reactivity and ligating properties of Me_2SeO in the presence of dirhodium complex **1** not only in solution but also in the vapor phase at elevated temperatures.

Three new donor−acceptor adducts **2**−**4** have been isolated from solution reactions, and these are the first coordination complexes of dimethyl selenoxide crystallographically characterized in the whole transition metal series. As a

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(17) We have obtained crystals of **4** as solvates with CH_2Cl_2 and ClH_2CCH_2Cl. In both cases all the crystal tried (over 10 total) have been shown to be twins. However, the twin refinement of $\mathbf{4}\cdot 2CH_2Cl_2$ was successful. The results for this compound are reported in Tables 1 and 2.

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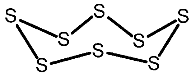
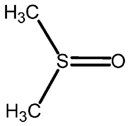
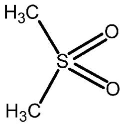
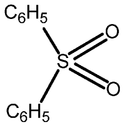
Table 3. Geometric Characteristics of "Free" and Coordinated to **1** Sulfur Molecules

Molecule	Bond, Angle	"Free" Ligand	Coord. Ligand
Cyclo-octasulfur 			μ_3-S,S',S"
	S-S	2.046	2.053
	S-S-S	108.2	107.2
		[18]	[8]
Dimethyl Sulfoxide 			μ_2-O
	S=O	1.49	1.50
	S-C	1.80	1.76
	C-S-O	105.9	104.6
	C-S-C	97.8	99.7
		[1c]	[2f]
Dimethyl Sulfone 			μ_2-O,O'
	S=O	1.45	1.44
	S-C	1.78	1.74
	O-S-O	117.2	116.6
	C-S-O	108.8	108.3
	C-S-C	103.4	106.7
		[19]	[20]
Diphenyl Sulfone 			μ_2-O,O'
	S=O	1.44	1.44
	S-C	1.77	1.76
	O-S-O	119.2	116.9
	C-S-O	108.1	108.0
	C-S-C	104.1	107.6
		[21]	[20]

result of these X-ray studies, the structure of dimethyl selenoxide has been proven to be the Me$_2$SeO type analogous to DMSO. A bridging mode of the Me$_2$SeO to the rhodium centers has been found in **2**, while complexes **3** and **4** both have terminally coordinated dimethyl selenoxide. In all adducts dimethyl selenoxide uses only the O-donor site for coordination. Geometrical parameters of the Me$_2$SeO molecules in O-bridging and O-terminal coordination modes were found to be very similar (Table 4). The Se−O bond distance is slightly longer in **2** than in **3** (1.704(6) versus 1.687(6) Å), while average Se−C distances as well as all angles about the selenium atom are very close for the two complexes.

There are no published X-ray data for dialkyl selenoxides except for the structures of a protonated dicyclohexyl selenoxide[23] and the selenolane five-membered ring based selenoxide.[24] Extrapolation of data from published studies on selenoxides of type Csp^{3}Csp^{2}Se(O)[25−28] and (Csp^2)$_2$SeO[29−33] suggests that the Se−O bond should be ca. 1.70 Å, as observed (Table 4). The observed C−Se bonds in the DMSeO complexes **2** and **3** are slightly shorter than expected from the literature examples. From data presented in Table 4 and from our previous experience, we may conclude that structural characteristics of the noncoordinated and the coordinated Me$_2$SeO molecules should be very close. Therefore, we can provide average characteristics for the Me$_2$SeO molecule in solution: a trigonal pyramid with Se−O 1.70 Å, Se−C 1.92 Å and $\Sigma_{X-Se-Y} = 301°$. The sum of the angles about the selenium atom is less than the expected value for pyramidal trisubstituted selenium with one lone pair (ca. 328.5°).

Structural information on Me$_2$SeO is useful for comparison with the results of theoretical calculations on this compound. Thus, calculations on Me$_2$SeO at the DFT (MP2)[34] level predict Se−O 1.672 (1.663) Å, C−Se 1.983 (1.948) Å, ∠CSeO 104.0° (103.8°), and ∠CSeC 94.4° (93.8°). Both Me$_2$SeO and Me$_2$SO are best described as possessing highly polarized X−O (X = Se, S) σ-bonds rather than X=O double bonds, with dipole moments of 4.77 D (DFT; 4.87 D MP2) and 4.45 D (DFT; 4.53 D MP2; 3.96 D experimental), respectively.

It is interesting to compare our structural data on Me$_2$SeO in **2** and **3** with results of the X-ray study of the protonated dialkyl selenoxide.[23] There is a small but noticeable elongation of the Se−O distance upon protonation, which can be interpreted as showing stronger interaction of DMSeO with the proton than with the rhodium centers of **1**.

Investigation of reactivity of Me$_2$SeO toward dirhodium tetraacetate, [Rh$_2$(O$_2$CCH$_3$)$_4$], which was shown to be a softer Lewis acid than **1** in solution reactions with DMSO,[22] revealed a difference in ligating properties of the two donor molecules. Dimethyl selenoxide was found to be insensitive to the Lewis acidity of the rhodium centers as it was O-terminally bound in both bis-adducts **3** and **4**. That contrasts with the coordination behavior of DMSO, which clearly revealed its ambidentate character in similar reactions with these two dirhodium complexes. Thus, the preferred coordination of DMSO ligands in the bis-adduct with [Rh$_2$(O$_2$CCH$_3$)$_4$] complex was found to be η^1-S, while in the bis-adduct with **1** it was η^1-O bound.[22]

So far the preference of the hard O atom of Me$_2$SeO for coordination to the metal center, rather than the soft Se atom, has been crystallographically confirmed in all adducts **2**−**4** isolated from solutions. This is in accord with the greater difference in electronegativities between selenium and oxygen compared to the situation with sulfur and oxygen.[23] It is also consistent with hydrogen-bonding studies concluding that DMSeO is a stronger base of the RX−O type than DMSO.[35] Lower reactivity of a selenophene 1-oxide toward further oxidation (compared to respective S-containing

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Table 4. Geometric Characteristics (Å and deg) of Selenoxide Compounds (R_2SeO)

compd	Se−O	Se−C	Se−C	O−Se−C	O−Se−C	C−Se−C	Σ_{X-Se-Y}	ref
Csp^3−Se(Rh−O−Rh)−Csp^3	1.704	1.91	1.93	100.6	103.3	98.0	301.9	this work (**2**)
Csp^3−Se(O−Rh)−Csp^3	1.687	1.92	1.94	100.5	102.1	98.4	301.0	this work (**3**)
Csp^3−Se(O−Rh)−Csp^3	1.696	1.916	1.926	101.7	101.9	96.1	299.7	this work (**4**)
Csp^3−Se(OH)−Csp^3 [a]	1.755	1.977	1.97	100.9	95.2	103.5	299.6	23
Csp^3−Se(O)−Csp^3 [b]	1.679	1.946	1.95	103.8	104.5	88.9	297.2	24
Csp^3−Se(O)−Csp^2 [c]	1.682	1.953	1.91	104.4	103.4	94.7	302.5	25
Csp^3−Se(O)−Csp^2 [d]	1.678	1.970	1.93	103.4	102.3	97.0	302.7	26
Csp^3−Se(O)−Csp^2 [e]	1.676	1.955	1.93	102.8	103.4	96.9	303.1	27
Csp^3−Se(O)−Csp^2 [f]	1.683	1.946	1.97	100.0	104.4	98.5	302.9	28
Csp^2−Se(O)−Csp^2 [g]	1.690	1.958	1.95	101.8	102.8	96.6	301.2	29
Csp^2−Se(O)−Csp^2 [h]	1.662	1.945	1.98	106.5	102.4	98.7	307.6	30
Csp^2−Se(O)−Csp^2 [i]	1.648	1.956	1.94	100.8	103.4	95.7	299.9	31
Csp^2−Se(O)−Csp^2 [j]	1.683	1.931	1.95	104.6	100.9	97.4	302.9	32
Csp^2−Se(O)−Csp^2 [k]	1.646	1.938	1.95	103.3	103.1	96.0	302.4	33

[a] Dicyclohexyl. [b] *trans*-3,4-Dihydroxy-1-selenolane. [c] 2-*exo*-Borneol, 4-methoxyphenyl. [d] Ethyl, *m*-tolyl. [e] 2-*exo*-Borneol, phenyl, clathrate. [f] 5′-Deoxyadenosine, phenyl. [g] 9-(Phenylseleno)dibenzothiophene, phenyl. [h] 2,4,6-Triisopropylphenyl, 4-(*p*-menthyloxycarbonyl)phenyl. [i] 3,3′-Bis(4-chloroquinolyl). [j] 4-Methoxyphenyl, phenyl, monohydrate. [k] Phenyl, 1-bromo-2-phenylethene.

molecules) has also been explained by decreased electron density on the selenium atom due to the highly polarized Se−O bond.[36] To force the Se-site coordination, it would be interesting to explore the phototriggered transformations μ^2-O → μ^2-S,O in the isolated crystalline monoadduct **2**, as intramolecular photochemical isomerization from Ru−O to Ru−S coordination has been previously observed in DMSO complexes of Ru(II).[4]

We were not able to prove the structure of Me_2SeO in the gas phase since dimethyl selenoxide showed limited thermal stability at elevated temperatures. Instead, we discovered a major decomposition pathway of Me_2SeO by successful entrapment of its reactive fragment, namely Me_2Se, formed in the vapor phase at 135−140 °C using complex **1** as an electrophilic trap. Dimethyl selenide was found to be the major fragment of this decomposition process, as its entrapment by **1** afforded crystals of complex **5** in moderate yield (ca. 35%). Chemical analysis also confirmed the identity of the isolated product, which is stable at room temperature. There are several[37] crystallographically characterized metal complexes that contain terminal dimethyl selenide ligands and only two other examples[37a,38] with bridging Me_2Se groups. For the latter two compounds average values of the Se−C bond and the C−Se−C angle for Me_2Se are close to the corresponding values obtained by microwave spectroscopy[39] and to the X-ray data for product **5** (Table 5).

Deoxygenation of sulfoxides to sulfides catalyzed by metal complexes with oxygen transfer to the metal center is a well-established process.[40] Although, the side product of the above reaction of **1** with Me_2SeO was not identified, the observed transformation confirms that the Me_2SeO molecule is less thermally stable than its sulfur analogue, which has been found to exist in vapor phase at temperatures at least up to 160 °C.[2f] The above thermal degradation reaction of Me_2SeO in the presence of dirhodium complex **1** in the gas phase is of interest as it provides an example of how environmentally important gas-phase transformations[41] of selenium-containing molecules can be studied with the use of the appropriate electrophilic metal complex traps.

Table 5. Geometric Characteristics (Å and deg) of Dimethyl Selenide

	microwave spectra[39]	calcd[33]		X-ray		
		DFT	MP2	ref 37a	ref 38	this work (**5**)
Se−C	1.943	1.970	1.948	1.951	1.925	1.92
				1.933	1.941	1.93
C−Se−C	96.11	96.9	95.9	96.59	99.11	98.3
M−Se				2.375	2.566	2.579
				2.377	2.561	2.601
M−Se−M				127.70	128.05	129.3
M−Se−C				107.1	107.2	106.2

This work illustrates the utility of the adduct formation approach to get structural information for molecules that are gaseous or liquid ligands or compounds with low melting temperatures. In addition, this technique also provides a route to examine decomposition reactions of thermally unstable molecules by entrapment of their reactive fragments formed at high temperatures. This will be extended to other small organoselenium molecules.

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Supporting Information Available: Three X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.asc.org.

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