Studies of Dirhodium(II) Tetra(trifluoroacetate). 5. Remarkable Examples of the Ambidentate Character of Dimethyl Sulfoxide

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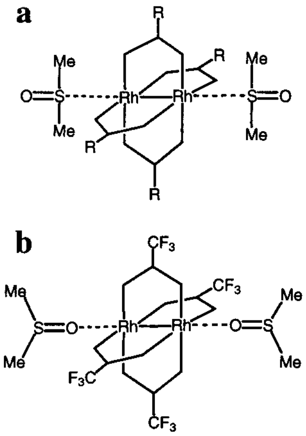
The ambidentate character of dimethyl sulfoxide, already known for dirhodium carboxylates, has been remarkably manifested in new ways. Three novel complexes of dirhodium(II) tetra(trifluoroacetate) with the DMSO ligand, namely, $[Rh_2(O_2CCF_3)_4]_m(DMSO)_n$ with m:n = 7:8 (**1**), 1:1 (**2**), and 3:2 (**3**), have been obtained by deposition from the vapor phase, and their crystal structures have been determined by X-ray crystallography. The crystallographic parameters are as follows: for **1**, monoclinic space group $P2_1/c$ with $a = 28.261(2)$ Å, $b = 16.059(4)$ Å, $c = 17.636(2)$ Å, $\beta = 92.40(4)°$, and $Z = 2$; for **2**, triclinic space group $P\bar{1}$ with $a = 8.915(2)$ Å, $b = 10.592(2)$ Å, $c = 11.916(2)$ Å, $\alpha = 84.85(1)°$, $\beta = 88.86(1)°$, $\gamma = 65.187(8)°$, and $Z = 2$; and for **3**, triclinic space group $P\bar{1}$ with $a = 8.876(2)$ Å, $b = 9.017(2)$ Å, $c = 19.841(3)$ Å, $\alpha = 101.91(2)°$, $\beta = 97.144(8)°$, $\gamma = 100.206(9)°$, and $Z = 1$. In the oligomeric molecule of **1**, six DMSO ligands bridge seven dirhodium tetra(trifluoroacetate) units in a bidentate fashion via S and O atoms, and two additional DMSO molecules terminate the chain. In the structure of the monoadduct $Rh_2(O_2CCF_3)_4(DMSO)$ (**2**), the dirhodium blocks are bridged through the O atoms of DMSO ligands, forming a one-dimensional polymeric chain. Compound **3** also has an infinite chain structure with the molecules of dimethyl sulfoxide acting in a bidentate μ-DMSO-*S*,*O* mode. Every second DMSO molecule is missing in **3**, so that two of every three $Rh_2(O_2CCF_3)_4$ units are associated through the O atoms of carboxylate groups to give the overall composition $[Rh_2(O_2CCF_3)_4]_3(DMSO)_2$.

Introduction

The ambidentate character of dimethyl sulfoxide (DMSO) has been remarkably demonstrated by its complexes with dirhodium(II,II) tetracarboxylates, $Rh_2(O_2CR)_4$. It has been shown that the mode of DMSO coordination can be controlled by simply changing the effective electronegativity of the carboxylate R group. The more electron-donating substituents (R = Me,[1] Et,[2] Ph[3]) cause the metal atom to prefer the coordination of Me_2SO ligands through their sulfur atoms (Chart 1a), whereas the strongly electron-withdrawing substituent (R = CF_3[2,4]) changes the preference to the oxygen atom (Chart 1b).

All of the compounds referred to above were synthesized by crystallization from solutions and are the bis adducts having the formula $Rh_2(O_2CR)_4(DMSO)_2$ with terminal monodentate coordination of the DMSO ligand to the axial positions of the dirhodium unit. Recently, we introduced a novel synthetic technique, solventless synthesis,[5] which allows for the isolation of adducts of the dirhodium(II) tetra(trifluoroacetate) that could not be obtained by conventional procedures in solvents. Using this procedure for the DMSO ligand, we have discovered three new compounds $[Rh_2(O_2CCF_3)_4]_m(DMSO)_n$ with m:n = 7:8 (**1**), 1:1 (**2**), and 3:2 (**3**).

Chart 1



In this paper, we present the crystal structures of **1**−**3**, in which DMSO ligands are attached to the dirhodium complexes in various bridging modes (Chart 2), whereby the ambidentate character of dimethyl sulfoxide is manifested in new ways.

Experimental Section

General Data. All of the experimental manipulations involving synthesis of the starting materials were carried out in a dry, oxygen-free, nitrogen atmosphere by employing standard Schlenk techniques. The anhydrous form of $Rh_2(O_2CCF_3)_4$ and the bis adduct $Rh_2(O_2CCF_3)_4(DMSO)_2$ were prepared according to literature procedures.[2,6] The IR spectra were recorded on a Perkin-Elmer 16PC FT-IR spectrophotom-

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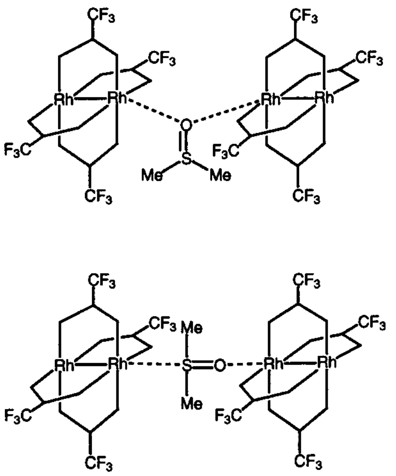
10.1021/ic9913076 CCC: $19.00

Chart 2



eter using a KBr pellet. Elemental analyses were performed by Canadian Microanalytical Sevices, Ltd. The EI/DP mass spectra were acquired using a VG Analytical 70S high-resolution, double-focusing, sectored (EB) mass spectrometer.

Synthesis of the $[Rh_2(O_2CCF_3)_4]_m(DMSO)_n$ Compounds. A small portion (~0.2 g) of a mixture of $Rh_2(O_2CCF_3)_4$ as a green powder and $Rh_2(O_2CCF_3)_4(DMSO)_2$ as blue crystals was sealed in an evacuated (10^{-2} atm) 11 × 60 mm Pyrex tube. The ampule was then placed in an electric furnace having a temperature gradient. The composition of the initial mixture was varied in molar ratio from 10:1 to 1:1, and the temperature of the "hot" zone of the tube was 100−160 °C in different experiments. The temperature of the "cold" zone was set 5−10 °C lower. The blue-violet crystals of **1** were obtained from the 1:1 initial mixture at 110 °C. The dark-green crystals of **3** were harvested from the 10:1 mixture at 100 °C. The intermediate compositions and higher temperatures produced the grass-green crystals of **2** as the main product, along with some of the other two compounds. The yields of the crystalline products were dependent on the time of heating and after 2−3 days were usually about 20−30%.

Anal. Calcd for **1**, $Rh_{14}S_8O_{64}F_{84}C_{72}H_{48}$: C, 16.53; O, 19.58; H, 0.92. Found: C, 16.73; O, 19.74; H, 1.08. Calcd for **2**, $Rh_2SO_9F_{12}C_{10}H_6$: C, 16.32; O, 19.56; H, 0.82. Found: C, 16.34; O, 19.51; H, 0.98. Calcd for **3**, $Rh_6S_2O_{26}F_{36}C_{28}H_{12}$: C, 15.79; O, 19.53; H, 0.57. Found: C, 15.79; O, 19.38; H, 0.70. MS (EI/DP, 300 °C, *m*/*z*) for **1**−**3**: 658 $[Rh_2(O_2CCF_3)_4^+]$, 544 $[Rh_2(O_2CCF_3)_3^+]$, 432 $[Rh_2(O_2CCF_3)_2^+]$, 319 $[Rh_2(O_2CCF_3)^+]$, 206 $[Rh_2^+]$. IR (KBr, cm^{-1}) for **1**: 1664.8 (s), 1305.4 (m), 1261.7 (m), 1192.0 (s), 1168.8 (s), 1079.0 (w), 1026.1 (w), 972.4 (m), 918.9 (w), 890.5 (m), 785.6 (m), 738.0 (s), 722.1 (s). IR (KBr, cm^{-1}) for **2**: 1665.9 (s), 1650.8 (s), 1620.0 (w), 1461.9 (w), 1227.5 (s), 1193.1 (s), 1172.6 (s), 1026.1 (w), 992.7 (w), 910.6 (m), 861.2 (m), 785.9 (m), 739.5 (s), 544.1 (m), 526.4 (m), 430.3 (w). IR (KBr, cm^{-1}) for **3**: 1669.2 (s), 1256.1 (s), 1229.3 (s), 1191.4 (s), 1168.2 (s), 1099.4 (m), 1054.1 (w), 860.7 (s), 804.1 (m), 785.4 (s), 739.4 (s), 539.9 (m), 528.4 (m).

X-ray Crystallographic Procedures. Single crystals of compounds **1**−**3** 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.[6] Each crystal was mounted on the tip of a quartz fiber with silicone grease, and the setup was quickly placed in the cold N_2 stream (−60 °C) of a low-temperature controller. Fifty reflections were used in cell indexing and more than 200 reflections in cell refinement. Axial images were obtained to confirm the Laue group and all dimensions. The data were corrected for Lorentz and polarization effects by the MADNES program.[7] Reflection profiles were fit, and values of F^2 and $\sigma(F^2)$ for each reflection were obtained by the program PROCOR.[8]

All calculations were done on a DEC Alpha workstation running VMS. The coordinates of rhodium and sulfur atoms for the structures were found in direct-method *E* maps using the structure solution program SHELXTL.[9] The positions of the remaining atoms were located after an alternating series of least-squares cycles and difference Fourier maps. The fluorine atoms of all CF_3 groups were found to be disordered over two or three different rotational orientations. For the structures of **2** and **3**, anisotropic displacement parameters were assigned to all non-hydrogen atoms except the disordered fluorine atoms. Hydrogen atoms were refined independently. For the structure of **1**, because of a poor ratio of the number of reflections to the number of parameters, only Rh, S, and O atoms were refined anisotropically. Hydrogen atoms of the DMSO ligands were included in the structure factor calculations at idealized positions. Relevant crystallographic data for compounds **1**−**3** are summarized in Table 1, and selected bond distances and angles are given in Tables 2−4.

Results and Discussion

Molecular Structures. Compound **1** adopts the monoclinic space group $P2_1/c$ with two oligomeric molecules $[Rh_2(O_2CCF_3)_4]_7(DMSO)_8$ (Figure 1) in the unit cell. The molecule itself is centrosymmetric, having an inversion center at the midpoint of the central dirhodium unit. The composition of **1** is unique as it is the only dimetal carboxylate adduct $M_2(O_2CR)_4L_x$ with $1 < x < 2$. Six molecules of dimethyl sulfoxide bridge seven dirhodium tetra(trifluoroacetate) units through their axial positions, and two additional DMSO molecules terminate the oligomeric chain. The chain is highly zigzagged because of acute Rh−O−S−Rh torsion angles ranging from 53° to 87°. The dimethyl sulfoxide bridging coordination is bidentate via the S and O atoms. Such a DMSO bonding mode has never been seen before, either for dimetal carboxylates or for chain compounds, and it is extremely rare in general (vide infra). In the crystal structure of **1**, we can recognize all three possible types of dirhodium units that differ by their axial coordination: three Rh_2 units with only O atoms at the ends, two with only S atoms, and two with both O and S atoms. This type of construction has no real precedent. The closest analogue to **1** was reported by Chisholm et al.[10] as the oligomeric dianion $[Rh_8(O_2CBu^t)_{16}(O_2CMe)_2(C_7H_8)_2]^{2-}$, which consists of four dimetal units bridged by carboxylato groups and terminated by toluene molecules.

The crystal structure of monoadduct $Rh_2(O_2CCF_3)_4(DMSO)$ (**2**) resembles one of the structures we recently published[5b] for the THF ligand. In fact, the two are isostructural. The oxygen atom of each dimethyl sulfoxide molecule bridges the axial positions of two dirhodium molecules, thereby producing a one-dimensional zigzag chain structure $[Rh_2(O_2CCF_3)_4(DMSO)]_\infty{}^1$ (Figure 2) that extends along the *a* direction of the unit cell. The zigzag arrangement arises from the nearly trigonal planar coordination of the DMSO oxygen atom where the Rh−O(DMSO)−Rh angle is 116.2(2)° (Table 3). As in the case of the THF ligand, the bridging is asymmetric with Rh−O(DMSO) distances of 2.299(5) and 2.375(5) Å and S−O(DMSO)−Rh angles of 128.8(3)° and 112.1(3)° for Rh(1) and Rh(2), respectively. This bridging μ-DMSO-*O* coordination mode is also uncharacteristic for dimethyl sulfoxide (vide infra) and has not been observed before for dimetal carboxylates.

Compound **3** also has an infinite zigzag chain structure (Figure 3). As in the molecule of **1**, the DMSO ligand acts in

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Table 1. Crystallographic Data for $[Rh_2(O_2CCF_3)_4]_m(DMSO)_n$ Molecules [m:n = 7:8 (**1**), 1:1 (**2**), and 3:2 (**3**)]

	1	**2**	**3**
formula	$Rh_{14}S_8O_{64}F_{84}C_{72}H_{48}$	$Rh_2SO_9F_{12}C_{10}H_6$	$Rh_6S_2O_{26}F_{36}C_{28}H_{12}$
fw	5230.32	736.03	2129.96
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a, Å	28.261(2)	8.915(2)	8.876(2)
b, Å	16.059(4)	10.592(2)	9.017(2)
c, Å	17.636(2)	11.916(2)	19.841(3)
α, deg		84.85(1)	101.91(2)
β, deg	92.40(4)	88.86(1)	97.144(8)
γ, deg		65.187(8)	100.206(9)
V, Å^3	7997(2)	1017.0(3)	1507.7(5)
Z	2	2	1
ρ_{calcd}, g cm^{-3}	2.172	2.404	2.346
μ, mm^{-1}	1.685	1.876	1.859
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
temp, °C	−60	−60	−60
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.0584, 0.1280	0.0428, 0.1072	0.0532, 0.1231
R1,[a] wR2[b] (all data)	0.0729, 0.1437	0.0471, 0.1123	0.0635, 0.1416

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

the bridging -*S*,*O* mode, thus yielding a pattern that is typical for dirhodium carboxylate complexes with bidentate ligands.[11] The only difference is that each second ligand is missing, so that two of every three $Rh_2(O_2CCF_3)_4$ units are associated through the O atoms of the carboxylate groups, resulting in the overall composition $[Rh_2(O_2CCF_3)_4]_3(DMSO)_2$. The “dimer of dimers” all have oxygen atoms of DMSO coordinated at both ends, while the single dirhodium unit has two S atoms at the axial positions. The chain is less zigzagged for **3** than for **1** and **2** because the Rh−O−S−Rh torsion angles are 135°. The 3:2 composition is the first that has been observed between 1:1 and 2:1 for polydentate ligands, and we might say that compound **3** is “unsaturated” by DMSO.

DMSO Coordination. The dirhodium(II,II) tetracarboxylates constitute the first class of compounds in which the ambidentate character of DMSO is fully manifested. Two types of monodentate (-*O* and -*S*) coordination modes were already known from solution chemistry under conditions of ligand excess. Here, we have discovered two additional μ coordination modes (μ-*O* and μ-*S*,*O*) from our solventless synthesis under the conditions of low concentration of dimethyl sulfoxide. The μ-DMSO-*S*,*O* moiety that bridges two transition metal centers[12] is extremely rare. It was reported for the first time in 1996[13] for the diruthenium(II,II) complex $[Ru_2(\mu\text{-Cl})(\mu\text{-H})(\mu\text{-DMSO-}S,O)Cl_2(DMSO\text{-}S)_4]$, and since then, it has been encountered[14] just once for $[Ru_2(\mu\text{-Cl})(\mu\text{-DMSO-}S,O)Cl_3(DMSO\text{-}S)_3(CO)_2]$. The Ru−O and Ru−S distances for bridging DMSO in these compounds were significantly different, but in general, they were shorter than those for corresponding monodentate coordination modes. In our case (compounds **1** and **3**), the bridging distances are very close to the known values of the Rh−O and Rh−S distances for monodentate coordination (Table 5).

Another bridging mode, μ-*O*, is more common for dimethyl sulfoxide and has been known for a long time, although there are few structurally characterized examples.[15] The bridging can be either symmetric or asymmetric and covers a broad range of both M···M distances for the connected atoms (from 3 to 4 Å) and M−O−M angles (67−109°). In the structure of the monoadduct $Rh_2(O_2CCF_3)_4(DMSO)$ (**2**), the difference in the $Rh-O_{br}$ distances is about 0.08 Å, and the Rh···Rh separation is 3.97 Å, which causes the bridging Rh−O−Rh angle to be 116°. The Rh−O distances in **2** are significantly longer than those for the terminal DMSO coordination in $Rh_2(O_2CCF_3)_4(DMSO)_2$ (Table 5). We have observed[5b] the same effect for the bridging coordination of THF to dirhodium(II) tetra(trifluoroacetate), where the $Rh-O_{br}$ distances are about 0.18 Å longer than terminal bonds.

IR Spectra. The S−O stretching frequencies, which are easily observed in IR spectra, have been known for a long time to be diagnostic of the DMSO binding mode.[16] The monodentate coordination of DMSO through the S atom causes an increase in the S−O bond order. For bis adducts, $Rh_2(O_2CR)_4(DMSO)_2$ (R = Me, Et, Ph), that corresponds to a shortening of the S−O bond length by about 0.04 Å compared to that in free DMSO molecule and an increase in ν_{SO} of 30−40 cm^{-1} (Table 6).[17] On the other hand, the O coordination of dimethyl sulfoxide to $Rh_2(O_2CCF_3)_4$ led to negligible elongation of the S−O bond and a substantial decrease of ν_{SO}. In the cases of bridging μ-*O* coordination of DMSO,[15] the S−O distance is within the range 1.50−1.56 Å. In the structure of the monoadduct (**2**), this

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Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Rh_2(O_2CCF_3)_4]_7(DMSO)_8$ (**1**)

Rh−Rh							
Rh(1)−Rh(1A)	2.398(3)	Rh(2)−Rh(3)	2.417(2)	Rh(4)−Rh(5)	2.425(2)	Rh(6)−Rh(7)	2.398(2)
Rh−O_{Ac} (av)							
Rh(1)−O(1−4)	2.03(1)	Rh−O(5−12)	2.03(1)	Rh−O(13−20)	2.03(1)	Rh−O(21−28)	2.04(1)
Rh−O_{DMSO}							
Rh(1)−O(29)	2.23(1)	Rh(3)−O(30)	2.27 (1)			Rh(6)−O(31)	2.23(1)
						Rh(7)−O(32)	2.24(1)
Rh−S							
		Rh(2)−S(1)	2.451(4)	Rh(4)−S(2)	2.410(4)		
				Rh(5)−S(3)	2.522(5)		
S−O							
S(1)−O(29)	1.50(1)	S(2)−O(30)	1.50(1)	S(3)−O(31)	1.47(1)	S(4)−O(32)	1.49(1)
O_{Ac}−Rh−O_{Ac} (av)							
O−Rh(1)−O	90.0(4)	O−Rh(2)−O	89.9(5)	O−Rh(4)−O	90.0(5)	O−Rh(6)−O	90.0(5)
		O−Rh(3)−O	90.0(5)	O−Rh(5)−O	88.9(5)	O−Rh(7)−O	89.9(5)
O_{Ac}−Rh−O_{ax}							
O−Rh(1)−O(29)	87.7(4)−96.3(4)	O−Rh(3)−O(30)	87.2(4)−95.7(4)			O−Rh(6)−O(31)	91.3(4)−92.6(4)
						O−Rh(7)−O(32)	87.3(4)−96.5(4)
O_{Ac}−Rh−S_{ax}							
		O−Rh(2)−S(1)	95.7(3)−89.6(4)	O−Rh(4)−S(2)	89.3(3)−94.3(3)		
				O−Rh(5)−S(3)	87.2(3)−98.6(3)		
Rh−Rh−O_{Ac} (av)							
Rh(1A)−Rh(1)−O	88.1(3)	Rh(3)−Rh(2)−O	87.8(3)	Rh(5)−Rh(4)−O	88.2(3)	Rh(7)−Rh(6)−O	88.0(3)
		Rh(2)−Rh(3)−O	88.0(3)	Rh(4)−Rh(5)−O	87.3(3)	Rh(6)−Rh(7)−O	88.1(3)
Rh−Rh−O_{ax}							
Rh(1A)−Rh(1)−O(29)	176.3(3)	Rh(2)−Rh(3)−O(30)	175.5(3)			Rh(7)−Rh(6)−O(31)	178.7(3)
						Rh(6)−Rh(7)−O(32)	175.0(3)
Rh−Rh−S_{ax}							
		Rh(3)−Rh(2)−S(1)	176.9(1)	Rh(5)−Rh(4)−S(2)	177.4(1)		
				Rh(4)−Rh(5)−S(3)	174.2(1)		
Rh−O−S							
Rh(1)−O(29)−S(1)	129.2(6)	Rh(3)−O(30)−S(2)	135.1(6)			Rh(6)−O(31)−S(3)	131.8(7)
						Rh(7)−O(32)−S(4)	123.3(7)
Rh−S−O							
		Rh(2)−S(1)−O(29)	120.4(4)	Rh(4)−S(2)−O(30)	120.3(5)		
				Rh(5)−S(3)−O(31)	127.4(5)		

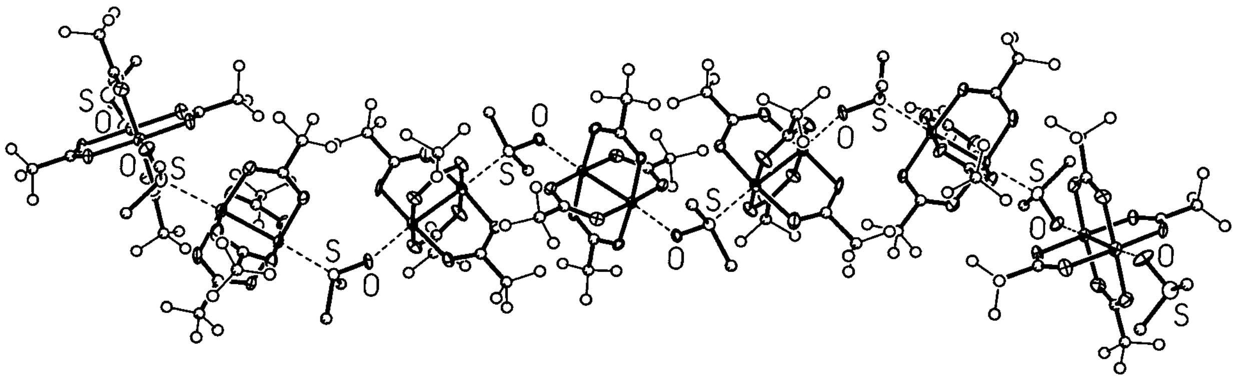


Figure 1. Perspective drawing of the $[Rh_2(O_2CCF_3)_4]_7(DMSO)_8$ molecule (**1**). Fluorine and carbon atoms are shown as spheres of arbitrary radii, with only one orientation of each CF_3 group depicted. Hydrogen atoms of DMSO groups are omitted. Axial interactions to the dirhodium units are drawn by dashed lines. Only S and O atoms of dimethyl sulfoxide are labeled for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[Rh_2(O_2CCF_3)_4(\mu\text{-DMSO-}O)]_\infty$ (**2**)

Rh−Rh	Rh(1)−Rh(1A)	2.407(1)	Rh(2)−Rh(2C)	2.416(1)
Rh−O_{Ac} (av)	Rh(1)−O(1−4)	2.038(5)	Rh(2)−O(5−8)	2.030(5)
Rh−O_{DMSO}	Rh(1)−O(9)	2.299(5)	Rh(2)−O(9)	2.375(5)
S−O	S(1)−O(9)	1.505(5)		
O_{Ac}−Rh−O_{Ac} (av)	O−Rh(1)−O	89.9(2)	O−Rh(2)−O	89.9(2)
O_{Ac}−Rh−O_{DMSO}	O(1)−Rh(1)−O(9)	86.5(2)	O(5)−Rh(2)−O(9)	88.7(2)
	O(2)−Rh(1)−O(9)	88.9(2)	O(6)−Rh(2)−O(9)	89.7(2)
	O(3)−Rh(1)−O(9)	97.8(2)	O(7)−Rh(2)−O(9)	95.7(2)
	O(4)−Rh(1)−O(9)	95.6(2)	O(8)−Rh(2)−O(9)	94.5(2)
Rh−Rh−O_{Ac} (av)	Rh(1A)−Rh(1)−O	87.9(1)	Rh(2C)−Rh(2)−O	87.9(2)
Rh−Rh−O_{DMSO}	Rh(1A)−Rh(1)−O(9)	173.2(1)	Rh(2C)−Rh(2)−O(9)	176.7(1)
Rh−O_{DMSO}−Rh	Rh(1)−O(9)−Rh(2)	116.2(2)		
Rh−O−S	Rh(1)−O(9)−S(1)	128.8(3)	Rh(2)−O(9)−S(1)	112.1(3)

Table 4. Selected Bond Distances (Å) and Angles (deg) for $\{[Rh_2(O_2CCF_3)_4]_3(\mu\text{-DMSO-}S,O)_2\}_\infty$ (**3**)

Rh−Rh	Rh(1)−Rh(2)	2.391(1)			Rh(3)−Rh(3A)	2.426(2)
Rh−O_{Ac} (av)	Rh(1)−O(1−4)	2.036(7)	Rh(2)−O(5−8)	2.039(7)	Rh(3)−O(9−12)	2.036(7)
Rh−L_{ax}	Rh(1)−O(1A)	2.386(6)	Rh(2)−O(13)	2.219(7)	Rh(3)−S(1)	2.449(3)
S−O	S(1)−O(13)	1.465(8)				
O_{Ac}−Rh−O_{Ac} (av)	O−Rh(1)−O	90.0(3)	O−Rh(2)−O	89.9(3)	O−Rh(3)−O	89.9(3)
O_{Ac}−Rh−L_{ax}	O(1)−Rh(1)−O(1A)	79.5(3)	O(5)−Rh(2)−O(13)	96.2(3)	O(9)−Rh(3)−S(1)	93.8(2)
	O(2)−Rh(1)−O(1A)	90.6(3)	O(6)−Rh(2)−O(13)	94.1(3)	O(10)−Rh(3)−S(1)	89.1(2)
	O(3)−Rh(1)−O(1A)	104.8(3)	O(7)−Rh(2)−O(13)	87.6(3)	O(11)−Rh(3)−S(1)	95.5(2)
	O(4)−Rh(1)−O(1A)	92.6(3)	O(8)−Rh(2)−O(13)	90.1(3)	O(12)−Rh(3)−S(1)	91.0(2)
Rh−Rh−O_{Ac} (av)	Rh(2)−Rh(1)−O	88.1(2)	Rh(1)−Rh(2)−O	88.0(2)	Rh(3A)−Rh(3)−O	87.6(2)
Rh−Rh−L_{ax}	Rh(2)−Rh(1)−O(1A)	168.0(2)	Rh(1)−Rh(2)−O(13)	175.9(2)	Rh(3A)−Rh(3)−S(1)	177.02(8)
Rh−O_{Ac}−Rh	Rh(1)−O(1)−Rh(1A)	100.5(3)				
Rh−O−S			Rh(2)−O(13)−S(1)	136.4(4)		
Rh−S−O					Rh(3)−S(1)−O(13)	119.0(4)

distance is 1.505(5) Å, and the S−O stretching frequency, 1026 cm^{-1} (Table 6), is again lowered.

For the bridging DMSO *μ-S,O*, the S−O bond lengths were found to be quite different in two known examples of diruthenium(II,II) compounds, namely, 1.508(5)[14] and 1.532(4) Å,[13] but longer than the corresponding distances for the S-bonded dimethyl sulfoxide ligands present in those complexes. We observed in the crystal structure of **3** a distinct shortening of the S−O distance [1.465(8) Å] relative to that in the free ligand [1.513(5) Å]. The ν_{SO} value of 1099 cm^{-1} was consistent with that observation. For compound **1**, there are four different S−O bonds: two having a length of 1.50(1) Å, one of 1.49(1) Å, and one of 1.47(1) Å. Because of the large uncertainties, these distances do not differ in a statistically significant sense. In the IR spectrum, there are two bands at 1028 and 1079 cm^{-1}. Presumably the first one arises from the terminal DMSO and the second from the bridging DMSO ligands.

Synthetic Aspect. Compounds **1**−**3** have been obtained by crystallization from the vapor phase, the technique which we already successfully used[5] for the synthesis of new $Rh_2(O_2CCF_3)_4$ adducts with different ligands. The only complex

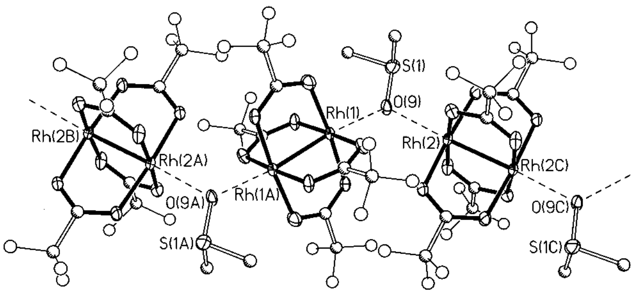


Figure 2. Fragment showing the arrangement of $Rh_2(O_2CCF_3)_4$ and DMSO units in the chain structure of the monoadduct (**2**). Atoms are represented by thermal ellipsoids at the 40% probability level. Fluorine and carbon atoms are shown as spheres of arbitrary radii, with only one orientation of each CF_3 group depicted. Hydrogen atoms of DMSO groups are omitted. Only Rh, S, and O(DMSO) atoms are labeled for clarity.

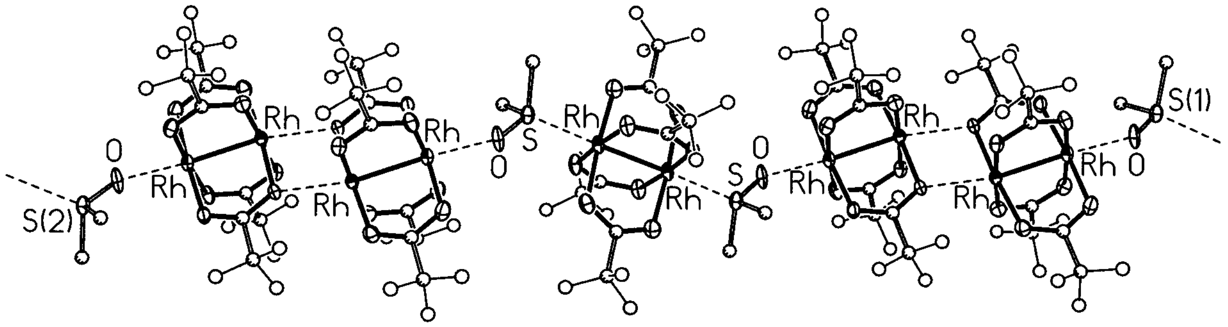


Figure 3. Fragment showing the arrangement of $Rh_2(O_2CCF_3)_4$ and DMSO units in the extended chain of $\{[Rh_2(O_2CCF_3)_4]_3(DMSO)_2\}_\infty$ (**3**). Atoms are represented by thermal ellipsoids at the 40% probability level. Fluorine and carbon atoms are shown as spheres of arbitrary radii, with only one orientation of each CF_3 group depicted. Hydrogen atoms of DMSO groups are omitted. Only Rh, S, and O(DMSO) atoms are labeled for clarity.

Table 5. Selected Distances (Å) and Angles (deg) in the Crystal Structures of the Dirhodium(II,II) Tetracarboxylate Complexes with Dimethyl Sulfoxide

$[Rh_2(O_2CR)_4]_m(DMSO)_n$	Rh−Rh	$Rh-O_t$	$Rh-O_{br}$	$Rh-S_t$	$Rh-S_{br}$	Rh−Rh−O	Rh−Rh−S	Rh−O−S	Rh−S−O	ref
$R = CF_3$ $m:n = 7:8$ (**1**)	2.398(3)−2.425(2)	2.24(1)	2.23(1)−2.27(1)		2.410(4)−2.522(5)	176.8(3)	176.2(1)	131.8(6)	122.7(5)	[a]
$R = CF_3$ $m:n = 3:2$ (**3**)	2.391(1), 2.426(2)		2.219(7)		2.449(3)	175.9(2)	177.02(8)	136.4(4)	119.0(4)	[a]
$R = CF_3$ $m:n = 1:1$ (**2**)	2.407(1)		2.299(5)			173.2(1)		128.8(3)		[a]
	2.416(1)		2.375(5)			176.7(1)		112.1(3)		
$R = CF_3$ $m:n = 1:2$	2.419(1)	2.236(3)				177.09(7)		132.4(2)		2
$R = Me$ $m:n = 1:2$	2.406(1)			2.451(1)			176.42(4)		123.3(2)	1
$R = Et$ $m:n = 1:2$	2.407(1)			2.449(1)			178.91(3)		119.4(2)	2
$R = Ph$ $m:n = 1:2$	2.405(1)			2.449(2)			177.46(4)		122.3(2)	3

[a] This work.

Table 6. Infrared Data for Dimethyl Sulfoxide Complexes

complex	DMSO bonding mode	S−O (Å)	ν_{SO} (cm^{-1})	ref
DMSO		1.513(5)[a]	1055	17
$Rh_2(O_2CPh)_4(DMSO)_2$	η^1-*S*	1.472(4), 1.482(4)	1094	3
$Rh_2(O_2CEt)_4(DMSO)_2$	η^1-*S*	1.460(4), 1.493(4)	1095	2
$Rh_2(O_2CMe)_4(DMSO)_2$	η^1-*S*	1.477(5)	1086	1
$Rh_2(O_2CCF_3)_4(DMSO)_2$	η^1-*O*	1.525(3)	939, 943	2
$[Rh_2(O_2CCF_3)_4]_7(DMSO)_8$ (**1**)	μ^2-*S,O*	1.47(1), 1.50(1)	1028, 1079	[b]
	η^1-*O*	1.49(1)		
$\{[Rh_2(O_2CCF_3)_4]_3(DMSO)_2\}_\infty$ (**3**)	μ^2-*S,O*	1.465(8)	1099	[b]
$[Rh_2(O_2CCF_3)_4DMSO]_\infty$ (**2**)	μ^2-*O*	1.505(5)	1026	[b]
$Ru_2Cl_4(DMSO)_4(CO)$	μ^2-*S,O*	1.508(5)	1010	14
	η^1-S	1.469(6)	1107, 1141	

[a] In a review (Calligaris, M.; Carugo, O. *Coord. Chem. Rev.* **1996**, *96*, 83), a value of 1.492(1) Å was suggested for "free" DMSO. However, we prefer the value actually found crystallographically for pure DMSO. Our qualitative comparisons remain valid in either case, however. [b] This work.

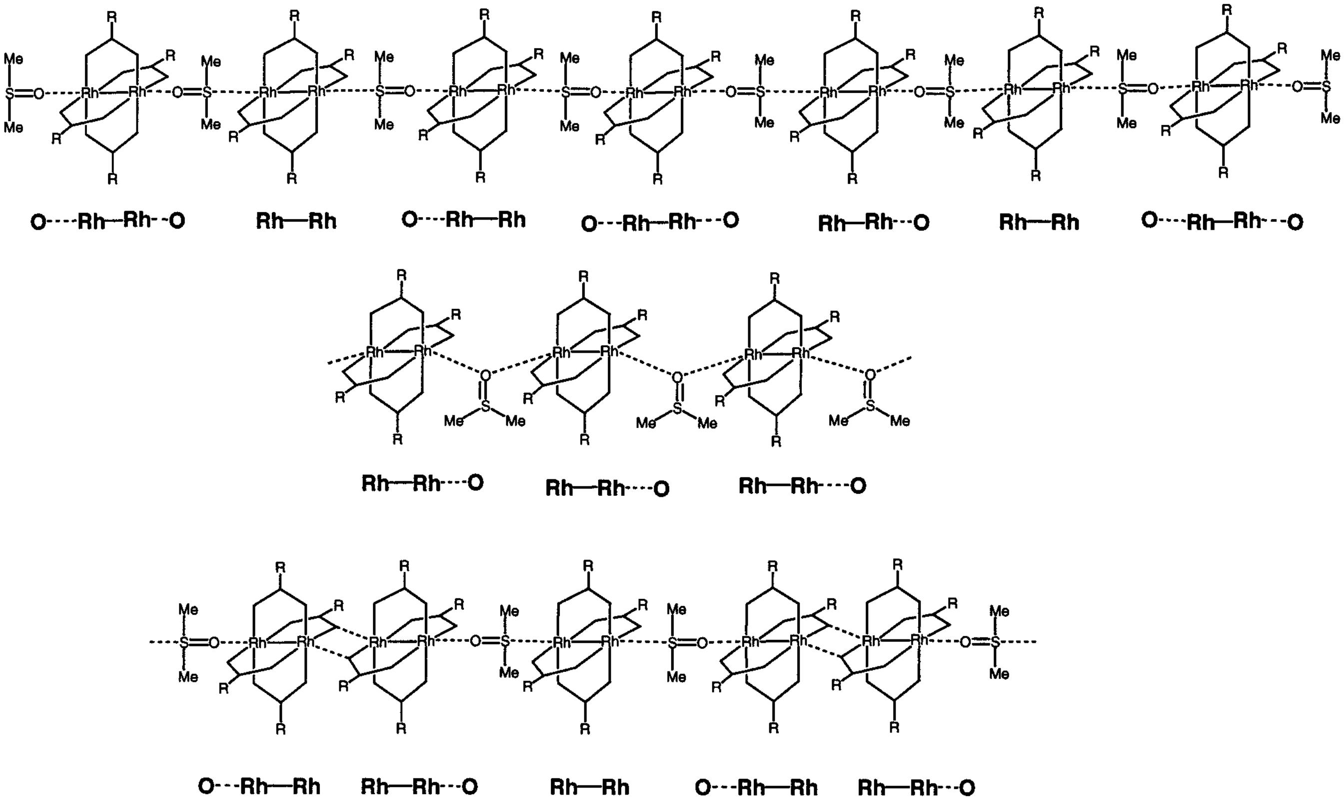
of dirhodium(II) tetra(trifluoroacetate) with dimethyl sulfoxide previously reported[2] was the bis adduct $Rh_2(O_2CCF_3)_4(DMSO)_2$ obtained from solution. The three new compounds $[Rh_2(O_2CCF_3)_4]_m(DMSO)_n$ described here all have compositions with $m:n > 1:2$, namely, 7:8 (**1**), 1:1 (**2**), and 3:2 (**3**). Earlier, using the same approach, we isolated two new compounds of $Rh_2(O_2CCF_3)_4$ with THF,[5b] but both of them had the same 1:1 composition.

We have already mentioned[5] that the most important steps in our solventless experiments occur in the gas phase or upon product deposition, and they depend on the concentrations of different molecules in the vapor. This, in turn, is mainly affected by the composition of the initial mixture and the temperature. In the present work, we clearly observe the influence of the first of these two parameters on the reaction pathway: the higher concentration of the ligand in the starting mixture favors the higher content of the ligand in the resulting compound.

The effect of temperature is more complicated. Obviously, the increase of the temperature at the beginning causes thermal decomposition of $Rh_2(O_2CCF_3)_4(DMSO)_2$ to the monoadduct and DMSO. All molecules of free dimethyl sulfoxide and some of the $Rh_2(O_2CCF_3)_4(DMSO)$ are subliming. A further increase of the heat leads to an increase of the concentration of monoadduct molecules that continue to vaporize until the moment when the temperature is high enough to strip the second DMSO molecule from the dirhodium complex. That induces another sharp growth of the ligand concentration in the vapor. After this point, the only contributing factor is an increasing appearance of ligand-free $Rh_2(O_2CCF_3)_4$ molecules in the reaction medium. That is why a full *P*−*T*−composition diagram of the $Rh_2(O_2CCF_3)_4$−DMSO system would be necessary to understand all of the equilibria that occur in the course of the process.

There is an important question about DMSO coordination to $Rh_2(O_2CCF_3)_4$ through the S atom (compounds **1** and **3**). It is certain that there are only O-bonded molecules in the solid state initially. Does the reorganization occur in the vapor phase, so that we have $[Rh_2 \cdots S]$ blocks there, or does it happen upon

Chart 3



product deposition? As shown in Chart 3, we can construct all of our compounds using only O-bonded blocks [O···Rh_2···O], [Rh_2···O], and “unligated’ [Rh_2] molecules. The chain of **2** (1:1) can obviously be made from the molecules of the monoadduct and compound **3** (3:2) from the monoadduct and $Rh_2(O_2CCF_3)_4$ units, whereas the oligomer **1** (7:8) requires all three types of these “building” blocks. This point of view is in accord with our description of the processes that occur in the $Rh_2(O_2CCF_3)_4$−DMSO system upon heating. Thus, the concept of recombination in the vapor phase to the S-bonded mode, although it cannot be completely ruled out, seems unnecessary.

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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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