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The first fully characterized neutral and cationic rhodium(I)-complexes containing DMSO as the only dative ligand; *S*-, *O*- and bridging *S*,*O*-bidentate binding modes

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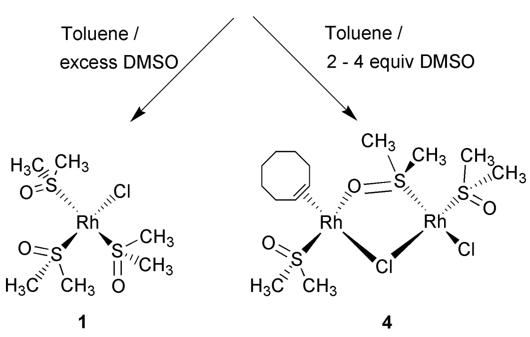
Isolation and characterisation of novel neutral and cationic Rh(I) complexes having only DMSO molecules as dative ligands give complexes showing *S*-, *O*- and bridging *S*,*O*-bidentate binding modes of DMSO.

Although Rh(I) systems show a wide spectrum of reactivity and have found many applications as homogeneous catalysts, fully characterised Rh(I) DMSO complexes, which contain no other dative ligands, are unknown.[1,2] In our effort to elucidate the chemistry of Rh(I)– and Ir(I)–DMSO systems, we have recently reported on the synthesis of Ir(I) DMSO complexes, which showed surprisingly similar reactivity to the corresponding phosphine systems towards water.[3]

We describe here the synthesis of neutral and cationic Rh(I) complexes stabilized by DMSO as the only dative ligand. These complexes were characterized by X-ray crystallography showing both *S*- and *O*-bonding of the DMSO molecule and some of their properties are described. In addition, we have characterized a binuclear rhodium complex which exhibits a rare example of an *S*,*O*-bridging DMSO ligand.

Reaction of a toluene suspension of $[RhCl(COE)_2]_2$ (COE = cyclooctene) with excess DMSO leads to the formation of the neutral complex RhCl(DM*S*O)$_3$ (**1**) as a yellow powder in 90% yield (Scheme 1). The ^{1}H NMR spectrum in CD_2Cl_2 (not shown) consists of a single broad resonance at 3.19 ppm indicating that dissociation of DMSO occurs rapidly on the NMR time scale.

In fact, a low temperature ^{1}H NMR analysis shows the appearance of two separate broad resonances at −30 °C, but even at −90 °C the peaks for the coordinated DMSO molecules are not sharp. The structure of **1** is supported by elemental analysis and orange crystals of **1** suitable for an X-ray analysis were obtained directly from a more dilute reaction mixture.[4]† An ORTEP drawing of complex **1** is shown in Fig. 1.‡ As expected, **1** has a square planar arrangement around the Rh centre with all three DMSO molecules bound *via* the sulfur atom and with Rh–S bond lengths of 2.27 and 2.29 Å (for the DM*S*O molecules *cis* to Cl) and 2.21 Å (for the DM*S*O *trans* to Cl) indicating that *S*-bound DMSO has a higher *trans* influence as compared with chloride. These relatively long metal–sulfur distances might explain the labile nature of the DMSO ligands in solution. Indirect evidence of the structure of **1** was obtained when a C_6D_6 suspension containing **1** was treated with excess pyridine giving a yellow solution of RhCl(C_5H_5N)(DM*S*O)$_2$ (**2**) and one equivalent of free DMSO. Treating **1** with one equiv. of dmbpy (dmbpy = 4,4′-dimethyl-2,2′-bipyridine) gave RhCl(dmbpy)(DM*S*O) (**3**) with concomitant loss of 2 equiv. of DMSO.[7,8] Interestingly, treatment of a dilute toluene solution of $[RhCl(COE)_2]_2$ with 2–4 equiv. of DMSO leads to formation of crystals, although in lower yield (Scheme 1). An X-ray study of the crystals reveals that the compound is the doubly-bridged dimer [(COE)(DM*S*O)Rh(μ-Cl)(μ-DMS*O*)RhCl(DM*S*O)] (**4**).‡ Structurally characterized sulfoxides bridging two transition metals are extremely rare and have been reported for two octahedral diruthenium complexes,[9,10] and for two octahedral rhodium(II) complexes.[11] In **4**, both metal atoms achieve a nearly square planar environment (Fig. 1). The S=O bond



Scheme 1

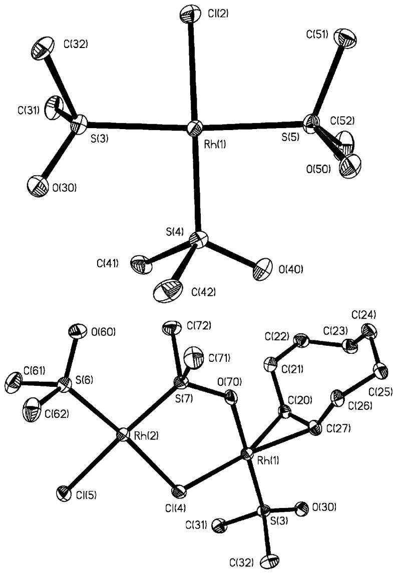


Fig. 1 ORTEP views of complexes **1** (above) and **4** (below). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°) for **1**: Rh(1)–S(4) 2.2095(11), Rh(1)–S(3) 2.2722(11), Rh(1)–S(5) 2.2874(11), Rh(1)–Cl(2) 2.3555(11), S(3)–O(30) 1.485(3), S(4)–O(40) 1.481(3), S(5)–O(50) 1.489(3); S(4)–Rh(1)–S(3) 93.72(4), S(4)–Rh(1)–S(5) 90.22(4), S(3)–Rh(1)–S(5) 169.86(4), S(4)–Rh(1)–Cl(2) 168.63(4), S(3)–Rh(1)–Cl(2) 86.84(4), S(5)–Rh(1)–Cl(2) 91.14(4). For **4**: Rh(1)–O(70) 2.112(2), Rh(1)–C(20) 2.133(3), Rh(1)–C(27) 2.154(3), Rh(1)–S(3) 2.1610(10), Rh(1)–Cl(4) 2.3812(10), Rh(2)–S(7) 2.1584(9), Rh(2)–S(6) 2.1965(10), Rh(2)–Cl(5) 2.3503(9), Rh(2)–Cl(4) 2.3785(10), S(3)–O(30) 1.479(2), S(6)–O(60) 1.480(2), S(7)–O(70) 1.521(2); O(70)–Rh(1)–C(20) 92.48(10), O(70)–Rh(1)–C(27) 91.28(10), C(20)–Rh(1)–C(27) 38.04(11), O(70)–Rh(1)–S(3) 174.08(6), C(20)–Rh(1)–S(3) 91.99(9), C(27)–Rh(1)–S(3) 89.85(9), O(70)–Rh(1)–Cl(4) 86.06(6), C(20)–Rh(1)–Cl(4) 157.34(8), C(27)–Rh(1)–Cl(4) 164.39(8), S(3)–Rh(1)–Cl(4) 91.30(3), S(7)–Rh(2)–S(6) 94.24(4), S(7)–Rh(2)–Cl(5) 176.96(3), S(6)–Rh(2)–Cl(5) 88.81(4), S(7)–Rh(2)–Cl(4) 90.14(4), S(6)–Rh(2)–Cl(4) 174.01(3), Cl(5)–Rh(2)–Cl(4) 86.83(3).

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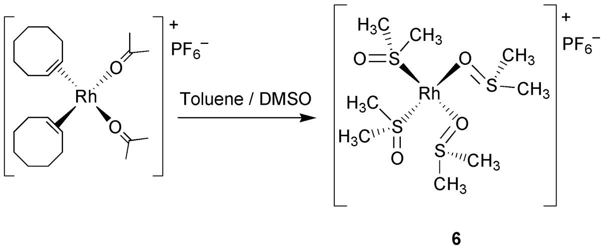
distance of the bridging DMSO is longer than in corresponding *S*-bound complexes and approaches the values found in the *O*-bonded DMSO molecules of [Rh(COD)(DMS*O*)$_2$]BF$_4$ (**5**) and [Rh(DMS*O*)$_4$]PF$_6$ (**6**) (see below) or of *O*-bonded Rh(III) DMSO systems.[12,13] Interestingly, the S(7)–Rh(2) distance of the bridging DMSO is significantly shorter than for the *S*-bonded DMSO molecule *trans* to chloride in **1**. Indeed, in complex **1**, we find generally longer metal–ligand bonds and this fact is in line with the relative stability of the unusual complex **4**.†

The cationic Rh(I) complexes [Rh(diene)DMSO(L)]X (L = phosphine, X = BF$_4^-$, PF$_6^-$)[14,15] were believed to have *O*-bonded DMSO based on IR spectroscopy data and their lability in solution {indeed, [Rh(COD)(DMS*O*)$_2$]BF$_4$ (**5**) was crystallized by us and the X-ray data show the expected structure,†‡}. We prepared the first cationic, all DMSO stabilized Rh(I) complex by treating a toluene slurry of [Rh(COE)$_2$(O=CMe$_2$)$_2$]PF$_6$ with excess DMSO (Scheme 2).[16] Precipitation in diethyl ether gave the complex [Rh(DM*S*O)$_2$(DMS*O*)$_2$]PF$_6$ (**6**) in 95% yield as a yellow powder.† The ^{1}H NMR of **6** at −20 °C in dichloromethane shows two sharp peaks at 3.11 ppm (*S*-bonded) and at 2.71 ppm (*O*-bonded) whereas the peak at 2.71 ppm is a broad singlet at room temperature.



6

Scheme 2

Interestingly, upon addition of only 2 equiv. of DMSO to a CD$_3$NO$_2$ solution of [Rh(COE)$_2$(O=CMe$_2$)$_2$]PF$_6$, displacement of the COE molecules took place, probably forming [Rh(DM*S*O)$_2$(O=CMe$_2$)$_2$]PF$_6$, without displacement of the acetone molecules. Treatment of complex **6** with 1 equiv. of 4,4′-dimethyl-2,2′-bipyridine resulted in selective substitution of the *O*-bonded DMSO molecules, leading to the isolation of [Rh(dmbpy)(DM*S*O)$_2$]PF$_6$ (**7**).[8] An X-ray crystallographic study of complex **6** confirmed that two DMSO ligands are bound *via* the sulfur atom and the other two DMSO molecules *via* the oxygen atom (Fig. 2),‡ as opposed to **1**, in which all the DMSO ligands are *S*-bound. As expected, the *O*-bonding mode is preferred with the harder, cationic metal center. The *S*-bonded molecules exhibit significantly shorter Rh–S bond distances compared to the neutral complex **1**. This can be explained by the more favourable arrangement with the *O*-bound DMSO molecules *trans* to them and is also reflected by the sharp peaks observed in ^{1}H NMR of this complex. Indeed, the *O*-bound DMSO is expected to have a significantly weaker *trans* influence as compared to the *S*-bound DMSO. The Rh–O distances fall in the range of the ones seen for **5**.

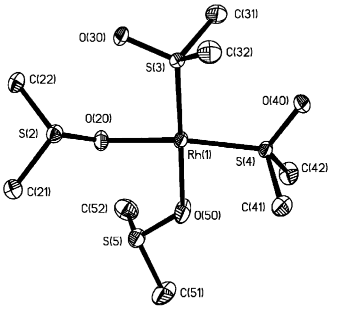


Fig. 2 ORTEP drawing of complex **6**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): Rh(1)–O(50) 2.099(3), Rh(1)–O(20) 2.112(3), Rh(1)–S(3) 2.1627(9), Rh(1)–S(4) 2.1643(10), S(2)–O(20) 1.539(3), S(4)–O(40) 1.486(3), S(5)–O(50) 1.530(3); O(50)–Rh(1)–O(20) 85.39(11), O(50)–Rh(1)–S(3) 178.90(10), O(20)–Rh(1)–S(3) 93.57(8), O(50)–Rh(1)–S(4) 86.14(9), O(20)–Rh(1)–S(4) 171.39(8), S(3)–Rh(1)–S(4) 94.89(4).

In summary, we have reported here the isolation and characterization of neutral and cationic Rh(I) complexes having only DMSO molecules as dative ligands. The X-ray crystal structure of the neutral derivative RhCl(DM*S*O)$_3$ showed that all DMSO molecules were *S*-bonded to the metal whereas with the harder metal center in the cationic [Rh(DM*S*O)$_2$(DMS*O*)$_2$]PF$_6$ both *S*- and *O*-bonding are involved. In addition, the first example of a square planar bimetallic complex with a bidentate *S*,*O*-bridging DMSO ligand was characterised. We are currently investigating the chemistry and the catalytic potential of these compounds.

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Notes and references

† *Selected data*: for **1**: ^{1}H NMR (CD$_2$Cl$_2$, 293 K): δ 3.19 (br, 18 H); IR (KBr): 1097 cm^{-1} (s, *S*=O); Anal. calc. for C$_6$H$_{18}$ClO$_3$RhS$_3$: C 19.33; H 4.87. Found: C 19.24; H 4.81%.

For **2**: ^{1}H NMR (C$_6$D$_6$): δ 3.01 (s, 6 H), 3.03 (s, 6 H), 6.33 (t, 6.5 Hz, 2 H), 6.60 (t, 7.7 Hz, 1 H), 8.78 (d, 4.9 Hz, 2 H). Anal. calc. for C$_9$H$_{17}$ClNO$_2$RhS$_2$: C 28.92; H 4.59; N 3.75. Found: C 28.78; H 4.48; N 3.87%.

For **4**: ^{1}H NMR (CD$_2$Cl$_2$, 293 K): δ 1.56 (m, br, 8 H), 1.96, 2.31 (m, br, 2 H each), 3.14–3.30 (several s, br, 18 H), 3.82 (m, 2 H).

For **5**: ^{1}H NMR (CD$_2$Cl$_2$): δ 1.71 (m, 4 H), 2.48 (m, 4 H), 2.76 (s, 12 H), 3.94 (s, br, 4 H); Anal. calc. for C$_{12}$H$_{24}$BF$_4$O$_2$RhS$_2$: C 31.74; H 5.33. Found: C 31.62; H 5.25%.

For **6**: ^{1}H NMR (CD$_2$Cl$_2$, 253 K): δ 2.71 (s, 6 H), 3.11 (s, 6 H); IR (KBr): 929 (s, S=*O*), 1101 cm^{-1} (s, *S*=O); Anal. calc. for C$_8$H$_{24}$F$_6$O$_4$PRhS$_4$: C 17.15; H 4.32. Found: C 16.89; H 4.31%.

‡ Structures **1**, **4**, **5** and **6** were solved by direct methods with SHELXS-97[5] and refined by full-matrix, least-squares based on F^2 with SHELXL-97.[6]

CCDC reference numbers 177298–177301. See http://www.rsc.org/suppdata/cc/b2/b200321j/ for crystallographic data in CIF or other electronic format.

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