Inorganica Chimica Acta, 46 (1980) 137–139
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Complexes of Osmium(II) with Dimethylsulfoxide

M. M. TAQUI KHAN, MEHREEN AHMED and ARUN KUMAR
Department of Chemistry, Osmania University, Hyderabad 7, India

Received March 19, 1980

A σ-bonded DMSO complex of Os(II) of the composition $\{Os(DMSO)_4[\sigma\text{-}CH_2S(O)CH_3]_2\}\cdot 2DMSO$ *(1) is reported. The complex has been characterised by elemental analysis, conductivity, dipole moment, infrared spectrum,* ^1H *and* ^{13}C *NMR spectra. In the complex two* $CH_2S(O)CH_3$ *groups are bonded to Os(II) in* trans *position, the equatorial positions being occupied by S-bonded DMSO ligands. The complex reacts with DPPE, 1,2-bis(diphenylphosphino)ethane, to form* $[Os(DMSO)_2(\sigma\text{-}CH_2S(O)CH_3)_2(DPPE)]$ *(2). Reaction with triphenylphosphine in the presence of HCl resulted in the formation of the cationic complex* $[Os(PPh_3)_6]Cl_2$ *(3). Reaction with triphenylarsine in the presence of HCl resulted in the formation of* $[Os(DMSO)_3(AsPh_3)_2Cl]Cl$ *(4). In cationic complexes (3) and (4) the bonded DMSO is completely replaced by phosphine or arsine ligands.*

Introduction

A large number of complexes of transition metal ions with dimethylsulphoxide [1–3] is known but no complex has so far been reported with osmium. The ruthenium complex $[Ru(NH_3)_5(DMSO)]X$ was thoroughly investigated by Senoff *et al.* [2]. Rempel *et al.* [4] obtained $RuCl_2(DMSO)_4$ by the hydrogenation of ruthenium trichloride in dimethylsulphoxide. Wilkinson and coworkers [5] prepared the above complex by refluxing ruthenium trichloride in DMSO. The X-ray structure of $RuCl_2(DMSO)_4$ was reported by Mercer and Trotter [6]. An attempt to prepare the osmium analogue of $RuCl_2(DMSO)_4$ resulted in a novel complex of osmium(II) with two dimethylsulphoxide σ(C)-bonded to the metal. The complex has been characterised and its substitution reactions with mono and bidentate phosphines and arsines have been carried out.

Experimental

Hydrated osmium trichloride was purchased from Alfa Inorganics. The ligands triphenylphosphine and 1,2-bis(diphenylphosphino)ethane (DPPE) were obtained from Ventron Corporation, U.S.A. Triphenylarsine was obtained from Maybridge Chemicals Co., U.K. Microanalysis of the complexes were performed by C.S.I.R.O., Australia. The infrared spectra were recorded on a Perkin Elmer 257 and the far IR on a Beckman IR-12 spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded with a Varian A-60-D and Varian XL-100 spectrophotometers, respectively using TMS as the internal standard.

Preparation of $\{Os(DMSO)_4[\sigma\text{-}CH_2S(O)CH_3]_2\}\cdot 2DMSO$ *(1)*

A solution of $OsCl_3\cdot 3H_2O$ (0.53 g, 1.5 mmol) or $(NH_4)_2OsCl_6$ (0.66 g, 1.5 mmol) in 40 to 50 ml of DMSO was refluxed for 40–50 h with a continuous bubbling of hydrogen. The temperature was maintained at 50 °C till the colour of the solution changed to chocolate-brown. The solution was concentrated to a small volume under vacuum and cooled. The white needle shaped crystals formed were recrystallized from methanol-ether mixture (MP = 105 °C).

Substitution Reactions

Refluxing 1 mmol of (1) with 2 mmol of DPPE in ethanol for 12 h followed by precipitation with petroleum ether, resulted in a light yellow coloured complex of the composition $\{Os(DMSO)_2(DPPE)[\sigma\text{-}CH_2S(O)CH_3]_2\}$ (2). Reaction of (1) with a large excess of $AsPh_3$ and PPh_3 in 3 *M* ethanolic HCl for six to ten hours resulted in the total displacement of the two σ-carbon-bonded DMSO ligands. The acid solutions were concentrated and poured into diethyl ether. Concentration of the etherial layer yielded complexes (3) and (4), respectively.

Results and Discussion

Conductivity measurements of (1) in DMA show that it is a non-electrolyte. Elemental analysis (Table I) indicates that there is no chloride ion in the complex. In the complexes of DMSO reported so far, DMSO is bound to a metal either through oxygen or through sulfur [1, 2, 5, 7]. It is generally observed

TABLE I. Analytical Data for the Complexes of Osmium with Dimethylsulfoxide.

Complex	Analysis*			
	Carbon %	Hydrogen %	Sulfur %	Chlorine %
1 $[Os(DMSO)_4[\sigma\text{-}CH_2S(O)CH_3]_2]$ 2·DMSO	25.21	6.06	32.10	0
	(25.62)	(5.66)	(31.49)	(0)
2 $[Os(DMSO)_2(\sigma\text{-}CH_2S(O)CH_3)_2(DPPE)]$	45.22	5.50	15.50	0
	(45.40)	(5.10)	(14.20)	(0)
3 $[Os(PPh_3)_6]Cl_2$	70.54	5.30	0	3.20
	(70.66)	(4.90)	(0)	(3.80)
4 $[Os(DMSO)_3(AsPh_3)_2Cl]Cl$	45.54	4.50	9.20	7.90
	(45.50)	(4.00)	(8.67)	(6.60)

*Calculated % in parenthesis.

TABLE II. Infrared Spectra of Complexes of Osmium with Dimethylsulfoxide

Complex	Metal–Ligand and other Ligand Frequencies[a]
1 $[Os(DMSO)_4(\sigma\text{-}CH_2S(O)CH_3)_2]$·2DMSO	460(s), 500(s), 690(sh), 710(w), 750(s), 920(m), 1110–1120(br), 1290(br), 1320(m), 1430(s), 2250(w), 2300(vw)
2 $[Os(DMSO)_2(\sigma\text{-}CH_2S(O)CH_3)_2(DPPE)]$	485(m), 510(s), 540(s), 555(sh), 680(s), 715(s), 730(sw), 750(m), 920(s), 980(m), 1010(m), 1180(s), 1100–1120(s), 1290(br), 1320(m), 1425(s)
3 $[Os(PPh_3)_6]Cl_2$	460, 500(s), 540(s), 680(s), 740(s), 760(m), 850–870 (w, br), 930(s), 990(s), 975(m)
4 $[Os(DMSO)_3(AsPh_3)_2Cl]Cl$	350(s), 480(s), 690(s), 720(s), 960(s), 930(vs), 990(m), 1020(m), 1060(w), 1080(s), 1110(br), 1190(s), 1290–1310(br), 1330(m), 1400(w), 1430(s)

[a] s = strong, m = medium, br = broad, sh = shoulder.

that in the complexes where DMSO is bonded through sulfur, the S–O stretching frequency is located at higher frequencies as compared to the free ligand due to an increase in the S–O bond order. In the oxygen bonded complexes of DMSO however the S–O stretch is observed at a lower frequency than in the ligand. In the IR spectra of (1) a broad band appeared at 1110–1120 cm^{-1} which is assigned to the $\nu(S{=}O)$ of the sulfur bonded DMSO. The osmium–sulfur and osmium–carbon stretching frequencies are observed at 460 and 500 cm^{-1}, respectively. There were no peaks in the region 1800–2200 cm^{-1} (Table II) indicating the absence of metal–hydride vibration. The PMR spectrum in $CDCl_3$ solution indicates two resonance singlets at $\tau = 2.6$ and $\tau = 6.9$ with intensity ratio 1:10. The former resonance is assigned to the $-CH_2$ protons which are shifted downfield from the normal methylene proton resonance due to the high deshielding of these protons. The peak at 6.9 τ is assigned to the methyl protons of the DMSO ligand. There was no separate peak for the free DMSO, but the intensity of the peak at 6.9 τ shows that it overlaps with the resonance of the coordinated DMSO groups. There was no indication of any hydride resonance in the upfield region of TMS. The ^{13}C NMR of (1) in $CDCl_3$ shows the negatively charged carbon atom of the $-CH_2$ group clearly different from the other carbons of the DMSO as a singlet in the downfield region at δ 204 ppm. The ^{13}C NMR of a number of carbene complexes with transition metals have been studied by Clark *et al.* [7]. The carbene carbon atoms show bands in the region δ = 246–252 ppm. The methyl carbon atoms of the DMSO ligands and the free DMSO are observed in the upfield region at δ 42 ppm. The integration of the peaks show that their ratio corresponds to the calculated value. The peaks in the region δ = 76–78 ppm are due to $CDCl_3$. The dipole moment of (1) in benzene solutions at 30 °C is 1.56 Debye units indicating that the two methylsulfonyl methylide ligands are *trans* to each other. Collins and Roper [8] have studied the complex $[OsCl(CO)(PPh_3)_2(\sigma\text{-}CH_2\text{–}SMe)]^+$ with a dimethylsulfonium methylide group coordinated to osmium.

To confirm the nature of binding of DMSO in (1), substitution reactions of the complex were carried out with phosphine and arsine ligands. Reaction of (1) with DPPE resulted in a yellow complex [2] which retains the σ-bonded DMSO groups. The IR spectrum of (2) shows a peak at 485 cm^{-1} assigned to σ-bonded DMSO. The band at 1100–1120 cm^{-1} is assigned to the sulfur-bonded DMSO groups. The ^1H NMR peak at 2.68 τ is assigned to the phenyl protons coupled together with the methylide protons of the two negatively charged DMSO ligands. The multiplet at 7.0 τ may be due to the four methylene protons of the DPPE ligand coupled together with the methyl protons of the four sulfur-bonded DMSO groups. The integration of these peaks agrees with the values calculated for the formulated complex $[Os(DMSO)_2(DPPE)(\sigma\text{-}CH_2S(O)CH_3)_2]$.

Substitution reactions on (1) in the presence of HCl however resulted in the displacement of all the DMSO groups by the monodentate phosphine and the σ(C)-bonded and one S-bonded DMSO groups by arsine ligands to form complexes (3) and (4), respectively. In the cationic complex (3) all the six PPh_3 ligands are coordinated to the metal. Complex (3) is novel since it cannot be prepared by any other method.

Conductivity measurements of (3) in DMA gave a conductance of 132 ohm^{-1} cm^2 eq^{-1} which is in the range expected for 2:1 electrolyte [9]. This is further supported by the absence of the ν(M–Cl) frequency in the IR spectrum of the complex in the region of metal–halogen stretching frequency. The NMR spectrum of (3) shows a single peak at 2.6 τ due to the phenyl protons. There was no band in the region 6.0 to 8.0 τ expected for the methyl groups of the DMSO ligands, indicating a complete displacement of DMSO.

Reaction of (1) with triphenylarsine resulted in the formation of a 1:1 electrolyte (4) with a conductance of 48.7 ohm^{-1} cm^2 eq^{-1} in DMA [9]. The IR spectrum of (4) shows the Os–Cl stretch at 350 cm^{-1}. The bands due to the coordinated DMSO ligands are observed at 480, 1080, 1110 and 1430 cm^{-1}. The 480 cm^{-1} band cannot be unequivocally assigned to ν(M–As) or ν(M–S) as both vibrations overlap in this region. The ^1H NMR spectrum of the complex gives the phenyl proton resonance as two peaks at 2.4 τ and 2.65 τ of almost equal intensities. The methyl resonance is observed at 7.0 τ. The intensity ratio of these peaks is in close agreement with the calculated ratio of protons. Complex (1) failed to react wlth PPh_3 or $AsPh_3$ in absence of HCl.

References

1 F. A. Cotton, R. Francis and Horrock Jr., *J. Phys. Chem., 64,* 1534 (1960).

2 C. V. Senoff, E. Maslowsky Jr. and R. G. Goel, *Can. J. Chem. 49,* 3585 (1971).

3 J. Selbin, W. E. Bull and L. H. Holmes Jr., *J. Inorg. Nucl. Chem., 16,* 219 (1961).

4 B. R. James, E. Ochiai and G. I. Rempel, *Inorg. Nucl. Chem. Lett., 7,* 781 (1971).

5 I. P. Evans, A. Spencer and G. Wilkinson, *J. Chem. Soc. (D),* 204 (1973).

6 A. Mercer and James Trotter, *J. Chem. Soc. (D),* 2480 (1975).

7 H. C. Clark, J. E. H. Ward and K. Yasfuku, *Can. J. Chem., 53,* 186 (1975).

8 T. J. Collins and W. R. Roper, *Chem. Comm.,* 901 (1977).

9 W. J. Geary, *Coord. Chem. Rev., 7,* 81 (1971).