COMPLEXES OF OSMIUM HALIDES WITH MONODENTATE AND BIDENTATE LIGANDS

M. M. TAQUI KHAN, S. SHAREEF AHAMED and ROBERT A. LEVENSON[†] Department of Chemistry, Nizam College, Hyderabad-500001, India

(Received 19 June 1975)

Abstract—Complexes of osmium halides with donor ligands L (L = PPh₃, AsPh₃, SbPh₃, PMePh₂, C₂H₄(AsPh₂)₂, PPr₂ⁿ Ph, CH₂(AsPh₂)₂) have been prepared. The IR and NMR spectra of complexes of the type *trans*-[OsCl₄L₂], *fac*-[OsX₃L₃] and *trans*-[OsX₂L₄] are recorded and discussed. For the *trans* complexes the halogen sensitive modes occur near those of the related [OsX₄]²⁻ species. Tentative assignments for ν (Os-Y) (Y = P, As, Sb) are discussed on the basis of the experimental results. Raman and ESR spectra of selected complexes have been recorded and are discussed. NMR data indicates the presence of monodentate diarsine ligands in *trans*-(OsCl₄(CH₂(AsPh₂)₂)₂)·C₂H₅OH.

INTRODUCTION

PLATINUM group metal ions have the ability to form stable complexes with donor groups containing elements of group V many of which are very good catalysts for the homogeneous hydrogenation and epoxidation of alkenes, and for other reactions such as hydroformylation and carbonylation[1]. Osmium complexes have been less extensively studied than those of other platinum metals and in this paper the preparation of a number of previously unreported complexes with mono and bidentate ligands is described and their structures are discussed.

EXPERIMENTAL

All preparations were carried out in an atmosphere of dry nitrogen using Schlenk tube techniques[2]. IR spectra were recorded in Nujol mulls on polythene plates using a Beckmann IR-12 spectrophotometer. The solid state Raman spectra were recorded on a Cary 82 Raman spectrometer equipped with a Coherent Radiation Model 52B Krypton ion laser using a defocussed beam of approx. 150 mw at 647.1 nm. NMR spectra were recorded with a Varian A-60 spectrometer. ESR spectra were taken on a Varian E-4 ESR spectrometer. Conductivity measurements in dimethylformamide at room temperature were made using a Toshniwal conductivity bridge. Microanalyses were performed at the Microanalytical Service Centre, CSIRO, Australia. Ammonium hexachlorosmate was purchased from Johnson Matthey, London. All ligands were obtained commercially and recrystallized from suitable solvents before use. Only representative preparations of the several types of compounds are given.

trans-Tetrachlorobis (triphenylphosphine) osmium (IV). A solution of 0.2 g (0.50 mmol) of $(NH_4)_2(OsCl_6)$ in 50 ml of concentrated hydrochloric acid and methanol (1:2) was refluxed for 30 min. To the hot solution was added a solution of triphenylphosphine (0.4 g, 1.5 mmol) in methanol (10 ml) and refluxing was continued for 2–3 hr. A yellow solid appeared which was filtered and washed with hot methanol and ether. Similarly prepared were trans-OsCl_4(PMePh_2)_2 (washed with methanol).

trans-Tetrachlorobis (triphenylarsine) osmium (IV). A solution of 0.2 g (0.50 mmol) of $(NH_4)_2[OsCl_6]$ in 40 ml of concentrated hydrochloric acid and 2-methoxyethanol (1:2) mixture was refluxed for 30 min. To the hot solution was added a solution of triphenylarsine (0.5 g, 1.75 mmol) in 15 ml of 2-methoxyethanol and refluxing was continued for 2-3 hr when the color had changed from yellow to orange-red. The volume was reduced by 0.5 and the remaining solution was stored in a refrigerator overnight. After addition of 10 ml of methanol the solution was heated, and on cooling a pale yellow precipitate appeared. The solid was transferred to a Schlenk tube and washed with acetone and methanol.

mer-Trichlorotris (triphenylstibine) osmium (III). (NH₄)₂[OsCl₆] (0.2 g, 0.50 mmol) in 50 ml of a 1:5 mixture of water and 2-methoxyethanol was refluxed for 30 min. To the above solution was added a solution of triphenylstibine (1.2 g, 3.4 mmol) in 15 ml of 2-methoxyethanol. After 3–4 hr of additional reflux a solid appeared which was filtered and washed with acetone.

trans-Tetrachlorobis(triphenylstibine)osmium(IV). This complex was prepared[3] by the oxidation of trichlorotris(triphenylstibine)osmium. OsCl₃(SbPh₃)₃ (0.2 g, 0.1 mmol) in 18 ml of carbontetrachloride was refluxed for 72 hr. The solvent was evaporated, and the solid obtained was recrystallized from methanol and acetone.

fac-Trichlorotris(triphenylphosphine)osmium(III). A solution of 0.2 g (0.50 mmol) of $(NH_4)_2[OsCl_6]$ in 30 ml of 2methoxyethanol and 15 ml of concentrated hydrochloric acid mixture was refluxed for 30 min. To the hot solution was added a solution of triphenylphosphine (0.5 g, 1.8 mmol) in 5 ml of 2-methoxyethanol and the refluxing was continued for 3-4 hr. The volume was reduced by 1.5 and the remaining solution was stored in a refrigerator overnight. After addition of 10 ml of methanol the solution was heated, and on cooling a yellow solid appeared which was washed with methanol, ether and finally dried.

fac-Tribromotris(triphenylstibine)osmium(III). A solution of 0.5 g (1.4 mmol) of triphenylstibine in 10 ml of methanol was refluxed for 10 min. $(NH_4)_2[OSBr_3]$ (0.2 g, 0.5 mmol) was dissolved in a 1:2 mixture of water and methanol and added to the above solution. After 1 hr of reflux, a solid appeared, which was washed with ether and dried. Similarly prepared was fac-OsBr_3(PPh_3), (recrystallized from methanol).

trans-Dichlorotetrakis (triphenylstibine) osmium (II). A solution of 0.2 g (0.50 mmol) of $(NH_4)_2[OsCl_6]$ in 40 ml of ethyleneglycol was refluxed for 20 min. To the hot solution was added a solution of triphenylstibine (1.2 g, 3.4 mmol) in 15 ml of acetone. The above solution was refluxed for 3-4 hr and the precipitate that appeared was filtered and washed with methanol and ether.

trans-Dibromotetrakis (triphenylstibine) osmium (II). To 1.0 g (3 mmol) of triphenylstibine in 20 ml of 2-methoxyethanol was added 0.2 g (0.3 mmol) of (NH₄)₂[OsBr₆] in 25 ml of 2-methoxyethanol and 10 ml of water. After 1 hr of reflux the dark-red solution changed to a colorless liquid. After an additional 0.5 hr of reflux a grey solid appeared which was filtered and washed with methanol and ether. Similarly prepared were trans-OsBr₂(PPh₃)₄ (washed with ether) and trans-OsBr₂(AsPh₃)₄ (washed with acetone and methanol).

[†]Texas A & M University, College Station, TX 77843, U.S.A.

trans-Dichlorobis-1,2bis(diphenylarsino)ethane osmium (II). A solution of 0.15 g (0.34 mmol) of $(NH_4)_2[OsCl_6]$ in 15 ml of water and 10 ml of ethanol was added to 1,2bis(diphenylarsino)ethane (0.17 g, 0.2 mmol) in 25 ml of ethanol. After 0.5 hr of reflux the yellow solution changed to orange-red. The solution was refluxed for an additional 1.5 hr and the precipitate obtained was washed with hot ethanol, ether and dried. Similarly prepared was trans-OsCl₄(CH₂(AsPh₂)₂)₂C₂H₅OH.

Triiodobis (1,2-bis (diphenylarsino)methane)osmium (III).(NH₄)₂[OsBr₆] (0·2 g, 0·3 mmol), potassium iodide (0·52 g, 3·4 mmol) and 1,2bis(diphenylarsino)methane (0·26 g, 0·3 mmol) were refluxed in 60 ml of a 1:5 mixture of water and ethanol for 1·5 hr. A dark blue solid was formed which was filtered, washed with hot ethanol, and dried.

Dithiocyanatotris (1,2-bis(diphenylarsino)methane) osmium. $(NH_4)_2[OsBr_6]$ (0.2 g, 0.4 mmol), ammoniumthiocyanate (0.85 g, 9 mmol) and diarsine (0.27 g, 0.3 mmol) were refluxed in 60 ml of a 1:5 water-ethanol mixture for 1.5 hr. The precipitate obtained was washed with hot ethanol and dried.

RESULTS AND DISCUSSION

The physical properties and analytical data are presented in Table 1.

IR and Raman spectra

Complexes of the type[OsCl₄L₂]. The IR spectra of the complexes (Table 2) favour a *trans*-geometry. Raman data for 1, 2 and 4 are presented in Table 3. A *trans*-configuration having one ν (M-X) mode (e_u) (IR

active) and two ν (M-X) modes $(a_{1g} + b_{1g})$ (Raman active) should be readily distinguishable from a cis C_{2v} molecule with 4 IR and Raman active vibrations $(2a_1 + b_1 + b_2)$. From the number of bands observed (Tables 2 and 3), it appears that [OsCl₄L₂](L = PPh₃, SbPh₃, AsPh₃, PPr₂ⁿ Ph, PMePh₂, CH₂(AsPh₂)₂) complexes have exclusively a *trans*-configuration.

The IR spectra (600-200 cm⁻¹) of $[OsCl_4L_2]$ are dominated by the occurrence of a single intense absorption *ca*. 310 cm⁻¹. This may be assigned to the IR active $e_{\mu}\nu(Os-Cl)$ mode of a *trans*-octahedral $[OsCl_4L_2]$ moiety. These assignments are in excellent agreement with those for spectra previously reported [4-6].

An intense Raman line, noncoincident with the strong IR band and at higher frequency accompanied by a weaker line at *ca*. 30 cm⁻¹ to lower frequency appeared in 1, 2 and 4. The strong Raman line may be assigned to the $a_{1g} \nu$ (Os-Cl) mode and its weaker counterpart to the b_{1g} mode of a *trans* D_{4h} skeleton. Similar absorptions have been observed for the complexes *trans*-[PtX₄(PEt₃)₂] (X = Cl, Br)[7].

The presence of a single sharp intense peak in the NMR spectra of 1, 2 and 3 at $3 \cdot 1\tau$, $2 \cdot 8\tau$, $3 \cdot 0\tau$ respectively is consistent with the *trans* geometry inferred from the IR and Raman spectra. The NMR spectrum of 4 shows a multiplet of protons centred at $2 \cdot 5\tau$ corresponding to the aromatic protons. The resonance corresponding to the methyl protons was observed as a triplet (1:2:1) centred

Table 1. Physical properties of osmium complexes

		Analyses, % [†] M. P.				
No.	Color	С	H	halide	P	(decomposed)
1 trans-OsCl4(PPh3)2	Yellow	50.9	3.6	17.0	-	218-220
		(51.7)	(3.7)	(19•1)		
2 trans-OsCl ₄ (AsPh ₃) ₂	Pale-	45.7	3.2	14.5		277280
	yellow	(45·7)	(3.2)	(15.0)		
3 trans-OsCl ₄ (SbPh ₃) ₂	Black	41.8	2.9	—		280-282
		(41.6)	(2.8)			
4 trans-OsCl ₄ (PMePh ₂) ₂	Yellow	42.3	3.6	_	8.0	198-200
		(42.6)	(3.5)		(8·4)	
\$5 trans-OsCl ₄ (PPr ₂ ⁿ Ph) ₂	Yellow	39.6	5.2	_	8.8	192–195
		(39•9)	(5.2)		(8.6)	
\$6 mer-OsCl ₃ (SbPh ₃) ₃	Green	48 ∙0	3.5	7.6		238-240
		(47.8)	(3.3)	(7.8)		
7 fac -OsCl ₃ (PPh ₃) ₃	Yellow	59.7	3.8	—	8.1	259-260
		(59-98)	(4.14)		(8.76)	
\$\$ fac-OsBr ₃ (SbPh ₃) ₃	Black	43.2	3.1			263-265
		(43.5)	(3.0)			
9 fac-OsBr ₃ (PPh ₃) ₃	Black	53.1	3.7	—		270-273
		(53-3)	(3.7)			
10 trans-OsCl ₂ (SbPh ₃) ₄	Light-	51.4	3.7	4.4		228-230
	grey	(51.6)	(3.6)	(4.2)		
11 trans-OsBr ₂ (SbPh ₃) ₄	Grey	48.8	3.5	—	_	279-282
		(49.1)	(3.4)			
12 trans-OsBr ₂ (PPh ₃) ₄	Light-	61.9	4∙4			202-205
	grey	(61.8)	(4·4)			
13 trans-OsBr ₂ (AsPh ₃) ₄	White	55.1	3.9			220-223
		(54.9)	(3.8)			
14 trans-OsCl ₂ (C ₂ H ₄ (AsPh ₂) ₂) ₂	Orange	50.8	4 ·1	5.9		208-210
		(50.6)	(3·9)	(5.8)		
15 trans-(OsCl ₄ (CH ₂ -	Brown	47.0	3.7	10.6	<u> </u>	182-185
$(AsPh_2)_2)_2)C_2H_5OH$		(47.2)	(3.8)	(10.7)		
16 $OsI_3(CH_2(AsPh_2)_2)_2$	Dark-	40.8	3.0	18.7		210-212
	blue	(40-6)	(3.0)	(18.5)		
17 $Os(SCN)_2(CH_2(AsPh_2)_2)_3$	Dark-	53.9	3.7		_	100-102
	pink	(53-7)	(3.8)			

†Required values in parentheses.

‡Reported previously but prepared by a different route[3].

 $\nu(Os-Y)$ $\nu(Os-X)$ (Y = P, As, Sb)Other bands (X = Cl, Br)No. 308(s) 495(s) 540(w), 510(sh), 430(s), 400(m), 250(w) 1 475(s) 2 330(s) 555(m) 3 310(sh) 455(s) 287(w), 265(w) 462(s), 433(m), 393(m), 345(w) 4 311(s, br) 502(s, br) 5 485(s) 495(sh), 408(s) 310(s, br) 6 307(s), 275(s, br) 465(sh) 7 304(s, br) 510(s, br) 500(sh.), 455(w) 455(s), 420(m), 398(w), 375(m), 275(s) 8 227(s) 460(sh) 502(s) 540(sh), 425(m), 400(w), 375(w) 9 230(s) 10 304(m) 465(sh) 550(m), 455(s), 275(s) 455(s), 425(m), 400(m), 375(w), 275(s) 225(m) 465(sh) 11 12 231(m) 513(s) 550(m), 458(m), 428(m), 415(m), 280(w) 485(sh), 425(w), 400(w), 325(w) 475(s) 13 230(m) 590(w), 540(w), 425(m), 395(m), 240(sh), 14 313(s) 465(s) 225(m) 575(m), 418(w), 395(m), 375(w), 325(w), 15 323(s) 465(s) 275(sh), 240(m) 570(s), 440(sh), 420(w), 400(m), 375(w), 16 470(s) 325(m), 280(w), 225(s).

Table 2. Far-IR spectra (600-200 cm⁻¹) of complexes

m, medium; s, strong; w, weak; br, broad; sh, shoulder.

Table	3. Rama	n spectra	of
	compl	exes	

Complex	ν (Os–Cl)
1	340(s), 310(w)
2	352(s), 325(s)
4	340(s), 309(w)

at 7.9τ . The methyl triplet is obtained because of the virtual coupling of the two *trans* phosphorous atoms [17].

Complexes of the type $[OsX_3L_3]$. Such complexes can exist as fac- and mer-isomers. Three IR active $(2_{a1} + b_1)$ metal-halogen stretching frequencies are expected for the mer-isomer, but only two for the fac-isomer $(a_1 + e)$. In the IR spectrum of 6 two bands were observed at 275 cm⁻¹ (s, br) and 307 cm⁻¹(m) which may be assigned to the ν (Os-Cl) frequencies of a mer-configuration. It is assumed that the third band expected for a mer-isomer is obscured by the broad 275 cm⁻¹ band. In the IR spectrum of 7, 8 and 9 only one osmium-halogen stretching frequency at 304(s, br), 227(s), and 230(s) cm⁻¹, respectively was observed compared to the 2 expected for a fac-isomer. The other band may be below 200 cm⁻¹ which was beyond the range of the instrument used.

In the NMR spectrum of compound 6 single peaks were observed for the phenyl protons at $2 \cdot 3\tau$ and $3 \cdot 15\tau$ in the ratio of 2:1. This is consistent with a *mer*-configuration. Multiplet peaks centred at $2 \cdot 25\tau$, $2 \cdot 8\tau$ and $3 \cdot 1\tau$ were observed for 7, 8 and 9 respectively consistent with a *fac*-configuration. Though the coordinated L(SbPh₃, PPh₃) groups are equivalent in the facial configuration, the multiplets are obtained because of the lack of a plane of symmetry through any of the M-L bonds [17, 18].

The ESR spectrum of **6** at 77K showed the presence of a rhombic "g" tensor. The values, $g_1 = 4.231$, $g_2 = 2.988$ and $g_3 = 2.486$ further support a *mer*-configuration for **6**. However, it was not possible to calculate "g" values for 7, since there was a broad featureless signal ($\Delta H \sim 150G$), indicating the presence of paramagnetic species.

Complexes of the type $[OsX_2L_4]$. These are octahedral d^6 complexes with halides trans to each other. The single

(Os-X) stretching frequency around 300 cm⁻¹ for the chloride and 230 cm⁻¹ for the bromide complexes is as expected for a D_{4h} configuration. The IR active (e_u) frequency ν (M-L) is observed as a single peak at 465 cm⁻¹ (L = SbPh₃), 520 cm⁻¹ (L = PPh₃) and 340 cm⁻¹ (L = AsPh₃).

Complexes with chelating diarsines. A strong intense absorption in 14 at 313 cm^{-1} is taken as indicating *trans*-chlorines. Moreover there was no significant absorption at 250–290 cm⁻¹, where the lower of the two bands associated with the vibrations of a *cis* Cl–Os–Cl moiety would be expected. The *trans*-isomer is also the more reasonable structure on steric grounds. The above arguments equally holds good in the case of 15.

The NMR spectrum of 15 shows in addition to the phenyl proton resonance, a singlet at 8.54τ . This peak can be assigned to the methylene protons of diarsine. So, both the diarsine ligands are monodentate and there is no reason to assume that the ligands are ambidentate. One would otherwise have expected difference in the chemical shifts of the methylene protons for the two modes of coordination [8, 9]. Conductivity experiments in dimethyl-formamide further indicate that 15 is not ionic. The presence of (SCN⁻) in 17 is indicated by the appearance of a strong band of medium intensity at 2070 cm⁻¹ (asymmetric stretch). Furthermore a band at 710 cm⁻¹ and the absence of peaks in the range 780–860 cm⁻¹ indicate that the thiocyanate is bonded to the metal through sulphur and not nitrogen [10].

ν (Os-P), ν (Os-As), ν (Os-Sb)

Our general approach to the assignment of these frequencies has been to look for bands in the spectra of the complexes which are not present in the spectra of the free ligands and which change in the appropriate way with the symmetry of the complexes. All of the bands in the free ligand spectrum will not necessarily appear in the complex, this is especially true if the ligand can adopt various orientations (*trans, gauche, etc.*).

Several papers [11-14] have appeared dealing with ν (M-P) and ν (M-As) stretching frequencies. Rivest *et al.* have previously made some tentative assignments for

 ν (M-P) and ν (M-As) frequencies [15]. The present work supports the conclusions of Rivest *et al.* since the ν (Os-P) and ν (Os-As) assignments are in a similar region of the spectrum. The ν (Os-Sb) stretching frequency appeared as a shoulder around 465 cm⁻¹. The difference in frequency between the Os-P and Os-As stretching modes may be due to two factors, namely the higher force constant of the Os-P bond (due to the stronger sigma donor properties of PPh₃ as compared to AsPh₃) and the lower reduced mass of (Os-P) species [16].

It was not possible to use the metal-phosphorous, metal-arsenic or metal-stibine stretching region of the spectrum for distinguishing cis- and trans- or fac- and *mer*-isomers because the number of bands is less than expected from symmetry considerations. No attempt was made to assign bending modes since ligand absorptions occur strongly in the same region.

REFERENCES

- 1. M. M. Taqui Khan and A. E. Martell, *Homogeneous Catalysis* by *Metal Complexes*, Vol. 1 and 2. Academic Press, New York (1974).
- 2. S. Herzog and J. Dehnert, Z. Chem. 4, 1 (1964).

- J. Chatt, G. J. Leigh, D. M. P. Mingos and R. J. Paske, J. Chem. Soc. (A), 2636 (1968).
- D. M. Adams and P. J. Chandler, J. Chem. Soc. (A), 1009 (1967).
- A. J. Carty, T. Hinsperger, L. Mihichuk and H. D. Sharma, Inorg. Chem. 9, 2573 (1970).
- J. Chatt, G. J. Leigh and D. M. P. Mingos, J. Chem. Soc. (A), 1674 (1969).
- J. Chatt, G. J. Leigh and D. M. P. Mingos, J. Chem. Soc. (A), 2972 (1969).
- 8. J. T. Mague and J. P. Mitchener, Inorg. Chem. 11, 2714 (1972).
- M. W. Anker, R. Colton and I. B. Tomkins, Aust. J. Chem. 21, 1143 (1968).
- 10. A. Turco and C. Pecile, Nature (London) 191, 66 (1961).
- P. Goggin and R. J. Goodfellow quoted by D. T. Rosevear and F. G. A. Stone, J. Chem. Soc. (A), 5275 (1965).
- 12. G. E. Coates and C. Parkin, J. Chem. Soc. (A), 421 (1963).
- 13. D. M. Adams and P. J. Chandler, Chem. Commun. 69 (1966).
- 14. F. R. Young III, R. A. Levenson, M. N. Memering and G. R. Dobson, *Inorg. Chim. Acta* in press.
- R. Rivest, S. Singh and C. Abraham, Can. J. Chem. 45, 3137 (1967).
- 16. J. R. Vanwazer, *Phosphorous and its Compounds*, Vol. 1. Interscience, New York (1958).
- 17. B. L. Shaw and A. C. Smithe, J. Chem. Soc. (A), 2784 (1968).
- J. M. Jenkins, M. C. Lupin and B. L. Shaw, J. Chem. Soc. (A), 1787 (1966).