

Complexes of osmium with tertiary arsines and carbonmonoxide

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Abstract. Osmium halides (Cl and Br) react with monotertiary arsines Ph_2RAs ($\text{R} = \text{Me, Et, Pr}$ and Bu) in alcoholic medium to give paramagnetic octahedral complexes of the type OsX_3L_3 ($\text{X} = \text{Cl, Br}$; $\text{L} = \text{Ph}_2\text{RAs}$) which further react with carbonmonoxide to give dihalo dicarbonyl complexes of osmium(II) of the type $\text{OsX}_2(\text{CO})_2\text{L}_2$. Similarly, osmium halides react with tertiary arsines in the presence of formaldehyde to give monocarbonyl complexes of osmium(II) of the type $\text{OsX}_2(\text{CO})\text{L}_3$. Structures have been assigned to all these compounds on the basis of IR and NMR studies.

Keywords. Osmium ; carbonmonoxide ; tertiary arsines ; IR spectra ; NMR spectra.

1. Introduction

Complexes of ruthenium and osmium stabilised by tertiary arsines have not been well investigated when compared to the corresponding compounds containing tertiary phosphines (Griffith 1967; McAuliffe 1973; Tripathi *et al* 1975; Reddy and Nanje Gowda 1977). Ruthenium and osmium are known to exhibit varied behaviour while reacting with tertiary phosphines and arsines depending on the experimental conditions. We have reported recently some of our investigations on the reactions of ruthenium halides with tertiary arsines (Leelamani and Reddy 1975; Srinivasamurthy *et al* 1977). It has been shown that ruthenium trihalides react with carbonmonoxide and/or monotertiary arsines under appropriate experimental conditions to give six coordinate complexes of the type RuX_3L_3 , RuX_2L_4 , $[\text{Ru}_2\text{X}_3\text{L}_6]\text{X}$, $\text{RuX}_2(\text{CO})_2\text{L}_2$ and $\text{RuX}_2(\text{CO})\text{L}_3$ ($\text{X} = \text{Cl, Br}$; $\text{L} = \text{Ph}_2\text{MeAs, Ph}_2\text{EtAs, Ph}_2\text{PrAs, Ph}_2\text{BuAs}$). It was, therefore, of interest to investigate the corresponding reactions involving osmium halides. These investigations are being reported here.

2. Experimental

Osmium salts $[\text{Na}_2\text{OsCl}_6]$ and $(\text{NH}_4)_2\text{OsBr}_6$ were supplied by Johnson Matthey Chemicals, London. The arsines Ph_2RAs ($\text{R} = \text{Me, Et, Pr, Bu}$) were prepared

by literature methods (Nanje Gowda 1975). IR (Nujol mulls), Far-IR (in polyethylene powder) and NMR (using CDCl_3 as solvent and TMS as internal standard) spectra were recorded with Specord 75 IR, Polytec FIR 30 Fourier spectrometer and Varian T-60 instruments, respectively. Microanalysis for carbon and hydrogen was carried out at the Universities of Sussex and Manchester, England. Halogen was estimated by sodium hydroxide fusion and subsequent titration by Volhard's method. The magnetic moment measurements were made at room temperature ($\sim 27^\circ \text{C}$) using a 'Gouy balance'.

**2.1. Trihalotris (tertiary arsine) osmium(III) compounds : $\text{OsX}_3(\text{Ph}_2\text{RAs})_3$
($\text{X} = \text{Cl}, \text{Br}$; $\text{R} = \text{Me}, \text{Et}, \text{Pr}, \text{Bu}$)**

To a solution of sodium chloroosmate or ammonium bromoosmate (0.1 mmol) in ethanol (30 ml) containing hydrohalic acid (0.5 ml), the arsine (0.4 mmol) was added and the mixture was refluxed on a steam-bath for about 6 hr. The required compound separated as shining coloured crystals on cooling overnight. The compound was washed successively with water, alcohol and dried in vacuo.

**2.2. Cis-dihalodicarbonylbis (tertiary arsine) osmium(II) compounds :
 $\text{OsX}_2(\text{CO})_2(\text{Ph}_2\text{RAs})_2$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{R} = \text{Me}, \text{Et}, \text{Pr}, \text{Bu}$)**

(a) Carbonmonoxide was bubbled through a suspension of $\text{OsX}_3(\text{Ph}_2\text{RAs})_3$ (0.1 mmol) in methoxyethanol (30 ml) at refluxing temperature, till a colourless solution was obtained. To this solution dropwise addition of water produced the carbonyl complex as shining white crystals. The crystals were washed with water, alcohol and dried in vacuo.

(b) A solution of sodium chloroosmate or ammonium bromoosmate (0.1 mmol) and the arsine (0.3 mmol) in methoxyethanol was refluxed for 30 min and carbon monoxide was bubbled through the resulting solution (under reflux) till the reddish brown colour changed to yellow. The reaction mixture was concentrated under reduced pressure and cooled to room temperature when shining yellow crystals separated. The crystals were filtered, washed with alcohol and dried in vacuo.

**2.3. Trans-dihalodicarbonylbis (tertiary arsine) osmium(II) compounds :
 $\text{OsX}_2(\text{CO})_2(\text{Ph}_2\text{RAs})_2$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{R} = \text{Me}, \text{Et}, \text{Pr}$)**

Carbonmonoxide was bubbled through a warm solution of $\text{OsX}_3(\text{Ph}_2\text{RAs})_3$ (0.1 mmol) in acetone (30 ml) in the presence of Zn/Hg (0.3 g) till a yellow solution was obtained. The solution was filtered and cooled in ice (or concentrated under reduced pressure) when yellow crystalline compound separated. The crystals were washed with alcohol and dried in vacuo.

**2.4. Dihalocarbonyltris (tertiary arsine) osmium(II) compounds ;
 $\text{OsX}_2(\text{CO})(\text{Ph}_2\text{RAs})_3$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{R} = \text{Me}, \text{Et}, \text{Pr}$)**

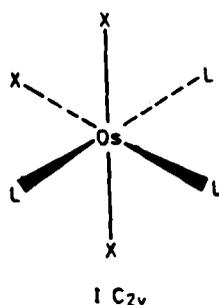
A mixture of sodium chloroosmate or ammonium bromoosmate (0.1 mmol), the tertiary arsine (0.3 mmol) and aqueous formaldehyde (5.0 ml; 37-41% w/v) in methoxyethanol (30 ml) was refluxed on a heating mantle for about 8 hr. Pale

yellow or pink crystals separated on cooling overnight. The crystals were washed with water, alcohol and dried in vacuo.

3. Results and discussion

Sodium chloroosmate and ammonium bromoosmate react with the arsines Ph_2RAs ($\text{R} = \text{Me, Et, Pr, Bu}$) in the mole ratio 1 : 4 in alcoholic medium in presence of the corresponding hydrohalic acid to give non-ionic, paramagnetic complexes of the formula OsX_3L_3 ($\text{X} = \text{Cl, Br}$; $\text{L} = \text{Ph}_2\text{RAs}$). The compound $\text{OsCl}_3(\text{Ph}_2\text{MeAs})_3$ has been reported earlier (Dwyer *et al* 1947). Attempts to prepare mononuclear and dinuclear halobridged complexes of osmium(II) of the formulae OsX_2L_4 and $[\text{Os}_2\text{X}_3\text{L}_6]\text{X}$ by using excess arsine (metal halide-arsine ratio of 1 : 8) as a reducing agent, as in the case of ruthenium halides were not successful. Similarly use of zinc-amalgam as a reducing agent also did not yield any osmium(II) compounds.

The observed magnetic moment values (table 1) of the trihalo compounds, OsX_3L_3 are in the range expected for spin-paired octahedral complexes of osmium(III) (Chatt *et al* 1968; Figgis and Lewis 1964). Because of their paramagnetic nature the PMR spectra of these compounds are not useful for assigning their structures. Similarly the metal halogen frequencies in the far-IR region are masked by other ligand bands and cannot be located. A meridional structure I may be assigned to the complexes on the basis of analogous structures shown by the corresponding tertiary phosphine complexes (Chatt *et al* 1969).



The trihalo complexes of osmium(III), OsX_3L_3 react with carbonmonoxide in refluxing methoxyethanol to give white crystalline complexes of osmium(II) of the type $\text{OsX}_2(\text{CO})_2\text{L}_2$. It is obvious that coordination of carbonmonoxide to the metal facilitates its reduction from +3 to +2 oxidation state. These dicarbonyl compounds are non-electrolytes in nitrobenzene and show two intense νCO peaks around 2000 cm^{-1} in the infrared (table 2) suggesting that the two carbonyls are located *cis* to each other. The proton NMR spectra of the compounds $\text{OsX}_2(\text{CO})_2\text{L}_2$ ($\text{X} = \text{Cl, Br}$; $\text{L} = \text{Ph}_2\text{MeAs, Ph}_2\text{EtAs}$) exhibit a single methyl or ethyl resonance pattern (table 2) due to the methyl or ethyl protons of the coordinated arsine ligands, indicating that the two arsines in each of the compounds are located in identical environments. Hence, these dicarbonyl compounds should have one of the two structures, II or III. On steric considerations it is likely that location of two

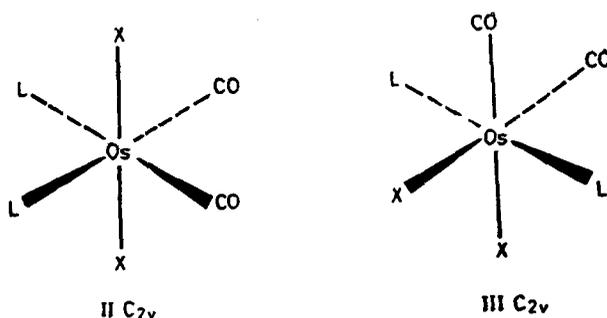


Table 1. Physical properties and analytical data of Os(III) complexes.

Compound	Colour	M.P. ($^{\circ}$ C)	$\mu_{\text{eff}}^{\text{b}}$ (BM)	Analytical data (%) ^a		
				C	H	X
$\text{OsCl}_3(\text{Ph}_2\text{MeAs})_3$	Brick red	175–77	1.980	45.4 (45.5)	3.9 (3.8)	9.5 (10.4)
$\text{OsBr}_3(\text{Ph}_2\text{MeAs})_3$	Dark violet	197–201	1.943	40.5 (40.2)	3.8 (3.4)	20.2 (20.6)
$\text{OsCl}_3(\text{Ph}_2\text{EtAs})_3$	Brick red	187–90	1.998	47.3 (47.1)	4.3 (4.2)	9.2 (9.9)
$\text{OsBr}_3(\text{Ph}_2\text{EtAs})_3$	Dark violet	189–92	1.943	41.3 (41.9)	3.8 (3.7)	18.9 (19.9)
$\text{OsCl}_3(\text{Ph}_2\text{PrAs})_3$	Orange red	208–10	NM	48.6 (48.5)	4.9 (4.6)	8.7 (9.6)
$\text{OsBr}_3(\text{Ph}_2\text{PrAs})_3$	Reddish brown	184–88	NM	43.3 (43.3)	4.0 (4.1)	18.7 (19.2)
$\text{OsCl}_3(\text{Ph}_2\text{BuAs})_3$	Orange red	166–68	NM	50.4 (49.8)	5.5 (4.9)	8.9 (9.2)
$\text{OsBr}_3(\text{Ph}_2\text{BuAs})_3$	Reddish brown	181–83	NM	44.5 (44.7)	4.9 (4.4)	18.1 (18.6)

^a Calculated values are in parentheses. ^b Magnetic moment values were measured at room temperature.

NM = not measured.

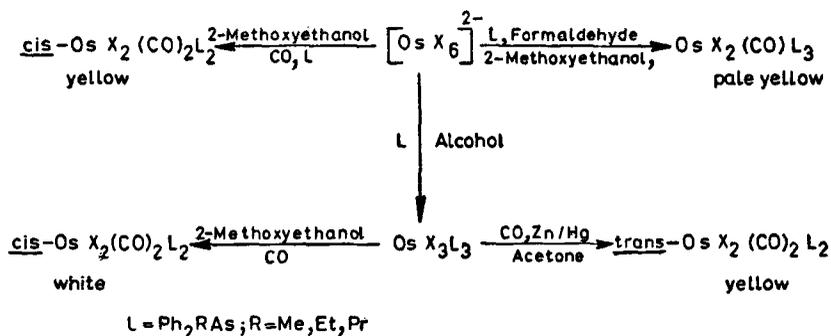
bulky arsines in *cis* positions would be less favourable and hence during substitution the arsine that gets replaced from complexes of structure I would be the one that is *trans* to a halogen. This way it is likely that the resulting complex would have structure III rather than II. As a supporting evidence the far-IR spectra of $\text{OsX}_3(\text{CO})_2(\text{Ph}_2\text{EtAs})_2$ show two intense bands due to $\nu_{\text{Os-Cl}}$ (281, 307 cm^{-1}) or $\nu_{\text{Os-Br}}$ (192, 211 cm^{-1}) which suggests *cis* location of halide groups. Similar observations have been made earlier in these laboratories with respect to nucleophilic substitution reactions involving complexes of rhodium of the type RhX_3L_3 (Nanje Gowda and Reddy 1974; Srinivasamurthy *et al* 1979) having structure I. It may also be noted that Chatt *et al* (1971) have assigned structure III for similar complexes of osmium with tertiary phosphines. We have also observed that bubbling of carbon monoxide through a methoxyethanol solution of osmium salt and arsine (Ph_2RAs) in the ratio 1 : 3 at refluxing temperature yields yellow crystalline products whose IR and NMR spectral results coincide with those of the above *cis*-dicarbonyls. There is, however, some difference in the colours of the dicarbonyls prepared by the two different routes. It is likely that this is due to difference

Table 2. Physical properties and analytical data of carbonyl complexes of osmium(II).

Compound	Colour	M.P. (°C)	νCO (cm ⁻¹)	Chemical shift ^b (τ)			Analytical data (%) ^a		
				CH ₃	CH ₂	CH	C	H	X
OsCl ₂ (CO) ₂ (Ph ₂ MeAs) ₂	White	178-80	1947, 2020	7.65s	..	41.8 (41.7)	3.3 (3.2)	..	
OsBr ₂ (CO) ₂ (Ph ₂ MeAs) ₂	White	205-06	1971, 2046	7.67s	..	37.6 (38.0)	2.9 (3.1)	17.9 (17.1)	
OsCl ₂ (CO) ₂ (Ph ₂ EtAs) ₂	White	205-06	1953, 2033	8.90t	7.20qt	43.2 (43.1)	3.6 (3.6)	8.5 (8.5)	
OsBr ₂ (CO) ₂ (Ph ₂ EtAs) ₂	White	235-38	1961, 2046	8.93t	6.93qt	39.1 (39.4)	3.3 (3.4)	..	
OsCl ₂ (CO) ₂ (Ph ₂ PrAs) ₂	White	235-38	1953, 2020	44.5 (44.6)	4.5 (3.9)	7.7 (8.2)	
OsBr ₂ (CO) ₂ (Ph ₂ PrAs) ₂	White	250	1953, 2033	40.3 (40.4)	3.6 (3.6)	16.4 (16.8)	
OsCl ₂ (CO) ₂ (Ph ₂ BuAs) ₂	White	179-80	1953, 2033	46.4 (45.9)	4.5 (4.3)	7.7 (8.0)	
OsBr ₂ (CO) ₂ (Ph ₂ BuAs) ₂	White	210-11	1953, 2027	41.2 (41.7)	3.8 (3.9)	15.8 (16.3)	
OsCl ₂ (CO) ₂ (Ph ₂ MeAs) ₂	Yellow	163-65	1970	7.90s	..	41.7 (41.7)	3.3 (3.2)	..	
OsBr ₂ (CO) ₂ (Ph ₂ MeAs) ₂	Yellow	188-91	1974	37.9 (38.0)	3.3 (3.1)	..	
OsCl ₂ (CO) ₂ (Ph ₂ EtAs) ₂	Yellow	185-88	1973	8.87t	7.40qt	42.9 (43.1)	3.7 (3.6)	..	
OsBr ₂ (CO) ₂ (Ph ₂ EtAs) ₂	Yellow	230	1980	39.5 (39.4)	3.6 (3.4)	..	
OsCl ₂ (CO) ₂ (Ph ₂ PrAs) ₂	Yellow	200-04	1966	44.4 (44.6)	4.7 (3.9)	..	
OsCl ₂ (CO) ₂ (Ph ₂ MeAs) ₂	Light pink	225-32	1880	8.43s	..	46.6 (46.9)	4.2 (3.8)	..	
				8.04s	
OsBr ₂ (CO) ₂ (Ph ₂ MeAs) ₂	Light yellow	220-22	1927	41.9 (43.2)	4.1 (3.5)	..	
OsCl ₂ (CO) ₂ (Ph ₂ EtAs) ₂	Light yellow	210	1913	9.47t	7.00qt	48.5 (48.5)	4.3 (4.2)	6.7 (6.7)	
				9.17t	8.07cm	
OsBr ₂ (CO) ₂ (Ph ₂ EtAs) ₂	Light yellow	219-21	1920	9.50t	8.00qt	44.9 (44.8)	4.0 (3.9)	..	
				9.20t	6.90cm	
OsCl ₂ (CO) ₂ (Ph ₂ PrAs) ₂	Light yellow	223-27	1933	49.1 (49.9)	4.6 (4.6)	6.0 (6.4)	
OsBr ₂ (CO) ₂ (Ph ₂ PrAs) ₂	Light yellow	240-42	1927	46.4 (46.2)	4.7 (4.3)	..	

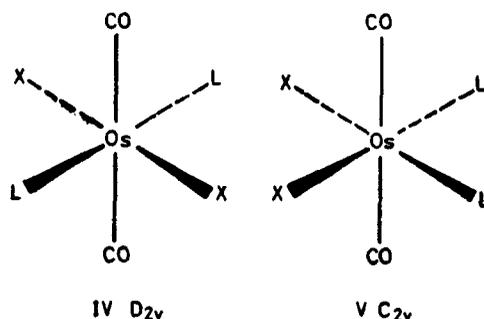
^a Calculated values are in parentheses. ^b s = singlet; t = triplet; qt = quartet; cm = complex multiplet.

in crystal packing rather than to difference in stereochemistry. The various reactions that have been carried out are shown in scheme 1.



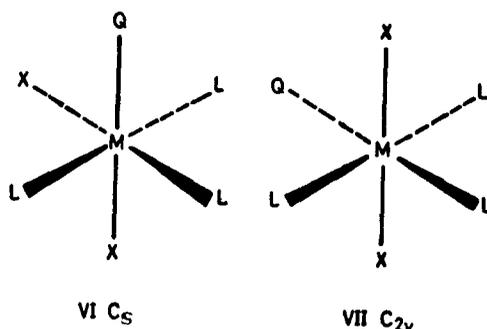
Scheme 1

When carbonmonoxide is passed through solutions of the trihalo compounds OsX₃L₃ (L = Ph₂RAs; R = Me, Et, Pr) in warm acetone in the presence of zinc-amalgam, yellow crystalline products which should also be formulated as OsX₂(CO)₂L₂ are obtained. These again give non-conducting solutions in nitrobenzene but show a single νCO peak around 2,000 cm⁻¹ (table 2) in the infrared suggesting a *trans* disposition of the two carbonyl groups. The PMR spectra of these compounds (R = Me, Et) show a single methyl or ethyl resonance pattern due to the coordinated arsines, which means that the arsines are located in an identical environment in each of the above compounds. The above results suggest that the dicarbonyls should have structure IV or V. Based on factors cited earlier



it is likely that the centrosymmetric structure IV would be more favourable than structure V for these compounds. Further, the far-IR spectra of the compounds OsX₂(CO)₂(Ph₂EtAs)₂ (X = Cl, Br) have been taken and these show a single νOs-X band (νOs-Cl = 316, νOs-Br = 235 cm⁻¹) supporting the assignment of structure IV for the above dicarbonyls. It is also found that when these *trans* dicarbonyls (configuration IV) are refluxed in methoxyethanol solvent they are converted to the more stable *cis* dicarbonyls of configuration III. Similar observations have been made by earlier workers with analogous complexes of ruthenium and osmium (Barnard *et al* 1976; Chatt *et al* 1971; James and Markham 1971).

Robinson and coworkers (Ahmed *et al* 1972) have found that the use of formaldehyde in a reaction involving sodium hexachloroosmate and triphenyl phosphine in methoxy-ethanol results in the formation of a hydridocarbonyl, $\text{OsHCl}(\text{CO})(\text{Ph}_3\text{P})_3$. Our attempts to isolate hydridocarbonyls under similar conditions using tertiary arsines resulted in the formation of non-ionic, monocarbonyl compounds of the formula $\text{OsX}_2(\text{CO})\text{L}_3$. These compounds show a carbonyl stretching band around 1900 cm^{-1} in the infrared and their PMR spectra ($\text{R} = \text{Me}, \text{Et}$) possess two methyl or ethyl resonance patterns (table 2) of relative intensity 2 : 1 indicating that two of the three arsines are *trans* to each other. The monocarbonyl compounds should therefore have either of the two structures, VI or VIII ($\text{M} = \text{Os}$;



$\text{L} = \text{Ph}_2\text{RAs}$; $\text{Q} = \text{CO}$). It has been shown earlier that in the NMR spectra of complexes with structure VI ($\text{M} = \text{Ir}$; $\text{Q} = \text{H}$; $\text{L} = \text{Ph}_2\text{EtAs}$) (Reddy and Leelamani 1973) the quartet due to methylene protons of the *trans* arsines is split due to the lower symmetry of the molecule, while the corresponding quartet of the methylene protons in the spectra of complexes with structure VII do not show any splitting. Examination of the PMR spectra of these complexes ($\text{M} = \text{Os}$; $\text{Q} = \text{CO}$; $\text{L} = \text{Ph}_2\text{EtAs}$) reveals that the methylene proton resonances of the *trans* arsines are indeed split indicating that the compounds have structure VI.

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