Complexes of osmium with tertiary arsines and carbonmonoxide

K G SRINIVASAMURTHY, N M NANJE GOWDA, E G LEELAMANI and G K N REDDY
Department of Chemistry, Central College, Bangalore University, Bangalore 560 001, India

MS received 9 August 1979; revised 1 February 1980

Abstract. Osmium halides (Cl and Br) react with monotertiary arsines Ph₂RAs (R = Me, Et, Pr and Bu) in alcoholic medium to give paramagnetic octahedral complexes of the type OsX₃L₃ (X = Cl, Br; L = Ph₂RAs) which further react with carbonmonoxide to give dihalo dicarbonyl complexes of osmium(II) of the type OsX₂(CO)₂L₂. Similarly, osmium halides react with tertiary arsines in the presence of formaldehyde to give monocarbonyl complexes of osmium(II) of the type OsX₂(CO)L₂. 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 RuX₃L₃, RuX₄L₄, [Ru₂X₅L₄]X, RuX₄(CO)₂L₂ and RuX₄(CO)L₃ (X = Cl, Br; L = Ph₂MeAs, Ph₂EtAs, Ph₂PrAs, Ph₂BuAs). It was, therefore, of interest to investigate the corresponding reactions involving osmium halides. These investigations are being reported here.

2. Experimental

Osmium salts [Na₂OsCl₄ and (NH₄)₂OsBr₄] were supplied by Johnson Matthey Chemicals, London. The arsines Ph₂RAs (R = Me, Et, Pr, Bu) were prepared
by literature methods (Nanje Gowda 1975). IR (Nujol mulls), Far-IR (in poly-
ethylene powder) and NMR (using CDCl₃ 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 
(≈ 27°C) using a ‘Gouy balance’.

2.1. Trihalotris (tertiary arsine) osmium(III) compounds : OsX₃(Ph₂RAs)₃ 
(X = CI, Br ; R = Me, Et, Pr, 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 :
OsX₃(CO)₂(Ph₂RAs)₂ (X = CI, Br ; R = Me, Et, Pr, Bu)

(a) Carbonmonoxide was bubbled through a suspension of OsX₃(Ph₂RAs)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 :
OsX₃(CO)₂(Ph₂RAs)₂ (X = CI, Br ; R = Me, Et, Pr)

Carbonmonoxide was bubbled through a warm solution of OsX₃(Ph₂RAs)₃ 
(0.1 mmol) in acetone (30 ml) in the presence of Zn/Hg (0.3 g) till a yellow solu-
tion 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 ;
OsX₃(CO) (Ph₂RAs)₃ (X = CI, Br ; R = Me, Et, 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 Ph₂RAs (R = 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 OsX₅L₅ (X = Cl, Br; L = Ph₂RAs). The compound OsCl₃(Ph₂MeAs)₂ has been reported earlier (Dwyer et al. 1947). Attempts to prepare mononuclear and dinuclear halobridged complexes of osmium(II) of the formulae OsX₅L₄ and [Os₂X₅L₄]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, OsX₅L₅ 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), OsX₅L₅ react with carbonmonoxide in refluxing methoxyethanol to give white crystalline complexes of osmium(II) of the type OsX₅(CO)₂L₅. 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 vCO 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 OsX₅(CO)₂L₅ (X = Cl, Br; L = Ph₃MeAs, Ph₃EtAs) 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.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>M.P. (°C)</th>
<th>$\mu^b_{\text{eff}}$ (BM)</th>
<th>Analytical data ($%$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OsCl$_2$(Ph$_3$MeAs)$_2$</td>
<td>Brick red</td>
<td>175-77</td>
<td>1.980</td>
<td>45.4 (45.5) 3.9 (3.8) 9.5 (10.4)</td>
</tr>
<tr>
<td>OsBr$_2$(Ph$_3$MeAs)$_2$</td>
<td>Dark violet</td>
<td>197-201</td>
<td>1.943</td>
<td>40.5 (40.2) 3.8 (3.4) 20.2 (20.6)</td>
</tr>
<tr>
<td>OsCl$_2$(Ph$_3$EtAs)$_2$</td>
<td>Brick red</td>
<td>187-90</td>
<td>1.998</td>
<td>47.3 (47.1) 4.3 (4.2) 9.2 (9.9)</td>
</tr>
<tr>
<td>OsBr$_2$(Ph$_3$EtAs)$_2$</td>
<td>Dark violet</td>
<td>189-92</td>
<td>1.943</td>
<td>41.3 (41.9) 3.8 (3.7) 18.9 (19.9)</td>
</tr>
<tr>
<td>OsCl$_2$(Ph$_3$PrAs)$_2$</td>
<td>Orange red</td>
<td>208-10</td>
<td>NM</td>
<td>48.6 (48.5) 4.9 (4.6) 8.7 (9.6)</td>
</tr>
<tr>
<td>OsBr$_2$(Ph$_3$PrAs)$_2$</td>
<td>Reddish brown</td>
<td>184-88</td>
<td>NM</td>
<td>43.3 (43.3) 4.0 (4.4) 18.7 (19.2)</td>
</tr>
<tr>
<td>OsCl$_2$(Ph$_3$BuAs)$_2$</td>
<td>Orange red</td>
<td>166-68</td>
<td>NM</td>
<td>50.4 (49.8) 5.5 (4.9) 8.9 (9.4)</td>
</tr>
<tr>
<td>OsBr$_2$(Ph$_3$BuAs)$_2$</td>
<td>Reddish brown</td>
<td>181-83</td>
<td>NM</td>
<td>44.5 (44.7) 4.9 (4.4) 18.1 (18.6)</td>
</tr>
</tbody>
</table>

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

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 OsX$_2$(CO)$_2$(Ph$_3$EtAs)$_2$ show two intense bands due to $\nu\text{Os}-\text{Cl}$ (281, 307 cm$^{-1}$) or $\nu\text{Os}-\text{Br}$ (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$_3$L$_3$ (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$_3$RAs) 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-dicarboxyls. There is, however, some difference in the colours of the dicarboxyls 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).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>M.P. (°C)</th>
<th>νCO (cm⁻¹)</th>
<th>Chemical shift ( \tau ) (Å)</th>
<th>Analytical data (%)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CH(_3)</td>
<td>CH(_4)</td>
</tr>
<tr>
<td>OsCl(_4)(CO)(_4)(Ph(_3)MeAs)(_4)</td>
<td>White</td>
<td>178-80</td>
<td>1947, 2020</td>
<td>7·65s</td>
<td>..</td>
</tr>
<tr>
<td>OsBr(_4)(CO)(_4)(Ph(_3)MeAs)(_4)</td>
<td>White</td>
<td>205-06</td>
<td>1971, 2046</td>
<td>7·67s</td>
<td>..</td>
</tr>
<tr>
<td>OsCl(_4)(CO)(_4)(Ph(_3)EtAs)(_4)</td>
<td>White</td>
<td>205-06</td>
<td>1953, 2033</td>
<td>8·90t</td>
<td>7·20qt</td>
</tr>
<tr>
<td>OsBr(_4)(CO)(_4)(Ph(_3)EtAs)(_4)</td>
<td>White</td>
<td>235-38</td>
<td>1961, 2046</td>
<td>8·93t</td>
<td>6·93qt</td>
</tr>
<tr>
<td>OsCl(_4)(CO)(_4)(Ph(_3)PrAs)(_4)</td>
<td>White</td>
<td>235-38</td>
<td>1953, 2020</td>
<td>..</td>
<td>..</td>
</tr>
<tr>
<td>OsBr(_4)(CO)(_4)(Ph(_3)PrAs)(_4)</td>
<td>White</td>
<td>250</td>
<td>1953, 2033</td>
<td>..</td>
<td>..</td>
</tr>
<tr>
<td>OsCl(_4)(CO)(_4)(Ph(_3)BuAs)(_4)</td>
<td>White</td>
<td>179-80</td>
<td>1953, 2033</td>
<td>..</td>
<td>..</td>
</tr>
<tr>
<td>OsBr(_4)(CO)(_4)(Ph(_3)BuAs)(_4)</td>
<td>White</td>
<td>210-11</td>
<td>1953, 2027</td>
<td>..</td>
<td>..</td>
</tr>
<tr>
<td>OsCl(_4)(CO)(_4)(Ph(_3)MeAs)(_4)</td>
<td>Yellow</td>
<td>163-65</td>
<td>1970</td>
<td>7·90s</td>
<td>..</td>
</tr>
<tr>
<td>OsBr(_4)(CO)(_4)(Ph(_3)MeAs)(_4)</td>
<td>Yellow</td>
<td>188-91</td>
<td>1974</td>
<td>..</td>
<td>..</td>
</tr>
<tr>
<td>OsCl(_4)(CO)(_4)(Ph(_3)EtAs)(_4)</td>
<td>Yellow</td>
<td>185-08</td>
<td>1973</td>
<td>8·87t</td>
<td>7·40qt</td>
</tr>
<tr>
<td>OsBr(_4)(CO)(_4)(Ph(_3)EtAs)(_4)</td>
<td>Yellow</td>
<td>230</td>
<td>1980</td>
<td>..</td>
<td>..</td>
</tr>
<tr>
<td>OsCl(_4)(CO)(_4)(Ph(_3)PrAs)(_4)</td>
<td>Yellow</td>
<td>200-04</td>
<td>1966</td>
<td>..</td>
<td>..</td>
</tr>
<tr>
<td>OsCl(_4)(CO)(_4)(Ph(_3)MeAs)(_4)</td>
<td>Light pink</td>
<td>225-32</td>
<td>1880</td>
<td>8·43s</td>
<td>..</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8·04s</td>
<td>..</td>
</tr>
<tr>
<td>OsBr(_4)(CO)(_4)(Ph(_3)MeAs)(_4)</td>
<td>Light yellow</td>
<td>220-22</td>
<td>1927</td>
<td>..</td>
<td>..</td>
</tr>
<tr>
<td>OsCl(_4)(CO)(_4)(Ph(_3)EtAs)(_4)</td>
<td>Light yellow</td>
<td>210</td>
<td>1913</td>
<td>9·47t</td>
<td>7·00qt</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9·17t</td>
<td>8·07cm</td>
</tr>
<tr>
<td>OsBr(_4)(CO)(_4)(Ph(_3)EtAs)(_4)</td>
<td>Light yellow</td>
<td>219-21</td>
<td>1920</td>
<td>9·50t</td>
<td>8·00qt</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9·20t</td>
<td>6·90cm</td>
</tr>
<tr>
<td>OsCl(_4)(CO)(_4)(Ph(_3)PrAs)(_4)</td>
<td>Light yellow</td>
<td>223-27</td>
<td>1933</td>
<td>..</td>
<td>..</td>
</tr>
<tr>
<td>OsBr(_4)(CO)(_4)(Ph(_3)PrAs)(_4)</td>
<td>Light yellow</td>
<td>240-42</td>
<td>1927</td>
<td>..</td>
<td>..</td>
</tr>
</tbody>
</table>

* Calculated values are in parentheses. \( s = \) 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.

When carbon monoxide is passed through solutions of the trihalo compounds OsX₅L₉ (L = Ph₂RAs; R = Me, Et, Pr) in warm acetone in the presence of zinc-amalgam, yellow crystalline products which should also be formulated as OsX₅(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 OsX₅(CO)₉(Ph₂EtAs)₉ (X = Cl, Br) have been taken and these show a single νOs–X band (Os–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, OsHCl(CO)(Ph₃P)₈. Our attempts to isolate hydridocarbonyls under similar conditions using tertiary arsines resulted in the formation of non-ionic, monocarbonyl compounds of the formula OsX₈(CO)L₃. These compounds show a carbonyl stretching band around 1900 cm⁻¹ in the infrared and their PMR spectra (R = Me, 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 (M = Os; L = Ph₃RAs; Q = CO). It has been shown earlier that in the NMR spectra of complexes with structure VI (M = Ir; Q = H; L = Ph₃EtAs) (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 (M = Os; Q = CO; L = Ph₃EtAs) reveals that the methylene proton resonances of the trans arsines are indeed split indicating that the compounds have structure VI.

Acknowledgements

The authors are indebted to Professor J Chatt and Dr D J Machin, England, for microanalysis. The authors are also thankful to Professor S Chandrasekhar and Dr S Venugopal, Raman Research Institute, Bangalore, for far-IR spectra and the authorities of Indian Institute of Science, for NMR spectra. One of the authors (KGS) is grateful to the University Grants Commission, New Delhi, for financial assistance (F.I.P).

References

Chatt J, Melville D P and Richards R L 1971 J. Chem. Soc. (A) 1169
Dwyer F P, Nyholm R S and Tyson B T 1947 *Proc. R. Soc. NS Wales* 81 272
Griffith W P 1967 *The chemistry of rarer platinum metals* (New York: Interscience)
McAuliffe C A 1973 *Transition metal complexes of phosphorus, arsenic and antimony ligands* (London: Macmillan)
Nanje Gowda N M 1975 *Some tertiary arsine and phosphine complexes of platinum group metals,* Ph.D. Thesis, Bangalore University