

Carbonyl and hydridocarbonyl complexes of ruthenium(II) and osmium(II) with tertiary arsines

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Abstract. Ruthenium halides (Cl and Br) react with monotertiary arsines- Ph_2RAs ($\text{R} = \text{Me, Et, Pr}^n$) in methoxyethanol, in the presence of aq. formaldehyde to give monocarbonyl complexes of ruthenium(II) of the type $\text{RuX}_2(\text{CO})(\text{Ph}_2\text{RAs})_3$. Carbonylation of an ethanolic solution containing ruthenium trichloride and the arsine at room temperature yield *trans* dicarbonyl compounds of the formula $\text{RuCl}_2(\text{CO})_2(\text{Ph}_2\text{RAs})_2$. The osmium monocarbonyls $\text{OsX}_2(\text{CO})(\text{Ph}_2\text{RAs})_3$ ($\text{X} = \text{Cl, Br}$; $\text{R} = \text{Me, Et}$) react with NaBH_4 in methanol to yield complexes of the composition $\text{OsHX}(\text{CO})(\text{Ph}_2\text{RAs})_3$. The ruthenium analogues $\text{RuHCl}(\text{CO})(\text{Ph}_2\text{RAs})_3$ have also been made. Structures have been assigned to all these compounds on the basis of IR and NMR spectral results.

Keywords. Ruthenium ; osmium ; carbon monoxide ; hydride ; tertiary arsines ; IR spectra ; NMR spectra.

1. Introduction

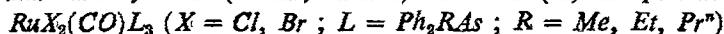
We have reported recently the isolation of carbonyl complexes of osmium of the formula $\text{OsX}_2(\text{CO})\text{L}_3$ where X is a halogen and L is a monotertiary arsine (Srinivasamurthy *et al* 1980) by refluxing a mixture of the metal halide and tertiary arsine in methoxyethanol in the presence of aq. formaldehyde. This method has now been extended to the isolation of the corresponding complexes of ruthenium. Similarly the isolation of dicarbonyl complexes of ruthenium of the formula $\text{RuX}_2(\text{CO})_2\text{L}_2$ (Leelamani and Reddy 1975 ; Srinivasamurthy *et al* 1977) where the two carbonyl groups occupy *cis* positions has also been reported earlier. An isomeric series of dicarbonyl complexes where the two carbonyl groups occupy *trans* positions have now been made. It is further found that under suitable conditions the monocarbonyl complexes of ruthenium and osmium may be converted to the hydrido compounds of the type $\text{MHX}(\text{CO})\text{L}_3$. These investigations are being reported here.

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2. Experimental

Ruthenium halides (RuCl_3 and RuBr_3) were supplied by Johnson Mathey Chemicals Ltd., London. The arsines Ph_2RAs ($\text{R} = \text{Me, Et, Pr}^n$) and the complexes $\text{RuCl}_3(\text{Ph}_2\text{RAs})_3$ and $\text{OsX}_2(\text{CO})(\text{Ph}_2\text{RAs})_3$ were synthesized as described elsewhere (Nanje Gowda 1975; Srinivasamurthy *et al* 1977, 1980). IR (Nujol mulls) and NMR (using CDCl_3 as solvent and TMS as internal standard) spectra were recorded with Carl Zeiss Specord 75 IR, Varian T-60 and Bruker WH 270 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.

2.1. Dihalocarbonyl tris (tertiary arsine) ruthenium(II) compounds :



A mixture of ruthenium trihalide (0.1 mmole), the tertiary arsine (0.3 mmole) and aq. formaldehyde (5.0 ml; 37–41% w/v) in methoxyethanol (25 ml) was refluxed on a heating mantle for about 6 hr. The required compound separated out on cooling. The crystals were filtered, washed with water and alcohol and dried *in vacuo*.

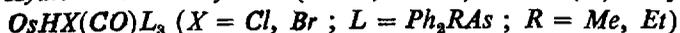
2.2. trans-Dichlorodicarbonyl bis (tertiary arsine) ruthenium(II) compounds :



(a) Carbon monoxide was bubbled through a solution containing ruthenium trichloride (0.1 mmole) and the arsine (0.3 mmole) in alcohol at room temperature for 15 min. The solution was left overnight when yellow crystals separated. The crystals were filtered, washed with alcohol and dried *in vacuo*.

(b) Carbon monoxide was bubbled through a suspension of RuCl_3L_3 (0.1 mmole) in warm acetone till the solution turned yellow. The yellow-solution was concentrated under reduced pressure and cooled, when yellow crystals separated. The crystals were filtered, washed with alcohol and dried *in vacuo*.

2.3. Hydridohalocarbonyl tris (tertiary arsine) osmium(II) compounds :



$\text{OsX}_2(\text{CO})\text{L}_3$ (0.1 g) and sodiumborohydride (0.2 g) were refluxed in about 30 ml methanol for 3–4 hr, when the required compound separated (often after reducing the volume of the solution under reduced pressure) as white crystals. The crystals were filtered, washed with alcohol, recrystallized from chloroform-ethanol and dried *in vacuo*.

2.4. Hydridochlorocarbonyl tris (tertiary arsine) ruthenium(II) compounds :

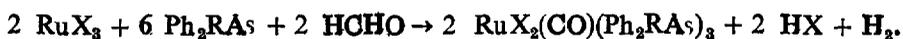


Ruthenium trichloride (0.1 mmole) in 10 ml ethanol was added to a boiling solution of arsine (0.4 mmole) in 25 ml ethanol followed by 5 ml aq. formaldehyde (37–41% w/v) and a solution of 0.2 g of KOH in 20 ml ethanol. The

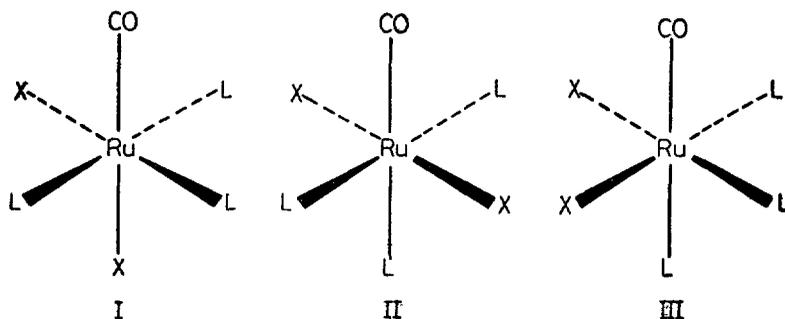
mixture was refluxed for 30 min and cooled to room temperature. The solution was filtered and left overnight when crude crystals of the hydridocarbonyl got separated. The solid was filtered, washed with alcohol and recrystallized from chloroform-ethanol and dried *in vacuo*.

3. Results and discussion

Ruthenium halides (RuCl_3 and RuBr_3) react with monotertiary arsines Ph_2RAs ($\text{R} = \text{Me, Et, Pr}^n$) in the mole ratio 1:3 in presence of aqueous formaldehyde in boiling methoxyethanol to produce yellow crystalline compounds of the formula $\text{RuX}_2(\text{CO})\text{L}_3$. These are diamagnetic, freely soluble in chloroform and give non-conducting solutions in nitrobenzene. It is likely that formaldehyde acts both as a reducing and as a carbonylating agent in these reactions (Evans *et al* 1968 ; Osborn *et al* 1966). The overall reaction for the formation of the carbonyl compound may be written as



Three configurations I to III are possible for these compounds. On steric grounds



configuration III where all the three bulky arsines are required to be located mutually *cis* to one another may be ruled out. The compounds show a ν_{CO} band around 1950 cm^{-1} (table 1) which lies in the same region as that shown by similar complexes of ruthenium with tertiary phosphines reported earlier and having configuration II. Carbonyl complexes of ruthenium with tertiary phosphines having configuration I have also been reported earlier (Chatt *et al* 1971 ; Jenkins *et al* 1966) and these have a ν_{CO} band around 1920 cm^{-1} .

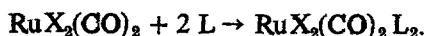
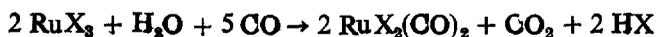
Further in the analogous complexes of osmium with $\text{L}(\text{Ph}_2\text{EtAs})_3$ and having configuration I there is no plane of symmetry across $\text{L}-\text{M}-\text{L}$. On account of this in the pmr spectra of these complexes the methylene quartets of the ethyl groups of the *trans* arsines occur as an overlapping complex multiplet confirming that the complexes indeed have configuration I (Srinivasamurthy *et al* 1980). However in the case of the monocarbonyl complexes of ruthenium being reported here the pmr spectra have a single quartet attributable to the methylene groups of the two *trans* arsines suggesting the existence of a plane of symmetry across $\text{L}-\text{M}-\text{L}$ and hence structure II for the complexes.

We have also reported earlier the isolation of dicarbonyl complexes of ruthenium of the formula $\text{RuX}_2(\text{CO})_2\text{L}_3$ where the two carbonyls are located *cis* to each other

Table 1. Physical properties and analytical data of carbonyl complexes of ruthenium(II)

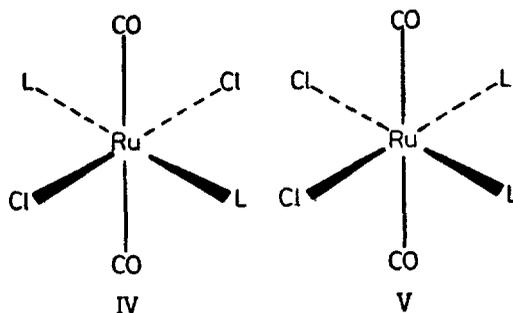
Compound	Colour	M.P. or Dec. P. (°C)	ν_{CO} (cm^{-1}) ^a	Chemical shift (τ) ^b		Analytical data (%) ^c		
				CH ₃	CH ₃	C	H	X
1	2	3	4	5	6	7	8	9
$\text{RuCl}_2(\text{CO})\text{L}_3$	Yellow	205-210	1940	7.97 s 8.50 s	..	51.5 (51.5)	4.1 (4.2)	6.8 (7.6)
$\text{RuBr}_2(\text{CO})\text{L}_3$	Yellow	214-216	1934	8.34 s 8.43 s	..	46.9 (47.0)	4.1 (3.8)	15.2 (15.6)
$\text{RuCl}_2(\text{CO})\text{L}'_3$	Yellow	192-198	1946	9.2 t 9.47 t	8.07 q 7.07 q	52.7 (52.9)	4.6 (4.6)	6.6 (7.3)
$\text{RuBr}_2(\text{CO})\text{L}'_3$	Yellow	193-195	1947	9.3 t 9.5 t	7.97 q 6.90 q	48.3 (48.5)	4.5 (4.2)	14.4 (15.0)
$\text{RuCl}_2(\text{CO})\text{L}''_3$	Yellow	211-213	1940	54.3 (54.3)	5.1 (5.0)	6.9 (7.0)
<i>trans</i> - $\text{RuCl}_2(\text{CO})\text{L}'_2$	Yellow	144-147	1994	7.92 s	..	47.3 (46.9)	3.7 (3.6)	..
* <i>trans</i> - $\text{RuCl}_2(\text{CO})\text{L}'_2$	Yellow	204-206	2010	48.1 (48.4)	4.3 (4.1)	8.9 (9.5)
<i>trans</i> - $\text{RuCl}_2(\text{CO})\text{L}''_2$	Yellow	179-182	2000	49.6 (49.7)	4.2 (4.4)	..

(Leelamani and Reddy 1975; Srinivasamurthy *et al* 1977). These were obtained by the addition of the arsine to the pale yellow solution obtained by passing carbon monoxide through a hot methoxyethanol solution of the metal halide. An isomeric series of dicarbonyl complexes where the two carbonyl groups occupy *trans* positions have now been made by replacing methoxyethanol by ethylalcohol as the reaction medium. Solutions obtained by passing carbon monoxide through ethanolic solutions of ruthenium halide have been shown to contain the species $\text{RuX}_2(\text{CO})_2$ (Berch and Davison 1973). The reduction of Ru(III) to Ru(II) by carbon monoxide may be assumed to take place in a way similar to that suggested for the carbonylation of rhodium trichloride in ethanol (Cotton and Wilkinson 1976). $\text{RuX}_2(\text{CO})_2$ so formed reacts with the arsine to give the final product.

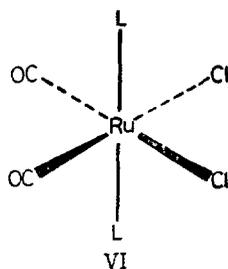


These compounds can also be made by bubbling carbon monoxide through a warm acetone solution of RuX_3L_3 .

These dicarbonyl complexes show a single ν_{CO} band around 2000 cm^{-1} in the infrared and a single methyl or ethyl resonance pattern in their pmr spectra (table 1) suggesting configuration IV or V for these compounds. On steric



considerations it is likely that location of two bulky arsines in *cis* positions as in configuration V would be less favourable. Hence we suggest the centrosymmetric structure IV for the compounds. It is further found that when these *trans* dicarbonyls are refluxed in methoxyethanol they are converted to *cis* dicarbonyls of configuration VI which show two ν_{CO} bands and are identical with those reported by us earlier (Leelamani and Reddy 1975; Srinivasamurthy *et al* 1977). Similar



observations have been made by earlier workers in the case of corresponding tertiary phosphine containing complexes (Chatt *et al* 1971 ; Stephenson and Wilkinson 1966 ; James and Markham 1971) and a mechanism has been proposed for such a conversion (Barnard *et al* 1976).

The monocarbonyl complexes of osmium of the formula $\text{OsX}_2(\text{CO})\text{L}_3$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{L} = \text{Ph}_2\text{RA}_3$; $\text{R} = \text{Me}, \text{Et}$) react with NaBH_4 in boiling methanol to yield hydridocarbonyl complexes of the formula $\text{OsHX}(\text{CO})\text{L}_3$. Under similar conditions the ruthenium monocarbonyls do not yield any hydrido compounds. However the ruthenium compounds of the formula $\text{RuHCl}(\text{CO})\text{L}_3$ can be made by reacting ruthenium chloride with the arsine in presence of alcoholic KOH and aqueous formaldehyde in boiling ethanol. Both the osmium and ruthenium hydridocarbonyls are white crystalline solids and soluble in chloroform and similar organic solvents. The osmium complexes show two absorption bands in the infrared—a strong band around 1900 cm^{-1} assignable to ν_{CO} and another weaker one around 2000 cm^{-1} assignable to $\nu_{\text{Os-H}}$ (table 2). In the case of ruthenium compounds, however, only a single but very strong absorption peak is found around 1900 cm^{-1} (table 2) which is clearly assignable to ν_{CO} . We believe that a $\nu_{\text{Ru-H}}$ also occurs in these compounds and this normally weak metal-hydrogen band is completely masked by the more intense ν_{CO} peak.

Replacement of a more electronegative halogen in the monocarbonyls by a less electronegative hydridic hydrogen to form the hydridocarbonyls increases the electron density at the metal. This facilitates greater π -bonding between metal and carbon monoxide and hence the ν_{CO} value of any hydridocarbonyl is less than that of the corresponding carbonyl. It has been found in several cases that the solvent sensitivity of the M-H stretching frequency of a hydrido compound is dependent on the group *trans* to the hydrogen. If a phosphine or arsine is *trans* to the hydridic hydrogen $\nu_{\text{M-H}}$ does not vary much with the nature of the solvent, while, if a halogen is *trans* to the hydrogen $\nu_{\text{M-H}}$ will have a higher value in a polar solvent than that in a non-polar solvent (Adams 1967 ; Geoffroy and Lehman 1977 ; Nanje Gowda and Reddy 1977). In the present investigation the M-H values do not show any appreciable change between polar (CHCl_3) and non-polar (C_6H_6) solvents, suggesting that the arsine is located *trans* to the hydridic hydrogen.

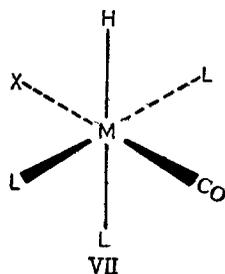
The presence of the metal-hydrogen bond in both the osmium and ruthenium complexes is confirmed by the pmr spectra of the compounds, which show a resonance peak in the high field side around 19τ (table 2). The compounds also show two sets of methyl and methylene proton resonance absorptions of relative intensity 1 : 2 due to the coordinated arsines indicating that two of the three arsines are occupying mutually *trans* positions in the octahedral complexes. The pmr spectral studies on a number of ruthenium and osmium hydridocarbonyl complexes have shown that in complexes having a halogen *trans* to the hydrogen, the hydridic hydrogen has a large chemical shift around 30τ or above when compared to the other isomers (Birnbaum 1971). Thus the presence of CO, phosphine or arsine in a position *trans* to the hydridic hydrogen is expected to result in a lower chemical shift around 20τ or less for the hydrogen. The hydridic hydrogen chemical shift values of the complexes under investigation are all around 19τ , suggesting the location of an arsine or CO *trans* to the hydrogen.

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

Compound	Colour	M.P. or Dec. P. (°C)	IR bands (cm ⁻¹) ^a			Chemical shift ^b			Analytical data (%) ^c		
			ν_{CO}	ν_{M-H}	τ_H	τ_{CH_3}	τ_{CF_3}	C	H	X	
RuHCl(CO)L ₃	White	155-156	1913	..	18.22	8.30 s	..	53.7	4.7	3.6	
RuHCl(CO)L' ₂	White	162-165	1920, 1900 sh	..	18.42	8.20 s 8.91 t	8.59 q	(53.4)	(4.5)	(3.9)	
OsHCl(CO)L ₃	White	165-166	1890	2000	18.79	9.35 t 8.20 s	7.69 cm	(54.9)	(4.9)	(3.8)	
OsHBr(CO)L ₃	White	180-182	1900	2002	19.19	8.56 s 8.15 s	..	(48.6)	(4.1)	(3.6)	
OsHCl(CO)L' ₂	White	192-193	1893, 1874 sh	1990	19.00	8.47 s 9.04 t	8.34 q	(46.5)	(3.9)	(7.7)	
OsHBr(CO)L' ₂	White	185-186	1900, 1890 sh	2000	19.43	9.38 t 8.93 t	7.31 cm 8.26 q	50.3 (50.2)	4.6 (4.5)	
						9.33 t	7.53 cm	(48.0)	(4.3)	(4.3)	

^a Calculated values are in parentheses. ^b NMR spectra were taken in CDCl₃ with TMS as internal standard. ^c Infrared spectra taken in nujol. L = Ph₂MeAs; L' = Ph₂EtAs; L'' = Ph₂Pr^oAs; C = carbon; H = hydrogen; X = halogen; s = singlet; t = triplet; q = quartet; q = quartet; cm = complex multiplet; sh = shoulder; * = compound reported earlier (Leelamani and Reddy 1975).

It has also been observed that in octahedral carbonyl complexes of the type $\text{RuHX}(\text{CO})\text{L}_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{L} = \text{Ph}_2\text{RAs}$; $\text{R} = \text{Me}, \text{Et}, \text{Pr}^n$) the chemical shift values of the hydridic hydrogen increases in the order $\text{Cl} < \text{Br} < \text{I}$, when the spacial arrangement of ligands around the metal is *cis*-H, X and *trans* X, CO (Birnbaum 1971). The chemical shift values of the hydridic hydrogen for the new complexes being reported here show similar trend. Further, because there is no plane of symmetry through L—M—L in structure VII, when L is Ph_2EtAs ,



the methylene quartet arising from the two *trans* arsines should get split in the pmr spectrum as explained earlier. The pmr spectra of the hydridocarbonyls containing Ph_2EtAs do show splitting of the methylene quartet. In the light of the above observations the new complexes may be assigned structure VII.

Acknowledgements

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