METAL-METAL BONDED COMPLEXES OF OSMIUM AND RUTHENIUM

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Abstract-The preparation and physical properties of complexes of the type OsCl₂XL₃, OsClX(L-L)₂ (where $X = SnCl_3 \text{ or } HgCl, L = PPh_3, AsPh_3, PPr_2^nPh, PMePh_2, L-L = C_2H_4(PPh_2)_2, CH_2(PPh_2)_2, CH_2(AsPh_2)_2, PA_2(AsPh_2)_2, PA_2(A$ $RuCl(SnCl_3)L_3$, $RuCl_2L_3HgCl$ and $RuCl_2(GeEt_2Cl)L_3$ (where $L = PPh_3$, AsPH_3, SbPh_3) are described. Metal-chlorine IR stretching frequencies ν (M-Cl) (M=Os, Ru, Sn, Hg) have been assigned. An increase in the Sn-Cl stretching frequency was observed upon coordination. IR spectra are reported for all complexes and for some of the complexes Raman spectra and conductivity data are also recorded and discussed.

INTRODUCTION

ALTHOUGH many metal-metal bonded complexes are known for the platinum metals [1-9], metal-metal bonded complexes of osmium have been little explored. The study of these complexes provide useful information not only on metal-metal bonding in osmium and ruthenium chemistry, but also provide new complexes for studies in homogeneous catalysis. In the present paper a number of complexes of osmium with Os-Sn and Os-Hg bonds and of ruthenium with Ru-Sn. Ru-Hg and Ru-Ge bonds are reported.

EXPERIMENTAL

All the complexes were prepared and the reactions conducted in a nitrogen atmosphere using Schlenk tube techniques. All solvents were purged with nitrogen prior to their use. Microanalysis of the compounds were performed by Microanalytical Service Centre, C.S.I.R.O., Australia. IR spectra of the complexes in Nujol mulls on polythene plates were recorded with a Beckman IR-12 spectrophotometer. 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. The spectra in the range 30-400 cm⁻¹ were recorded on a FIS-13 spectrophotometer. The conductivity measurements were made on a Toshinwal conductivity bridge in dimethylformamide solution at 30°. Ammoniumhexachloroosmate and ruthenium trichloride hydrate were purchased from Johnson Matthey, London. The ligands triphenylphosphine (PPh₃) triphenylarsine (AsPh₃), triphenylantimony (SbPh₃), di-npropylphenylphosphine (PPr2"Ph), methyldiphenylphosphine (PMePh₂), bis-1,2diphenylphosphinoethane (C₂H₄(PPh₂)₂), bis-1,2diphenylphosphinomethane $(CH_2(PPh_2)_2)$ his-1,2diphenylarsinomethane (CH₂(AsPh₂)₂) and diethylgermanium dichloride (GeEt₂Cl₂) were purchased from Ventron Corporation, U.S.A. BDH AnalaR grade stannous chloride and mercuric chloride were used.

Dichloro - (trichlorostannato) - tris - (triphenylphosphine) osmium(III)

A mixture of 0.2 g (0.5 mmol) of ammoniumhexachloroosmate(IV) and 0.3 g (1.6 mmol) of stannous chloride in 25 ml of concentrated hydrochloric acid and 35 ml of ethanol was refluxed for 0.5 hr. To the hot solution was added a solution of triphenylphosphine (0.5 g, 1.9 mmol) in 10 ml of methanol. A brown solid appeared which was refluxed for an additional 3 hr. The precipitate was filtered, washed with methanol, ether and dried. A similar method of preparation was used for OsCl(SnCl₃)(AsPh₃)₄ (recrystallized from chloroform) OsCl(SnCl₃) (SbPh₃)₄ (washed with ether and acetone); OsCl₂(SnCl₃) (PMePh₂)₃ (washed with

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dichloromethane and methanol); OsCl(SnCl₃) (CH₂(PPh₂)₂)₂ (recrystallized from benzene and methanol); OsCl(SnCl₃)- $(C_2H_4(PPh_2)_2)_2$ (washed with methanol and benzene).

Chlorotetrakis(triphenylphosphine)(osmium(II) - bis - dichloromercury(II)

To a solution of (0.2 g, 0.5 mmol) of ammoniumhexachloroosmate(IV) in 40 ml of water and methanol (1:3) mixture was added mercuric chloride (0.3 g, 1 mmol) in 10 ml of methanol and the solution refluxed for 20 min. To the hot solution was added a solution of triphenylphosphine (0.5 g, 1.9 mmol) in 10 ml of methanol. After refluxing for an extra 3-4 hr a white precipitate appeared, which was filtered and washed with hot methanol, ether and dried. Similarly prepared were [OsCl2(AsPh3)3].2HgCl2 methanol, ether (washed with and acetone): $[OsCl(C_2H_4(PPh_2)_2)_2]$ ·2HgCl₂ (washed with benzene and hot methanol); [OsCl₂(CH₂(PPh₂)₂)₂]·HgCl₂ (washed with benzene and methanol); [OsCl(CH2(AsPh2)2)2]·2HgCl2 (washed with benzene and methanol.

Chlorotetrakis(triphenylstibine)osmium(I) - dichloromercury(II)

A mixture of (0.2 g, 0.5 mmol) of ammoniumhexachloroosmate(IV) in 35 ml of 2-methoxyethanol, 7 ml of water and 0.3 g (1 mmol) of mercuric chloride in 5 ml of 2-methoxyethanol was refluxed for 30 min. To the hot solution was added a solution of triphenylstibine (0.5 g, 1.4 mmol) in 2-methoxyethanol (10 ml). After refluxing for 3 hr, a brown precipitate was obtained which was washed with methanol, ether and dried.

Dichlorotris - (diphenylmethylphosphine) - osmium (II) - dichloromercury(II)

To a solution of (0.2 g, 0.5 mmol) of ammoniumhexachloroosmate(IV) in 45 ml of water and ethanol (1:3) mixture was added mercuric chloride (0.3 g, 1 mmol). To the hot solution was added a solution of diphenylmethylphosphine (1 mmol) in 10 ml of ethanol. A black precipitate appeared, which was washed with methanol and dried.

Preparation of the complexes of the type RuCl(SnCl₃)(RPh₂)₃

200 mg (0.8 mmol) of ruthenium trichloride hydrate was dissolved in 10 ml of ethanol and refluxed for 1 hr with a stannous chloried solution obtained by dissolving 1 g (4 mmol) of SnCl₂·2H₂O in 25 ml of a 1:1 mixture of concentrated hydrochloric acid and ethanol. To the hot solution, about 1 g (3-4 mmol) of RPh₃ (R=P, As or Sb) in 10 ml of methanol or ethanol was added. A brownish yellow (R=P), greenish yellow (R=As) or scarlet red (R=Sb) microcrystalline powder separated. The precipitates were washed with hot methanol, ether and dried and purified by thin layer chromatography [10].

Preparation of complexes of the type RuCl₂(RPh₃)₃·HgCl₂

200 mg (0.8 mmol) of ruthenium trichloride hydrate was dissolved in 10 ml of acetone and taken into a three necked flask. About 400 mg (1.5 mmol) of mercuric chloride was dissolved in

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10 ml of acetone and added to the flask. The mixture was refluxed for 1 hr. A hot solution of about 1 g (3-4 mmol of the ligand (PPh₃, AsPh₃ or SbPh₃) was added to the mixture and refluxed for an additional 30 min. Brown (R=P) reddish brown (R=As) and scarlet red (R=Sb) colored microcrystalline powders deposited at the bottom of the flask. The finely divided substances were washed repeatedly with acetone to remove excess of RPh₃ (R=P, As or Sb) and HgCl₂. Further purification of the complexes was done by TLC.

Preparation of the complexes of the type RuCl₂(GeEt₂Cl)(RPh₃)₃

250 mg (1 mmol) of rutheniumtrichloride hydrate was dissolved in 20 ml of tetrahydrofuran and mixed with 1 g (6 mmol) of diethylgermaniumdichloride dissolved in 25 ml of tetrahydrofuran (THF). The mixture was refluxed for one hour under nitrogen and 1 g (3-4 mmol) of RPh₃ (R=P, As or Sb) in 10 ml of THF was added to the hot mixture which was further refluxed for 45 min. A greenish (R=P), brownish (R=As) or scarlet red (R=Sb) powder was obtained. The complex was purified by repeated washing with THF and finally with ether and dried.

Analytical data for the complexes are presented in Table 1 and IR spectral data in Tables 2-4.

RESULTS AND DISCUSSION

In solution, the free SnCl_3^- ion is pyramidal and displays two stretches at 297 cm⁻¹ and 256 cm⁻¹[11]. A considerable increase in the Sn-Cl stretching frequency was observed upon coordination to ruthenium or osmium. In every case, the band was broad and asymmetric and the two (SnCl₃⁻) frequencies were not always resolved. The increase in the Sn-Cl stretching frequency on coordination to ruthenium or osmium may be due to the back donation of electron density from suitable ruthenium or osmium orbitals to the empty 4d orbitals of tin by a $d-d_{\pi}$

Table 1.	Anal	vtical	data†	of	osmium	and	ruthenium	comp	lexes
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	Complex	Colour	С	Н	Cl	P or Sb, As	Conductivity (M ⁻¹ cm ² ohm)
1.	OsCl ₂ (SnCl ₃)(PPh ₃) ₃	Brown	50.85	3.6	14.1	7.5	
			(50-94)	(3.5)	(13-95)	(7.3)	
2.	OsCl(SnCl ₃)(AsPh ₃) ₄	Red	53.0	3.7	8.6		_
			(52.5)	(3.6)	(8.5)		
3.	OsCl(SnCl ₃)(SbPh ₃) ₄	Pale-	46.4	3.32	—		_
		yellow	(46·4)	(3.22)			
4.	$OsCl_2(SnCl_3)(PMePh_2)_3$	Yellow	43-2	3.6	16.5	8∙4	_
			(43.0)	(3.5)	(16·3)	(8.5)	
5.	OsCl ₂ (SnCl ₃)(PPr ₂ "Ph) ₃	Pale-	40.1	5.4	16.8	9.6	
		yellow	(40·4)	(5.3)	(16·6)	(9.7)	
6.	$OsCl(SnCl_3)(CH_2(PPh_2)_2)_2$	Yellow	49.4	3.5	11.9	9.8	-
			(49.2)	(3.6)	(11.7)	(10.1)	
7.	$OsCl(SnCl_3)(C_2H_4(PPh_2)_2)_2$	Yellow	49 ∙6	3.9	11.5	9.6	_
			(50.0)	(3.9)	(11.4)	(9.9)	A
8.	[OsCl(PPh ₃) ₄]·2HgCl	Grey	47.6	3.4	9.6	7.0	8.63
			(47.82)	(3.32)	(9-8)	(6-86)	0.50
9.	[OsCl(AsPh ₃) ₃]·2HgCl ₂	Black	37.3	2.63	12.5	13.00	9.58
		_	(37.6)	(2.67)	(12.4)	(13-0)	10 70
10.	[OsCl(SbPh ₃) ₄]·HgCl ₂	Brown	45.4	3.0	5.7		10.70
			(45.2)	(3.15)	(5-58)		
11.	[OsCl ₂ (PMePh ₂) ₃]·HgCl ₂	Black	42.0	3.5	12-2	8.4	11.02
			(41-3)	(3.44)	(12.53)	(8.2)	10.10
12.	$[OsCl_2(CH_2(PPh_2)_2)_2] \cdot HgCl_2$	White	46.11	3.5	11.2	9.3	12-13
		~	(46.13)	(3.38)	(10.9)	(9.53)	17 59
13.	$[OsCl(C_2H_4(PPh_2)_2)_2] \cdot 2HgCl_2$	Grey	39.90	3.12	(7.0)	(11.2)	13.38
		n 1 1	(39.9)	(3.06)	(7.9)	(11.3)	14.65
14.	[OsCl(CH ₂ (AsPh ₂) ₂) ₂]·2HgCl ₂	Dark red	34.9	2.7	(10.4)		14.03
		D	(33-1)	(2.0)	(10.4)	Q. 1	
15.	$RuCl(SnCl_3)(PPn_3)_3$	Brownisn	30°2 (56.4)	(2.02)	(12.25)	(8.1)	—
16		Greenish	(30.4)	(3.40)	(12.33)	(0.1)	_
16.	RUCI(SnCl ₃)(ASPn ₃) ₃	valleur	(50.6)	(3.47) (2.50)	(11.08)		
17	D.C. C. C. V. C. D. V	Scorlat	(50.0)	2.10	10.0	25.5	
17.	KUCI(SIICI₃)(SUPII₃) 3	Scallet	(15.6)	(3.17)	(9.98)	(25.7)	
10	IBucl (DDb.) LUgCl	Brown	54.3	3.63	11.49	7.7	4.65
10.		DIOWI	(52.7)	(3.66)	(11.52)	(7.57)	
10	[PuCl.(AsPh.).].HoCl.	Reddish	47.7	3.29	10.35	18.4	5.72
12.	[Ruci2(7131 113)3] 116012	brown	(47.62)	(3.30)	(10.40)	(18.28)	
20	(RuCl_(ShPh_)_]·HeCl_	Scarlet	43.2	3.01	9.30	24.4	6.86
20.		Demite	(43.17)	(2.99)	(9.43)	(24.33)	
21	RuCl ₂ (GeEt ₂ Cl)(PPh ₂) ₁	Green	62-01	4.92	9·51	``	-
2			(61.87)	(4.89)	(9.46)		
22.	RuCl ₂ (GeEt ₂ Cl)(AsPh ₃) ₃	Brown	54-42	4.40	8.50		
			(54-38)	(4.37)	(8.47)		
23.	RuCl ₂ (GeEt ₂ Cl)(SbPh ₃) ₃	Scarlet red	56-2	3.88	6.12	19.5	
			(56-15)	(3.9)	(6-15)	(19-47)	

†Calculated values in parenthesis.

Table 2. IR spectral data (cm ⁻¹)				
Complex	ν(Os–Cl)	ν(M-Cl) (M=Sn or Hg)	ν (Os-L) (L=P, As, Sb)	
1	340	310, 265	500	
2	315	325, 280	475	
3	310	275	455	
4	300	312	500	
5	295	302	485	
6	298	303	498	
7	315	275	490	
8	315	296, 255	495	
9	330	350, 290, 245	460	
10	305	325, 275, 263	465	
11	320	295, 275	490	
12	305	365	505	
13	340	290, 260	485	
14	· 325	275	465	

Table 3. Raman spectral data (cm⁻¹)

Complex	v(Os-Cl)	ν (Sn–Cl)
1	339	346, 308
2	315	324, 281
7	313	270

Table 4. IR spectral data (cm⁻¹)

Complex	v(M-Cl) (Ru, Sn or Hg)	ν(Ru-L) (L=P, As or Sb)	ν(Ru-M) (M=Sn or Hg)
15	320(br)	438(m)	219(m)
16	315-320(br)	460(s)	209(m)
17	305(s)	412(m)	199(s)
	315(sh)		
18		440(m)	177(m)
19		420(m)	175-178(m)
20		410(m)	172(m)
		415(sh)	. /

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

interaction. This strengthens the Sn-Cl bond by allowing synergic back donation to Cl. On close examination of the spectra of tin-bonded ruthenium and osmium complexes the M-Cl (M = ruthenium, osmium) stretching frequency is observed as a weak band or shoulder on the Sn-Cl stretching frequency. Any separate assignment of the M-Cl frequency is thus speculative.

The Raman spectrum of compound 1 shows an intense line at 346 cm⁻¹, non-concident with the strong IR band at *ca.* 30 cm⁻¹ to lower frequency. This Raman line may be due to some impurity in the complex or to a second Os-Cl frequency. The Raman band at 339 cm⁻¹ coincides with the IR band assigned to ν (Os-Cl). The M-Cl (M=Os, Sn) stretching frequencies in compounds 2 and 7 appeared in the Raman spectra at almost the same frequencies as in the IR spectra, as expected from molecules of such low symmetry.

It has been reported[12] that (Hg-Cl) stretching

frequencies generally appear around 250-300 cm⁻¹. Similar absorption peaks were observed in the complexes reported in this paper. It was not possible to assign ν (Os-Sn) and ν (Os-Hg) frequencies because these frequencies are too close to Hg-Cl or Sn-Cl frequencies.

The IR spectra of 18, 19, 20 showed a peak of medium intensity at 177, 175–178 and 172 cm⁻¹, respectively, characteristic of a ν (Ru-Hg) frequency[5]. The peaks corresponding to ν (Ru-Sn) frequencies[13] appeared in 15, 16 and 17 at 219, 209 and 199 cm⁻¹ respectively.

Nyholm and Vrieze[14, 15] prepared M-Hg(M=Rh or IR) complexes by addition of HgCl₂ to the d^8 Ir(I) and Rh(I) to form Ir(III) and Rh(III) mercury-bonded complexes. This oxidative addition may be considered to have taken place by the transfer of two electrons from Ir(I) and Rh(I) ions to a HgCl⁺ group (obtained by the dissociation of HgCl₂ into HgCl⁺ and Cl⁻). In the case of the ruthenium-mercury and osmium-mercury complexes, depending on the polarity of the Os-Hg or Ru-Hg bond, coordinated HgCl or HgCl⁺ species may be present. The oxidation state of the metal ion in such complexes is thus very difficult to assign. In the case of 2:1 adducts it is also possible that 1 mol of HgCl₂ is loosely bound in the lattice. In the absence of any X-ray data, the complexes in Table 1 have thus been merely written as 1:1 or 2:1 adducts.

In ruthenium-germanium bonded complexes, the ν (Ru-Ge) frequency is expected around 300-400 cm⁻¹. Since metal-halogen and ligand frequencies also occur in the same region, it was not possible to assign unequivocally a band in the above region to the ν (Ru-Ge) frequency. The presence of a Ru-Ge bond is however inferred from elemental analysis and the stability of the compounds in solution. The formation of chloro-bridged Ru-Ge compounds are excluded on the basis of the absence of frequencies corresponding to chloro-bridges. Such compounds are also expected to be much less stable than Ru-Ge bonded complexes.

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