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SYNTHESIS AND REACTIONS OF OSMIUM NITROSYL COMPLEXES

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Abstract—Nitrosyl halides NOX (X = Cl, Br) reacted with osmium carbonyl complexes $[OsH(CO)ClL_3]$, $[Os(CO)Cl_2L_3]$ and $[OsH_2(CO)L_3]$ ($L = PPh_3$, $AsPh_3$) to give osmium nitrosyl complexes $[Os(NO)X_3L_2]$, $[Os(NO)ClBr_2L_2]$ and $[Os(NO)Cl_2BrL_2]$ and osmium carbonyl complexes $[Os(CO)_2X_2L_2]$ (X = Cl, Br; $L = PPh_3$, $AsPh_3$). Low valent osmium nitrosyl complexes $[Os(NO)X(AsPh_3)_3]$ (X = Cl, Br) were prepared by refluxing $[Os(NO)X_3(AsPh_3)_2]$ with excess $AsPh_3$. Reaction of sulphur with $[Os(NO)X_3(PPh_3)_2]$ resulted in the formation of novel thionitro complexes $[Os(NSO)X_2(PPh_3)_2]$. $[Os(NO)Cl_3(PPh_3)_2]$ reacted with $[Na(S_2CNR_2)\cdot xH_2O]$ (R = Et. Me) under different reaction conditions to produce the complexes $[Os(NO)Cl_2(S_2CNR_2)(PPh_3)]$ and $[Os(S_2CNR_2)_3]$. The products have been characterized by elemental analyses, magnetic measurements, IR and electronic spectral studies.

The activation of nitrosyl halides in homogeneous systems by metal complexes, has received considerable attention because of the possible synthetic applications as well as interest in the catalytic processes.[1–15] Osmium nitrosyl complexes of the type $[Os(NO)X_3L_2]$ ($L = PPh_3$, $AsPh_3$, $SbPh_3$) have been prepared previously by (a) the reaction of $[OsX_6]^{2-}$ with NO or MNTS in the presence of ligand L ($L = PPh_3$, $AsPh_3$, $SbPh_3$),[16] (b) the reactions of $OsCl_3$ with NOX (X = Cl, Br, Br_3 or NO_2) in the presence of triphenylphosphine or triphenylarsine[17] and (c) the reactions of NOX (X = Cl, Br) with some osmium(II) complexes.[18] Synthesis of osmium(0) complexes $[Os(NO)X(PPh_3)_3]$ (X = Cl, Br) have also been reported.[18–19]

The formation of either nitrato or nitro/nitrito complexes in the reactions of nitrosyl complexes with O_2,[20–25] and the formation of the Fe—N(O)S moiety,[26] in the reaction of sodium nitroprusside with SH^- or S^{2-}, prompted us to undertake the reaction of osmium nitrosyl complexes with sulphur. Sulphur ligands stabilize several nitrosyl complexes, but to the best of our knowledge no sulphur derivative of the osmium nitrosyl complex has been reported. Herein we wish to report (i) the reactions of osmium carbonyl complexes with nitrosyl chloride and nitrosyl bromide, (ii) synthesis of $[Os(NO)X(AsPh_3)_2]$, (iii) the reactions of $[Os(NO)X_3L_2]$ (X = Cl, Br; $L = PPh_3$) with sulphur and (iv) the reactions of $[Os(NO)Cl_3(PPh_3)_2]$ with $[Na(S_2CNR_2)]$ (R = Et, Me).

EXPERIMENTAL

All the reagents used were AnalaR or of chemically pure grade. The solvents were dried and freshly distilled before use. Hydridochlorocarbonyltris(triphenylphosphine)osmium(II), dichlorocarbonyltris(triphenylphosphine)osmium(II), dihydridocarbonyltris (triphenylphosphine) osmium (II), hydridochlorocarbonyltris (triphenylarsine) osmium (II), dichlorocarbonyltris(triphenylarsine)osmium(II), dihydridocarbonyltris(triphenylarsine)osmium(II), nitrosyl chloride and nitrosyl bromide were prepared by literature methods.[27–31] A saturated solution of NOCl and *ca* a 2 M solution of NOBr in CH_2Cl_2 have been used in these reactions. $[Na(S_2CNR_2)\cdot xH_2O]$ (R = Et or Me) salts were used as purchased from Flucka.

The analyses for sulphur, chloride and bromide

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in the complexes were carried out using standard methods.[32,33] Carbon, hydrogen and nitrogen analyses were performed using a Carlo Erba 1106 Thomas CH-analyser 35 and Coleman N-analyser 29. For the estimation of phosphorus and arsenic, samples were decomposed with sodium peroxide, sugar and sodium nitrate in the ratio 20 : 1 : 3 in a Parr bomb crucible and extracted with water. The solution was neutralized with dilute H_2SO_4 and an excess of concentrated H_2SO_4 (0.5 cm^3) added. This was heated until the evolution of SO_3 fumes ceased, then cooled and diluted with water. From the filtrate of the solution, phosphorus and arsenic was estimated by standard methods.[34] The results are reported in Table 1.

The IR spectra have been recorded in the range 4000–250 cm^{-1} with a Perkin–Elmer 580 spectrophotometer at the R.S. Instrument Centre of the Indian Institute of Technology, Bombay. Samples were prepared as KBr pellets. Important IR frequencies are given in Table 2. The electronic spectra have been recorded using a Shimadzu 160 spectrophotometer. Magnetic measurements were carried out by Gouy's method at room temperature

Table 1. Colour and analytical data of osmium complexes

Compounds	Colour	Analysis % found (calc.) C	H	N	Cl/Br	S	P/As
$Os(NO)Cl_3(PPh_3)_2$	Red	50.6	3.4	1.5	12.7	—	7.4
	Brown	(50.8)	(3.5)	(1.6)	(12.5)		(7.3)
$Os(NO)Cl_2Br(PPh_3)_2$	Red	48.4	3.5	1.7	8.2	—	7.2
	Brown	(48.2)	(3.3)	(1.6)	(7.9)		(6.9)
$Os(NO)ClBr_2(PPh_3)_2$	Brown	45.9	3.0	1.6	3.9	—	6.8
		(46.0)	(3.2)	(1.4)	(3.8)		(6.6)
$Os(NO)Br_3(PPh_3)_2$	Brown	43.8	3.2	1.2	—	—	6.5
		(43.9)	(3.0)	(1.4)			(6.3)
$Os(CO)_2Cl_2(PPh_3)_2$	White	54.4	3.4	—	8.6	—	7.5
		(54.2)	(3.6)		(8.4)		(7.4)
$Os(CO)_2Br_2(PPh_3)_2$	White	49.1	3.1	—	17.5	—	6.8
		(49.0)	(3.2)		(17.2)		(6.7)
$Os(NO)Cl_3(AsPh_3)_2$	Red	46.2	3.4	1.6	11.5	—	16.2
	Brown	(46.0)	(3.2)	(1.5)	(11.3)		(16.0)
$Os(NO)Cl_2Br(AsPh_3)_2$	Brown	43.8	3.2	1.6	7.4	—	15.4
		(43.9)	(3.0)	(1.4)	(7.2)		(15.2)
$Os(NO)ClBr_2(AsPh_3)_2$	Brown	42.2	2.8	1.5	3.6	—	14.8
		(42.0)	(2.9)	(1.4)	(3.4)		(14.6)
$Os(NO)Br_3(AsPh_3)_2$	Brown	40.1	2.7	1.1	—	—	14.2
		(40.3)	(2.8)	(1.3)			(14.0)
$Os(CO)_2Cl_2(AsPh_3)_2$	White	49.2	3.4	—	7.8	—	16.3
		(49.1)	(3.2)		(7.6)		(16.1)
$Os(CO)_2Br_2(AsPh_3)_2$	White	44.6	2.7	—	—	—	14.9
		(44.8)	(2.9)				(14.7)
$Os(NO)Cl(AsPh_3)_3$	Green	55.4	3.7	1.3	3.2	—	19.3
		(55.2)	(3.8)	(1.2)	(3.0)		(19.2)
$Os(NO)Br(AsPh_3)_3$	Green	53.0	3.8	1.2			18.6
		(53.2)	(3.7)	(1.1)			(18.5)
$Os(NSO)Cl_2(PPh_3)_2$	Green	51.2	3.7	1.5	8.5	3.9	7.5
		(51.0)	(3.5)	(1.6)	(8.4)	(3.8)	(7.3)
$Os(NSO)Br_2(PPh_3)_2$	Green	46.3	3.1	1.6	—	3.6	6.8
		(46.1)	(3.2)	(1.5)		(3.4)	(6.6)
$Os(NO)Cl_2(S_2CNEt_2)(PPh_3)$	Brownish	39.1	3.4	3.7	10.3	9.3	4.6
	Yellow	(39.4)	(3.6)	(4.0)	(10.1)	(9.1)	(4.4)
$Os(S_2CNEt_2)_3$	Brown	28.5	4.9	6.5	—	30.4	—
		(28.4)	(4.7)	(6.6)		(30.3)	
$Os(NO)Cl_2(S_2CNMe_2)(PPh_3)$	Khakhi	37.3	3.0	4.3	10.7	9.7	4.8
		(37.4)	(3.1)	(4.2)	(10.5)	(9.5)	(4.6)
$Os(S_2CNMe_2)_3$	Brown	19.5	3.3	7.5	—	35.2	—
		(19.6)	(3.3)	(7.6)		(34.9)	

Table 2. Melting point and important IR frequencies (cm^{-1}) of osmium complexes

Compounds	ν(NO)	ν(CO)	ν(NSO)	ν(Os—Cl)	ν(CN)	M.p. (°C)
$Os(NO)Cl_3(PPh_3)_2$	1850	—	—	325, 310	—	260
$Os(NO)Cl_2Br(PPh_3)_2$	1860	—	—	320	—	> 280
$Os(NO)ClBr_2(PPh_3)_2$	1855	—	—	310	—	> 280
$Os(NO)Br_3(PPh_3)_2$	1860	—	—	—	—	> 280
$Os(CO)_2Cl_2(PPh_3)_2$	—	2040, 1973	—	329	—	> 280
$Os(CO)_2Br_2(PPh_3)_2$	—	2035, 1970	—	—	—	> 280
$Os(NO)Cl_3(AsPh_3)_2$	1847	—	—	322, 312	—	> 280
$Os(NO)Cl_2Br(AsPh_3)_2$	1858	—	—	318	—	> 280
$Os(NO(ClBr_2(AsPh_3)_2$	1852	—	—	312	—	> 280
$Os(NO)Br_3(AsPh_3)_2$	1856	—	—	—	—	> 280
$Os(CO)_2Cl_2(AsPh_3)_2$	—	2038, 1972	—	—	—	> 280
$Os(CO)_2Br_2(AsPh_3)_2$	—	2035, 1970	—	—	—	> 280
$Os(NO)Cl(AsPh_3)_3$	1635	—	—	310	—	140
$Os(NO)Br(AsPh_3)_3$	1630	—	—	—	—	130
$Os(NSO)Cl_2(PPh_3)_2$	—	—	1237, 1052	325	—	210
$Os(NSO)Br_2(PPh_3)_2$	—	—	1235, 1055	—	—	215
$Os(NO)Cl_2(S_2CNEt_2)(PPh_3)$	1810	—	—	330	1530	275
$Os(NO)Cl_2(S_2CNMe_2)(PPh_3)$	1800	—	—	330	1542	180
$Os(S_2CNEt_2)_3$	—	—	—	—	1540	225
$Os(S_2CNMe_2)_3$	—	—	—	—	1535	> 280

(25°C), using mercury tetrathiocyanato cobaltate(II) as calibrant. Melting points were determined by the capillary method and are uncorrected.

(a) *Reactions of* NOX (X = Cl *or* Br) *with* [OsH(CO)ClL$_3$], [Os(CO)Cl$_2$L$_3$] *or* [OsH$_2$(CO)L$_3$] (L = PPh$_3$ *or* AsPh$_3$)

The experiments were performed similarly and the reaction of NOCl with [OsH(CO)Cl(PPh$_3$)$_3$] is described as a representative example.

A saturated solution of NOCl (25 cm^3) in dichloromethane was added dropwise to a stirred solution of [OsH(CO)Cl(PPh$_3$)$_3$] (0.2 g) in dichloromethane (20 cm^3). The reaction mixture was refluxed for 20 min. On addition of hot methanol (60 cm^3), the red brown crystals of [Os(NO)Cl$_3$(PPh$_3$)$_2$] which separated out, were filtered, washed with methanol, diethylether and dried *in vacuo*.

On keeping the filtrate for 3 h, a white compound [Os(CO)$_2$Cl$_2$(PPh$_3$)$_2$] separated out, which was filtered, washed with methanol, ether and dried *in vacuo*.

Similarly the complexes [Os(NO)Cl$_3$L$_2$] and [Os(CO)$_2$Cl$_2$L$_2$] (L = PPh$_3$ or AsPh$_3$) were isolated by the reactions of NOCl with [OsH(CO)Cl(AsPh$_3$)$_3$], [Os(CO)Cl$_2$L$_3$] or [OsH$_2$(CO)L$_3$] and the complexes of the type [Os(NO)ClBr$_2$L$_2$] and [Os(CO)$_2$Br$_2$L$_2$]; [Os(NO)Cl$_2$BrL$_2$] and [Os(CO)$_2$Br$_2$L$_2$]; [Os(NO)Br$_3$L$_2$] and [Os(CO)$_2$Br$_2$L$_2$] were isolated by the reactions of NOBr with [OsH(CO)ClL$_3$], [Os(CO)Cl$_2$L$_3$] and [OsH$_2$(CO)L$_3$], respectively.

(b) *Reactions of* AsPh$_3$ *with* [Os(NO)X$_3$(AsPh$_3$)$_2$] (X = Cl *or* Br)

Triphenylarsine (1.0 g) was added to a solution of [Os(NO)X$_3$(AsPh$_3$)$_2$] (0.2 g) in benzene (25 cm^3). The resulting solution was refluxed for 50 h and then concentrated to 5 cm^3 under reduced pressure. On addition of *n*-hexane, green complexes of [Os(NO)X(AsPh$_3$)$_3$] precipitated out which were centrifuged, washed with *n*-hexane and dried *in vacuo* (yield 0.13 g, 52% for X = Cl; 0.10 g, 44% for X = Br).

(c) *Reactions of sulphur with* [Os(NO)X$_3$(PPh$_3$)$_2$] (X = Cl *or* Br)

To a solution of [Os(NO)Cl$_3$(PPh$_3$)$_2$] (0.85 g, 1 mmol) in benzene (100 cm^3), was added sulphur (0.064 g, 0.25 mmol). The reaction mixture was refluxed for 4 h, whereby its colour changed from orange to green. It was concentrated to 5 cm^3 under reduced pressure. On addition of *n*-hexane, the green complex [Os(NSO)Cl$_2$(PPh$_3$)$_2$] precipitated and was centrifuged, washed with hexane and dried *in vacuo*. It was recrystallized with benzene–hexane (1 : 3) (yield 0.25 g, 30%).

The green complex [Os(NSO)Br$_2$(PPh$_3$)$_2$] was isolated by a similar procedure using [Os(NO)

$Br_3(PPh_3)_2]$ (0.98 g, 1 mmol) and sulphur (0.064 g, 0.25 mmol) (yield 0.22 g, 22%).

(d) *Reaction of* $[Na(S_2CNR_2)\cdot xH_2O]$ *with* $[OsNOCl_3(PPh_3)_2]$ (R = Et, Me)

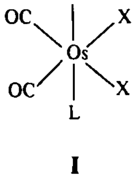
(i) The compounds $[Os(NO)Cl_3(PPh_3)_2]$ (0.2 g) and $[Na(S_2CNR_2)\cdot xH_2O]$ (0.1 g) were stirred in benzene (25 cm^3) for 5 h. The resulting solution was filtered and reduced to 5 cm^3 under reduced pressure. On addition of *n*-hexane brownish–yellow complexes $[Os(NO)Cl_2(S_2CNR_2)(PPh_3)]$ separated, filtered, washed with water and dried *in vacuo*.

(ii) Compounds $[Os(NO)Cl_3(PPh_3)_2]$ (0.2 g) and $[Na(S_2CNR_2)\cdot xH_2O]$ (0.5 g) were refluxed in benzene (25 cm^3) for 4 h. The resulting solution was filtered and reduced to about 5 cm^3 under reduced pressure. On addition of *n*-hexane, the brown complex $[Os(S_2CNR_2)_3]$ separated, this was centrifuged, washed with water, cold ethanol and dried *in vacuo*.

RESULTS AND DISCUSSION

Reactions of nitrosyl halides NOX (X = Cl, Br) with $[OsH(CO)ClL_3]$, $[Os(CO)Cl_2L_3]$ and $[OsH_2(CO)L_3]$ (L = PPh_3, $AsPh_3$) gave osmium nitrosyl complexes $[Os(NO)X_3L_2]$, $[Os(NO)ClBr_2L_2]$ and $Os(NO)Cl_2BrL_2$ in good yield (50–70%) and osmium carbonyl complexes $[Os(CO)_2X_2L_2]$ (X = Cl, Br; L = PPh_3, $AsPh_3$) in low yield (8–10%).

The IR spectra of $[Os(NO)X_3L_2]$, $[Os(NO)ClBr_2L_2]$ and $[Os(NO)Cl_2BrL_2]$ exhibited intense bands in the region 1840–1860 cm^{-1} due to the nitrosyl stretching frequency and in the region 340–300 cm^{-1} (in chloro complexes) due to ν(Os—Cl). The IR spectra of osmium dicarbonyl complexes $[Os(CO)_2X_2L_2]$ (X = Cl, Br; L = PPh_3, $AsPh_3$) which agreed with those previously reported,[35-37] exhibit two strong ν(CO) vibrations (Table 2) consistent with a *cis*-configuration (**I**).



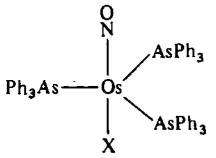
I

The complexes $[Os(NO)X_3(AsPh_3)_2]$ (X = Cl, Br), on refluxing with triphenylarsine in benezene for 50 h afforded green complexes $[Os(NO)X(AsPh_3)_3]$:

$$Os(NO)X_3(AsPh_3)_2+AsPh_3 \xrightarrow[\text{reflux}]{\text{benzene}} Os(NO)X(AsPh_3)_3+\cdots. \quad (1)$$

The complex $[Os(NO)Cl(AsPh_3)_3]$ is a green coloured solid, a non-electrolyte and its solution is air sensitive. The IR spectrum of $[Os(NO)Cl(AsPh_3)_3]$ shows a strong band at 1635 cm^{-1} due to ν(NO) and at 310 cm^{-1} due to ν(Os—Cl).

The electronic spectrum in benzene shows bands at 13400, 15750, 20200 and 25120 cm^{-1}. Complex $[Os(NO)Br(AsPh_3)_3]$ is a green coloured solid, a non-electrolyte and its solution is air sensitive. The IR spectrum of $[Os(NO)Br(AsPh_3)_3]$ shows a strong band at 1630 cm^{-1} due to ν(NO). The electronic spectrum in benzene shows bands at 13330, 15670, 19610 and 25000 cm^{-1}. The corrected nitrosyl stretching frequencies, ν(NO), calculated by Ibers empirical rules,[38] fall above 1610 cm^{-1}. This is evidence for the presence of a linear nitrosyl group in these complexes. Combining the rules which have been suggested by Ibers,[39] and Hoffmann *et al*,[40] for penta-coordinated nitrosyl complexes, with the empirical rules of stereochemistry, the geometry about the osmium atom can be described as distorted trigonal bipyramid with equatorial triphenylarsine ligands and the NO group *trans*axial to X (X = Cl, Br) and the molecule has C_{3v} symmetry (**II**).



II

The reaction of sulphur with $[Os(NO)X_3(PPh_3)_2]$ (X = Cl, Br) in benzene results in the formation of thionitro complexes, $[Os(NSO)X_2(PPh_3)]$

$$Os(NO)X_3(PPh_3)_2+\tfrac{1}{4}S_8 \xrightarrow{\text{benzene}} Os(NSO)X_2(PPh_3)_2+\cdots. \quad (2)$$

These complexes are green coloured solids, stable under nitrogen atmosphere and paramagnetic compounds, with magnetic moments μ = 1.70, 1.72 BM, respectively. The IR spectra of $[Os(NSO)X_2(PPh_3)_2]$ show absorption bands in the region 1230, 1050 and 575 cm^{-1} due to ν_{asym}(NSO), ν_{sym}(NSO) and δ(NSO), respectively.[41,42] The electronic spectrum of $[Os(NSO)Cl_2(PPh_3)_2]$ shows bands at 19800, 21500, 25640 and 36360 cm^{-1}.

Stirring the benzene solution of $[Os(NO)Cl_3(PPh_3)_2]$ with $[Na(S_2CNR_2)]$ (R = Et, Me) afforded the nitrosyl complexes [Os(NO)$Cl_2(S_2CNR_2)(PPh_3)$]

$$Os(NO)Cl_3(PPh_3)_2 + Na(S_2CNR_2) \xrightarrow[\text{stirring}]{\text{benzene}} Os(NO)Cl_2(S_2CNR_2)(PPh_3). \quad (3)$$

Refluxing the complex [$Os(NO)Cl_3(PPh_3)_2$] with excess [$Na(S_2CNR_2)$] gave osmium(II) complexes [$Os(S_2CNR_2)_3$]:

$$Os(NO)Cl_3(PPh_3)_2 + \text{excess}\ Na(S_2CNR_2) \xrightarrow[\text{reflux}]{\text{benzene}} Os(S_2CNR_2)_3. \quad (4)$$

The IR spectra of the complexes [$Os(NO)Cl_2(S_2CNR_2)(PPh_3)$] (R = Et, Me) show intense bands at 1810 and 1800 cm^{-1} due to ν(NO), respectively, in addition to the absorption bands due to S_2CNR_2 and (PPh_3) ligands. The ν(CN) frequency in these complexes appears at 1530 and 1542 cm^{-1}, respectively. It is shifted to higher energy compared with the free ligand, as a result of increased double bond character upon coordination to the metal centre.[43,44]

The electronic spectra of [$Os(NO)Cl_2(S_2CNEt_2)(PPh_3)$] show absorption bands at 23690, 30300 and 34480 cm^{-1}. The electronic spectra of [$Os(S_2CNEt_2)_3$] show bands at 35714 cm^{-1} and a very weak band at 20200 cm^{-1}. A study of dithiolic acids assigned the high energy absorption to π–π^* transitions.[45] The IR spectra of [$Os(S_2CNR_2)_3$] (R = Et, Me) show no band due to ν(NO), indicating the absence of the NO group in the complexes. The complexes [$Os(S_2CNR_2)_3$] are paramagnetic with magnetic moments $\mu = 1.80$, 1.83 BM, respectively.

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