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Thionitrosyl Complexes of Ruthenium(II) and their Reactions with NOX ($X = Cl, Br, Br_3, NO_2$) in Presence of Excess PPh_3, $AsPh_3$, $SbPh_3$ and Py

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The reactions of trithiazyltrichloride in tetrahydrofuran with $RuCl_2(PPh_3)_3$, $RuBr_2(PPh_3)_3$, $RuCl_3(AsPh_3)_2 \cdot MeOH$ *and* $RuBr_3(AsPh_3)_2 \cdot MeOH$ *give crystalline thionitrosyl complexes* $Ru(NS)Cl_3(PPh_3)_2$, $Ru(NS)Br_2Cl(PPh_3)_2$, $Ru(NS)Cl_3(AsPh_3)_2$, $Ru(NS)Br_2Cl(AsPh_3)_2$ *and two novel mixed ligand thionitrosyls* $Ru(NS)Cl_3(PPh_3)(AsPh_3)$ *and* $Ru(NS)Cl_3(AsPh_3)(SbPh_3)$. *On irradiation with UV light in air these compounds form a pentacoordinated species* $Ru(NS)X_3L$ *and the corresponding oxides of triphenylphosphine, arsine or stibine. When* $Ru(NS)X_3L$ *is treated with excess L', mixed thionitrosyl complexes are obtained. On treating these with NOX* ($X = Cl, Br, Br_3$) *mixed nitrosyl complexes are obtained, presumably through a pentacoordinated species as an intermediate in the presence of excess ligand L'* ($L = PPh_3, AsPh_3$; $L' = PPh_3, AsPh_3, SbPh_3$, *Py*). *The reactions of dinitrogen trioxide in presence of an excess of the corresponding ligand give nitrosyl nitrato complexes of the general form* $Ru(NO)(NO_3)X_2L_2$.

Introduction

Although the existence of stable nitrosyls has long been regarded as a normal part of transition metal chemistry, compounds containing NS as coordinated ligand synthesized in recent years are few in number [1–11]. The reason for the relative rarity of such complexes is the lack of a suitable thionitrosylating agent. The NS group may be bonded to the metal ion analogous to NO, *viz.*, as bridged [5] or terminal in which it may behave either as a three (linear NS^+) [6] or as a one-electron donor (bent NS^-) [7]. The embryonic state of thionitrosyl chemistry has provoked us to work on the syntheses and structural aspects of new and novel metal thionitrosyls with a view to gain more insight into the understanding of bonding with the metal ions. In this paper we wish to report the preparation and characterizations of some mixed thionitrosyls and nitrosyls of ruthenium(II). Their structures are postulated by powder X-ray data.

Experimental

All reagents were Analar or of chemically pure grade. All the solvents were dried and distilled before use.

Trithiazyl trichloride, nitrosyl chloride, nitrosyl bromide, nitrosyl tribromide, dinitrogen trioxide, dichlorotris(triphenylphosphine)ruthenium(II), dibromotris(triphenylphosphine)ruthenium(II), trichlorobis(triphenylarsine)methanol ruthenium(III), tribromobis(triphenylarsine)methanol ruthenium(III) were prepared according to the literature methods [12–17].

A. Preparation of Complexes

(i) $RuCl_3(NS)L_2$ ($L = PPh_3$ *or* $AsPh_3$)

30 ml of THF solution of $(NSCl)_3$ (*ca.* 4 mmol) was added to a solution (75 ml) of the corresponding ruthenium complex $RuCl_2(PPh_3)_3$ or $RuCl_3(AsPh_3)_2 \cdot MeOH$ (0.3 mmol) in dichloromethane followed by vigorous stirring for 30 minutes. 100 ml of methanol was added to the resulting solution whereupon shining brown crystals of the phosphine complex appeared immediately. In the case of the arsine complex precipitation did not take place, and the resulting solution was heated on a water bath for about 10 minutes to remove dichloromethane: 1.2 g (*ca.* 4 mmol) of $AsPh_3$ was added, whereby the shining crystals of the arsine complex appeared. The product precipitate was collected, and washed with methanol and ether: it was recrystallized by dissolving in boiling dichloromethane (*ca.* 250 ml), evaporating

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the solution to small volume, and adding about 75 ml of hot methanol. The compound thus obtained was separated, washed and dried *in vacuo* at room temperature. The analytical data corresponded very well with the formula $RuCl_3(NS)L_2$ (L = PPh_3 or $AsPh_3$).

(ii) $RuClBr_2(NS)L_2$ (L = PPh_3 or $AsPh_3$)

The procedures for the syntheses of the complexes were exactly the same as those given in (i) except that $RuBr_2(PPh_3)_3$ or $RuBr_3(AsPh_3)_2\cdot$MeOH was used in place of $RuCl_2(PPh_3)_3$ or $RuCl_3(AsPh_3)_2\cdot$MeOH, respectively. The analytical data conformed with the proposed formula.

(iii) $RuCl_3(NS)LL'$ (L = PPh_3, $AsPh_3$; L′ = PPh_3, $AsPh_3$ or $SbPh_3$; L ≠ L′)

(a) $RuCl_3(NS)(PPh_3)(AsPh_3)$: A solution of approximately one mmol of $RuCl_3(NS)(PPh_3)_2$ and 5 mmol of $AsPh_3$ in 200 ml of chloroform after refluxing for 8 hours, was concentrated to nearly half the volume, followed by the addition of 100 ml of hot methanol whereupon shining brown crystals of $RuCl_3(NS)(PPh_3)(AsPh_3)$ appeared. These were collected, washed with methanol and ether and recrystallized by the same procedure as given in (i). The analyses corresponded to the proposed formula.

All efforts to replace phosphine by $SbPh_3$ under these experimental conditions failed. $RuCl_3(NS)(PPh_3)(SbPh_3)$ could therefore not be synthesized.

(b) *$RuCl_3(NS)(AsPh_3)(SbPh_3)$:* This was prepared by the procedure similar to that given for $RuCl_3(NS)(AsPh_3)_2$ in (i), except that triphenylstibene was added in place of $AsPh_3$, after concentrating the stirred solution. The analyses of the brown crystals corresponded to the proposed formula.

B. Reactions of NOCl with $RuCl_3(NS)L_2$ (L = PPh_3 or $AsPh_3$) in the Presence of PPh_3, $AsPh_3$, $SbPh_3$, Py. Formation of $RuCl_3(NO)LL'$ (L = PPh_3, $AsPh_3$; L′ = PPh_3, $AsPh_3$, $SbPh_3$ and Pyridine)

A saturated solution (30 ml) of NOCl in CH_2Cl_2 was added to 100 ml dichloromethane solution of $RuCl_3(NS)L_2$ (*ca.* 2 mmol), followed by stirring for 30 minutes. The resulting solution was divided into four parts.

Part 1

Approximately 5 mmol of solid PPh_3 or $AsPh_3$ were dissolved in the solution, followed by the addition of 50 ml of methanol. The resulting solution was refluxed on a water bath for five minutes, when shining orange-brown crystals of $RuCl_3(NO)L_2$ appeared in this solution. Crystals were centrifuged, washed with methanol and ether, and dried *in vacuo.*

Part 2, 3 and 4

Approximately 5 mmol of solid PPh_3 or $AsPh_3$, $SbPh_3$ and pyridine were added separately to solutions of parts 2, 3 and 4 respectively followed by 50 ml of MeOH. On refluxing the solutions 2, 3 and 4 separately for 30 minutes the respective mixed complexes $RuCl_3(NO)LL'$ (L = PPh_3, $AsPh_3$; L′ = PPh_3, $AsPh_3$, $SbPh_3$, pyridine L ≠ L′) precipitated out and were treated as described for part 1.

Two important points must be noted in these preparations.

(1) From the solutions of part 1–4, it is impossible to precipitate out the complex without adding solid PPh_3, $AsPh_3$, $SbPh_3$ or pyridine. Even after complete evaporation of the solvent, an oily mass remained from which all our attempts to separate crystalline materials failed. (2) Starting from $RuCl_3(NS)AsPh_3)_2$ it was not possible to separate $RuCl_3(NO)(AsPh_3)(PPh_3)$ on addition of PPh_3 in the solution of Part B. Under such experimental conditions both ($AsPh_3$) molecules were substituted by PPh_3 and the crystals of $RuCl_3(NO)(PPh_3)_2$ were obtained.

C. Reactions of NOCl with $Ru(NS)Br_2ClL_2$ (L = PPh_3, $AsPh_3$) in the Presence of PPh_3 or $AsPh_3$, $SbPh_3$ or Pyridine. Formation of $Ru(NS)Br_2Cl(LL')$

The procedures to carry out the reactions were similar to the ones given in B for the syntheses of $RuCl_3(NO)LL'$ except that $Ru(NS)Br_2ClL_2$ was taken in place of $RuCl_3(NS)L_2$. The reactions products obtained were $Ru(NO)Br_2Cl(LL')$ (L′ = PPh_3, $AsPh_3$, $SbPh_3$ or pyridine).

D. Reactions of NOBr with $RuCl_3(NS)L_2$ (L = PPh_3, $AsPh_3$) in the Presence of Excess of L. Formation of $Ru(NO)BrCl_2L_2$

15 ml of dichloromethane solution of NOBr (*ca.* 2 *M*) was added dropwise to a solution (100 ml) of $Ru(NS)Cl_3L_2$ (*ca.* 1 mmol) in dichloromethane and the mixture was stirred for about 30 minutes, followed by the addition of 100 ml of methanol. The resulting solution was heated on a water bath for ten minutes and nearly 7 mmol of L (PPh_3 or $AsPh_3$) was added whereupon shining brownish orange crystals of $Ru(NO)BrCl_2L_2$ appeared which were separated, washed with methanol and ether and recrystallized by the method described earlier.

E. Reactions of NOBr with $Ru(NS)Br_2ClL_2$ (L = PPh_3, $AsPh_3$) in the Presence of Excess L. Formation of $Ru(NO)Br_3L_2$

The procedure for these reactions were the same as that given in D except that $Ru(NS)Br_2ClL_2$ was used in place of $Ru(NS)Cl_3L_2$. The product was found to be $Ru(NO)Br_3L_2$.

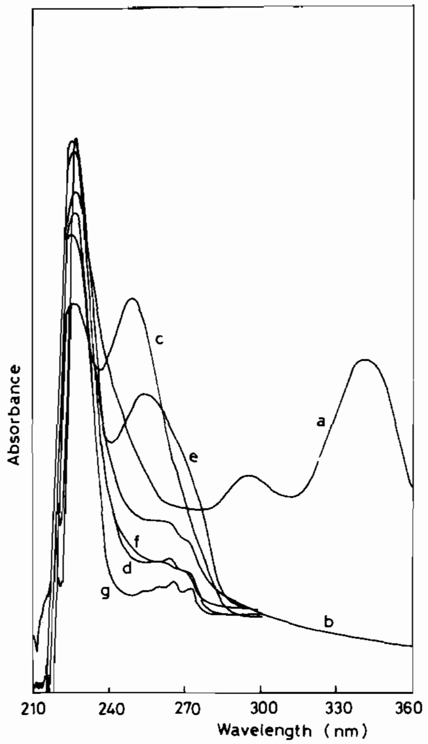


Fig. 1. UV spectra of: (a) $Ru(NS)Cl_3(AsPh_3)_2$; (b) $Ru(NS)Cl_3(AsPh_3)_2$ after exposure to the UV radiation; (c) $AsPh_3$; (d) $AsPh_3$ after exposure to the UV radiation; (e) $SbPh_3$; (f) $SbPh_3$ after exposure to the UV radiation; (g) $O{=}PPh_3$.

F. Reactions of $NOBr_3$ with $Ru(NS)Cl_3L_2$ or $Ru(NS)Br_2ClL_2$ ($L = PPh_3, AsPh_3$) in the Presence of L. Formation of Complexes of $Ru(NO)Br_2ClL_2$ or $Ru(NO)Br_3L_2$

Reactions were carried out by methods similar to that given in D or E except that $NOBr_3$ solution in dichloromethane was used in place of NOBr. $Ru(NS)Cl_3L_2$ and $Ru(NS)Br_2ClL_2$ gave $Ru(NO)Br_2ClL_2$ and $Ru(NO)Br_3L_2$, respectively.

G. Reactions of N_2O_3 with $Ru(NS)Cl_3L_2$ or $Ru(NS)Br_2ClL_2$ in the Presence of an Excess L

N_2O_3 gas was bubbled through a 50 ml dichloromethane solution of the complex for ten minutes and the mixture was subsequently stirred for 30 minutes. 100 ml of methanol was added to the resulting solution, followed by approximately 7 mmol of L. The solution was then heated on a water bath for about 10 minutes, whereby the product appeared as shining crystals which were separated as given in F. The complexes were recrystallized by dissolving in 50 ml of dichloromethane and adding 100 ml of hot methanol. $Ru(NS)Cl_3L_2$ and $Ru(NS)Br_2ClL_2$ gave $Ru(NO)Cl_2(NO_3)L_2$ and $Ru(NO)ClBr(NO_3)L_2$, respectively.

Photolysis Experiments

Following preliminary experiments of photolysis of MPh_3 (M = P, As, Sb) and $Ru(NS)Cl_3(AsPh_3)_2$ were also carried out.

(i) Photolysis of PPh_3, $AsPh_3$ or $SbPh_3$

Three separate very dilute solutions of MPh_3 (M = P, As, Sb) in CH_2Cl_2 were prepared and their electronic spectra (A) (Fig. 1) in the UV region (200–400 nm) were recorded. The solutions were photolysed with a UV lamp ($\lambda = 376$ nm) for about 10 minutes and their spectra (B) were recorded in the UV region (Fig. 1). The solutions of MPh_3 were evaporated to dryness before exposing them to the UV radiation (solid C), and also after exposing them to the UV radiation (solid D). The melting points and other analytical and physical data of solids C and D correspond to those of MPh_3 and $O{=}MPh_3$, respectively.

The UV spectra of very dilute solution of $O{=}PPh_3$ were also recorded (Fig. 1) and compared with those of MPh_3 after exposure to UV radiations (spectra B). The spectra were found to be identical.

(ii) Photolysis of $Ru(NS)Cl_3(AsPh_3)_2$ in the Presence of Excess of $SbPh_3$. Formation of $Ru(NS)Cl_3(AsPh_3)(SbPh_3)$

Approximately one mmol of $Ru(NS)Cl_3(AsPh_3)_2$ and six mmol of $SbPh_3$ were dissolved in 50 ml of dichloromethane and irradiated with a 376 nm UV source for one hour. 100 ml of methanol was added to the resulting solution and kept for 15 minutes, whereupon shining brown crystals of $Ru(NS)Cl_3(AsPh_3)_2(SbPh_3)$ appeared. These crystals were filtered, washed with methanol and ether, and dried *in vacuo*.

After evaporation of the filtrate under reduced pressure at room temperature and fractional crystallization, a white solid was obtained which was identified as $O{=}AsPh_3$ after comparing with a standard sample.

The analyses of the complexes for halogens, phosphorus, arsenic and sulfur were carried out by standard methods [18]. Carbon, hydrogen and nitrogen analyses were carried out by the Microanalytical section of the Indian Institute of Technology, Kanpur, India.

Infrared spectra of the complexes were recorded with a Perkin Elmer Model-580 Infrared Diffraction Grating Spectrophotometer in the region 4000–200 cm^{-1}. Samples were prepared as KBr pellets. Ultraviolet spectra were recorded with a Cary model-17 recording spectrophotometer. X-ray powder diffraction pattern of the complexes were recorded with General Electric XRD-6/diffractometer. Conductivity measurements were made on an Elico conductivity meter type CM-80 of milimolar solutions in nitro-

TABLE 1. Elemental Analyses of the Complexes (Numbers in Parenthesis are Calculated Values).

Compound	C	H	N	X	S	P/As
Ru(NS)Cl$_3$(PPh$_3$)$_2$	55.8	3.7	1.8	13.9	4.0	7.9
	(55.6)	(3.9)	(1.8)	(13.7)	(4.1)	(8.0)
Ru(NS)Br$_2$Cl(PPh$_3$)$_2$	49.8	3.7	1.8	22.1	3.5	7.3
	(49.9)	(3.5)	(1.6)	(22.5)	(3.7)	(7.1)
Ru(NS)Cl$_3$(AsPh$_3$)$_2$	49.7	3.6	1.8	12.4	3.5	17.0
	(49.9)	(3.5)	(1.6)	(12.3)	(3.7)	(17.3)
Ru(NS)Br$_2$Cl(AsPh$_3$)$_2$	45.1	3.4	1.4	20.0	3.6	15.4
	(45.3)	(3.2)	(1.5)	(20.4)	(3.4)	(15.7)
Ru(NS)Cl$_3$(PPh$_3$)AsPh$_3$)	52.7	3.5	1.9	13.0	3.9	
	(52.6)	(3.7)	(1.7)	(12.9)	(3.9)	
Ru(NS)Cl$_3$(AsPh$_3$)(SbPh$_3$)	47.1	3.5	1.6	11.8	3.4	
	(47.4)	(3.3)	(1.5)	(11.6)	(3.5)	
Ru(NO)Cl$_3$(PPh$_3$)$_2$	56.6	4.2	1.6	14.0		7.9
	(56.7)	(4.0)	(1.8)	(13.9)		(8.1)
Ru(NO)Cl$_3$(AsPh$_3$)(SbPh$_3$)	48.4	3.6	1.4	12.0		
	(48.2)	(3.4)	(1.6)	(11.9)		
Ru(NO)Cl$_3$(PPh$_3$)(SbPh$_3$)	50.9	3.7	1.4	12.3		
	(50.7)	(3.5)	(1.6)	(12.5)		
Ru(NO)Cl$_3$(PPh$_3$)(AsPh$_3$)	53.3	3.9	1.6	13.4		
	(53.6)	(3.7)	(1.7)	(13.2)		
Ru(NO)Cl$_3$(PPh$_3$)(Py)	47.9	3.5	4.6	18.5		5.2
	(47.7)	(3.5)	(4.8)	(18.4)		(5.3)
Ru(NO)BrCl$_2$(PPh$_3$)(Py)	44.1	3.4	4.7	24.0		4.8
	(44.3)	(3.2)	(4.5)	(24.2)		(5.0)
Ru(NO)Cl$_3$(AsPh$_3$)$_2$	50.5	3.7	1.5	12.7		17.3
	(50.9)	(3.5)	(1.6)	(12.5)		(17.6)
Ru(NO)Cl$_3$(AsPh$_3$)(Py)	44.2	3.6	4.3	17.2		11.8
	(44.3)	(3.2)	(4.5)	(17.1)		(12.0)
Ru(NO)BrCl$_2$(AsPh$_3$)(Py)	41.0	2.8	4.1	22.4		10.9
	(41.4)	(3.0)	(4.2)	(22.6)		(11.2)
Ru(NO)Cl$_2$(NO$_3$)(AsPh$_3$)$_2$	49.0	3.2	3.4	8.3		17.0
	(49.3)	(3.4)	(3.2)	(8.1)		(17.1)
Ru(NO)BrCl(NO$_3$)(AsPh$_3$)$_2$	47.0	3.5	3.1	12.4		16.1
	(46.9)	(3.3)	(3.0)	(12.5)		(16.3)
Ru(NO)Cl$_2$(NO$_3$)(PPh$_3$)$_2$	54.6	3.7	3.8	9.2		7.6
	(54.8)	(3.8)	(3.5)	(9.0)		(7.8)
Ru(NO)BrCl(NO$_3$)(PPh$_3$)$_2$	52.0	3.4	3.5	13.6		7.1
	(51.9)	(3.6)	(3.4)	(13.8)		(7.4)
Ru(NO)BrCl$_2$(AsPh$_3$)$_2$	48.6	3.5	1.5	17.0		16.5
	(48.3)	(3.4)	(1.6)	(16.9)		(16.7)
Ru(NO)Br$_2$Cl(AsPh$_3$)$_2$	46.0	3.1	1.5	20.5		
	(46.1)	(3.2)	(1.5)	(20.8)		
Ru(NO)Br$_3$(AsPh$_3$)$_2$	44.1	3.4	1.5	24.2		15.0
	(44.0)	(3.1)	(1.4)	(24.4)		(15.2)
Ru(NO)BrCl$_2$(PPh$_3$)$_2$	53.4	3.5	1.5	18.6		
	(53.6)	(3.7)	(1.7)	(18.7)		
Ru(NO)Br$_2$Cl(PPh$_3$)$_2$	50.6	3.5	1.5	22.6		
	(50.8)	(3.6)	(1.6)	(22.9)		
Ru(NO)Br$_3$(PPh$_3$)$_2$	48.1	3.6	1.5	26.5		
	(48.3)	(3.6)	(1.6)	(26.8)		

benzene. Magnetic measurements were carried out using a Gouy balance at room temperature. All the compounds are found to be nonconducting and diamagnetic.

Results and Discussion

The reactions of RuBr$_2$(PPh$_3$)$_3$ and RuCl$_2$(PPh$_3$)$_3$ with (NSCl)$_3$ yield diamagnetic complexes Ru(NS)-

TABLE II. Color, m.p. and Important I.R. Frequencies of the Complexes.

Compound	Color	M.P.[a] °C	νNS cm^{-1}	νNO cm^{-1}	Other important I.R. frequencies in cm^{-1}
$Ru(NS)Cl_3(PPh_3)_2$	Reddish brown	197–8	1310		
$Ru(NS)Br_2Cl(PPh_3)_2$	Reddish brown	195–6	1308		
$Ru(NS)Cl_3(AsPh_3)_2$	Reddish brown	>260	1305		
$Ru(NS)Br_2Cl(AsPh_3)_2$	Reddish brown	>260	1300		
$Ru(NS)Cl_3(PPh_3)(AsPh_3)$	Reddish brown	247–8	1300		
$Ru(NS)Cl_3(AsPh_3)(SbPh_3)$	Reddish brown	218–20	1299		
$Ru(NO)Cl_3(PPh_3)_2$	Orange	245		1875	
$Ru(NO)Cl_3(AsPh_3)(SbPh_3)$	Orange	decomp. 230		1830	
$Ru(NO)Cl_3(PPh_3)(SbPh_3)$	Orange	230		1832	
$Ru(NO)Cl_3(PPh_3)(AsPh_3)$	Orange	>260		1872	
$Ru(NO)Cl_3(PPh_3)(Py)$	Reddish brown	224–6		1863	1600, 1450, 1220, 1068
$Ru(NO)BrCl_2(PPh_3)(Py)$	Reddish brown	222–4		1862	1600, 1450, 1220, 1068
$Ru(NO)Cl_3(AsPh_3)_2$	Orange	>260		1875	
$Ru(NO)Cl_3(AsPh_3)(Py)$	Reddish brown	>260		1855	1600, 1450, 1665
$Ru(NO)BrCl_2(AsPh_3)(Py)$	Reddish brown	>260		1854	1598, 1397, 1068
$Ru(NO)Cl_2(NO_3)(AsPh_3)_2$	Orange	>260		1874	1518, 1269, 985
$Ru(NO)BrCl(NO_3)(AsPh_3)_2$	Orange	>260		1869	1510, 1267, 980
$Ru(NO)Cl_2(NO_3)(PPh_3)_2$	Orange	238–40		1873	1515, 1272
$Ru(NO)BrCl(NO_3)(PPh_3)_2$	Orange	237		1873	1515, 1271
$Ru(NO)BrCl_2(AsPh_3)_2$	Orange	>260		1870	
$Ru(NO)Br_2Cl(AsPh_3)_2$	Orange	>260		1869	
$Ru(NO)Br_3Cl(AsPh_3)_2$	Orange	>260		1869	
$Ru(NO)BrCl_2(PPh_3)_2$	Orange	242–3		1874	
$Ru(NO)Br_2Cl(PPh_3)_2$	Orange	242		1874	
$Ru(NO)Br_3(PPh_3)_2$	Orange	239–40		1872	

[a] Melting points are taken on a Fischer-Johns melting point apparatus and are uncorrected.

$ClBr_2(PPh_3)_2$ and $Ru(NS)Cl_3(PPh_3)_2$. When the latter is refluxed with $AsPh_3$ in chloroform one molecule of PPh_3 is substituted by $AsPh_3$ producing a mixed ligand complex $Ru(NS)Cl_3(PPh_3)(AsPh_3)$. Their IR spectra show bands around 1310 cm^{-1} and 330 cm^{-1} assigned to $\nu(NS^+)$ and terminal $\nu(RuCl)$, respectively, in addition to all the characteristic bands of PPh_3 and $AsPh_3$. This suggests the oxidation state of ruthenium at +2, which is also corroborated by diamagnetism. The reactions of $RuX_3(AsPh_3)_2\cdot MeOH$ ($X = Cl$, Br) are, however, slightly complicated. Both result in an oily mass which could not be crystallized under any conditions. Presumably the oil is a mixture of a number of complexes along with a pentacoordinated one, indicated by the fact that the addition of any ligand like $SbPh_3$, $AsPh_3$, *etc.* to the reaction mixture yields shining crystals of the mixed ligand complex of the type $Ru(NS)X_3(AsPh_3)L$. Furthermore triphenylarsine sulfide is recovered from the filtrate after removing the oily mass. The IR spectra of the complex $Ru(NS)X_3(AsPh_3)L$ shows a band around 1300 cm^{-1} assigned to $\nu(NS^+)$. The characteristic bands of triphenylarsine, as well as those of L, also appear in the spectra.

Substitution reactions of $RuCl_3(NS)L_2$ ($L = PPh_3$, $AsPh_3$) with various other ligands proceeded *via* dissociative mechanisms to form a five-coordinated intermediate $Ru(NS)Cl_3L$, supported by the photolytic studies of these compounds in the UV region. Figure 2(a) and (b) illustrate the difference in the UV spectra of $Ru(NS)Cl_3(PPh_3)_2$ in dichloromethane before and after exposing the solution with UV radiation. The intensities of the bands at 333 nm and 293 nm present in the spectrum of the compound before exposure are reduced drastically after exposing with UV radiations, and new bands appeared at 272 nm, 265 nm and 259 nm. The change is found to be irreversible indicating the formation of some new species. It was further observed that the UV spectrum of the photolyzed Ru(NS)-

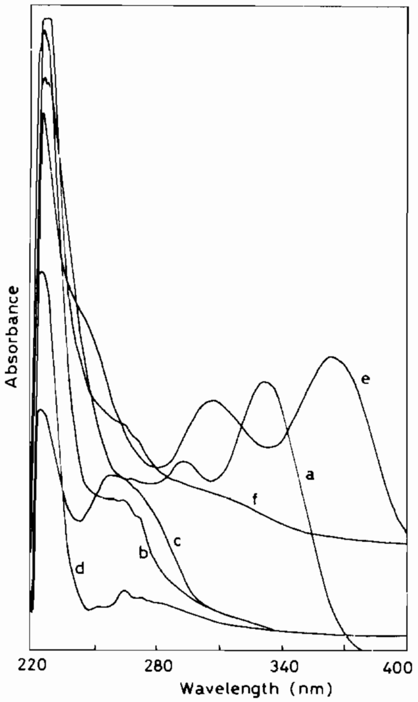


Fig. 2. UV spectra of: (a) $Ru(NS)Cl_3(PPh_3)_2$; (b) $Ru(NS)Cl_3(PPh_3)_2$ after exposure to the UV radiation; (c) PPh_3; (d) PPh_3 after exposure to the UV radiation; (e) $Ru(NS)Cl_3(AsPh_3)(SbPh_3)$; (f) $Ru(NS)Cl_3(AsPh_3)(SbPh_3)$ after exposure to the UV radiation.

$Cl_3(PPh_3)_2$ matches with that of the phosphine oxide (Fig. 1(g)). Similar changes are also observed in the spectra of PPh_3 before and after exposing its solution in dichloromethane to UV radiation. Furthermore, $OPPh_3$ is recovered from a slightly concentrated solution of PPh_3 after irradiation for about 30 minutes. It thus appears that the irradiation catalyzes the oxidation of PPh_3. Since the photolyzed products of $Ru(NS)Cl_3(PPh_3)_2$ give practically the same spectra as that of $OPPh_3$, one of the phosphine molecules in the complex presumably is photolabile, which after dissociation gets oxidized to $OPPh_3$, leaving a pentacoordinated species in solution.

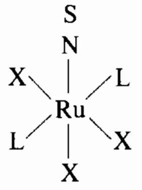
$$Ru(NS)Cl_3(PPh_3)_2 \rightleftharpoons Ru(NS)Cl_3(PPh_3) + PPh_3 \xrightarrow[O_2]{h\nu} Ru(NS)Cl_3(PPh_3) + OPPh_3$$

Identification of the photolytic products of $Ru(NS)Cl_3(AsPh_3)_2$ and $Ru(NS)Cl_3(AsPh_3)(SbPh_3)$ in dichloromethane solution after irradiation match with the literature reported UV spectra of $OAsPh_3$ and $OSbPh_3$, respectively [19, 20]. The formation of five coordinated species after irradiation is also confirmed by photolyzing a dichloromethane solution of $Ru(NS)Cl_3(AsPh_3)_2$ in the presence of an excess of $SbPh_3$ for a longer period, whereupon a mixed ligand thionitrosyl complex $Ru(NS)Cl_3(AsPh_3)(SbPh_3)$ is separated after irradiation. The analytical and IR data of the compound are identical to those of one obtained thermally.

The thionitrosyl group in the thionitrosyl complexes is found to be substituted by NO when they are treated with NOX (X = Cl, Br, Br_3, NO_2). However, the complex could not be separated out from the solution unless a minimum of ten-fold of some coordinating ligand ($AsPh_3$, $SbPh_3$, Py, *etc.*) is added to the solution, whereby mixed ligand complexes of the type $RuX_3(NO)PPh_3(L)$ are separated out. It appears that in these reactions a five coordinated species also is forming, which could not be separated [21, 22]. It is possible to prepare a number of mixed ligand complexes of the type $Ru(NO)X_3LL'$ with the help of this method. One of the interesting new compounds prepared by this method is $Ru(NO)(NO_3)X_2L_2$ by treatment of a suitable thionitrosyl with N_2O_3. In addition, the number of bromides substituted in the complex $Ru(NO)X_3L_2$ is found to be more when $NOBr_3$ was used as nitrosylating agent.

Structure of Thionitrosyls

X-ray powder pattern data showed that all the thionitrosyls $Ru(NS)X_nY_{3-n}LL'$ (X or Y = Cl or Br; LL' = PPh_3, $AsPh_3$, $SbPh_3$) were found to be isomorphous with $Ru(NO)Cl_3(PPh_3)_2$ whose structure has been previously determined [23]. It is therefore possible to assign the following structure to all the thionitrosyls:



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