Reactivity of $RuCl_3(EPh_3)_2S$ (E=P, As; S=DMSO, DMF, THF, CH_3CHO, CH_3CN, CS_2, $(CH_3)_2CO$) towards 2,4,6-Trichloro-1,3,5,2,4,6-trithiatriazine and Substitution Reactions of $Ru(NS)Cl_3(EPh_3)(E'Ph_3)$(E=P, As; E′=P, As, Sb) with N-Donor Heterocyclic Ligands

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Synopsis. 2,4,6-Trichloro-1,3,5,2,4,6-trithiatriazine, $N_3S_3Cl_3$, reacts with Ru(III) complexes of the type $RuCl_3(EPH_3)_2S$ to form an intermediate which further reacts with PPh_3, $AsPh_3$, and $SbPh_3$ to form $Ru(NS)Cl_3(EPh_3)_2$ or $Ru(NS)Cl_3(EPh_3)(E'Ph_3)$. Besides, substitution reactions of $Ru(NS)Cl_3(EPh_3)_2$ and $Ru(NS)Cl_3(EPh_3)(E'Ph_3)$ with pyridine, γ-picoline, pyrazine, and pyrazole have been carried out. The compounds were characterized by physicochemical methods.

2,4,6-Trichloro-1,3,5,2,4,6-trithiatriazine, $N_3S_3Cl_3$, is air sensitive and unstable in different solvents. It interacts with metal salts or complexes affording various interesting products containing NS^+, N_2S_2, $N_2S_2^{2-}$, $N_3S_2^{3-}$, $NSCl^{2-}$, NSCl, etc. as coligands.[1–7] The use of $N_3S_3Cl_3$ as a synthetic reagent for thionitrosyl complexes depends upon the reaction conditions and no definite suggestion has yet been made in this direction. The problem is, therefore, still in an embryonic state. Since we are interested in the metal thionitrosyl synthesis, we have chosen ligand-exchange reactions as a possible potential route for their synthesis. This communication reports the reactions of $N_3S_3Cl_3$ with ruthenium complexes having coordinated solvent molecules. Substitution reactions of $Ru(NS)Cl_3(EPh_3)_2$ and $Ru(NS)Cl_3(EPh_3)(E'Ph_3)$ (E=P, As; E′=P, As, Sb) with N-donor heterocyclic bases and their interconversion reactions with $E''Ph_3$ (E″=P, As, Sb) have also been described.

Experimental

All the chemicals used were of Analar or chemically pure grade. Solvents were dried prior to use by the conventional methods. 2,4,6-Trichloro-1,3,5,2,4,6-trithiatriazine and $RuCl_3(EPh_3)_2S$ (E=P, As; S=DMSO, DMF, THF, CS_2, $(CH_3)_2CO$, CH_3CN, CH_3CHO) were prepared by the literature methods.[8,9]

Reactions. (A) Reactions of $N_3S_3Cl_3$ with $RuCl_3(EPh_3)_2S$ (E=P, As; S=DMSO, DMF, THF, CH_3CN, CH_3CHO, CS, $(CH_3)_2CO$). A typical reaction has been carried out as follows. A saturated mint-green solution of trichlorotrithiatriazine in THF (10 ml) was added with stirring to a solution of $RuCl_3(EPh_3)_2S$ (ca. 0.26 mmol) in 40 ml of dichloromethane. The stirring was continued for an hour. A red colored solution was obtained, 50 ml of methanol was added to it, followed by the addition of EPh_3 (ca. 0.06 mmol) whereupon a brown microcrystalline compound was obtained which was separated, washed with methanol, water, methanol, and finally with ether. It was dried under vacuum (yield, ca. 70%). The analytical data corresponded with the formula given in Table 1.

The same compounds $Ru(NS)Cl_3(EPh_3)_2$ were also obtained, though in low yields, using zinc as reducing agent[†] in place of the EPh_3.

(B) Reactions of $Ru(NS)Cl_3(EPh_3)(E'Ph_3)$(E=P, As; E′=P, As, Sb) with Heterocyclic Bases L (L=Pyridine, γ-Picoline, Pyrazine, Pyrazole). (i) $Ru(NS)Cl_3(EPh_3)(E'Ph_3)$ (ca. 0.14 mmol) in 40 ml of chloroform was refluxed with the heterocyclic base (ca. 0.4 mmol) for a few hours (cf. Table 1) whereby the color of the solution was changed from orange to red-brown. The resulting solution was concentrated to about 10 ml. The addition of petroleum ether (40—60 °C) to the concentrate yielded a compound which was separated. It was recrystallized 2—3 times from benzene/petroleum ether (40—60 °C).

(ii) A solution of $Ru(NS)Cl_3(EPh_3)(E'Ph_3)$ (ca. 0.12 mmol), and base (0.7 mmol) in 40 ml of chloroform was refluxed for a few hours. The resulting solution was concentrated to nearly half its volume, followed by the addition of hexane whereby a compound was precipitated. It was separated, thoroughly washed with benzene, ether and recrystallized several times with dichloromethane/hexane.

The reactions described in section B were also carried out in benzene yielding the same compounds.

Measurements. The measurements on the complexes and the analyses were done as reported elsewhere.[10,11] These data matched extremely well with the formula of the complexes given in Table 1.

Results and Discussion

Reactions of $N_3S_3Cl_3$ with $RuCl_3(EPh_3)_2S$ (E=P, As; S=CH_3CHO, DMSO, DMF, THF, CH_3CN) yielded yellowish brown literature known diamagnetic complexes $Ru(NS)Cl_3(EPh_3)_2$[11] freely soluble in halohydrocarbons. Their purity were tested by TLC and by comparing their physical data (mp, mixed mp, X-ray powder pattern, and other spectral data) with those of the authentic sample. Their identical nature with the authentic samples were further confirmed by (1) their IR spectra which displayed the expected band around 1310 cm^{-1} attributable to terminal $(NS)^+$ group besides the characteristic bands of EPh_3 (E=P, As, Sb) and by (2) ^{31}P NMR data[12] (δ 13.3).

X-Ray powder diffraction data of these substituted complexes were carried out and compared with the powder pattern of $Ru(NS)Cl_3(PPh_3)_2$. Both the compounds were found to be isomorphous. $Ru(NS)Cl_3(PPh_3)_2$ was an octahedral complex with two phosphines trans to each other which was confirmed by the X-ray crystal structure of isomorphous osmium analogue.[13] We assumed that the substituted products

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[†] In the reactions of $RuCl_3(EPh_3)_2S$ (S=DMSO, DMF, CS_2) with $N_3S_3Cl_3$, the solution obtained after stirring and zinc reduction yielded $Ru(NS)Cl_3(EPh_3)_2$ as a precipitate in a very low yield and from the filtrate after its concentration, a black material obtained. The black material was not charaterized.

Table 1. Thionitrosyl Complexes of Ruthenium(II). Characterization Data of Complexes

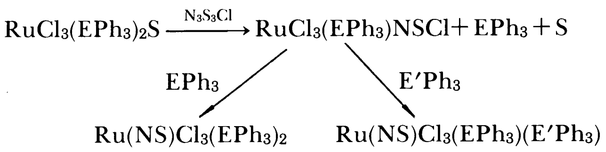
Sl. No.	Reactant (Procedure)	Ligand	Time for refluxing	Product Color, Mp/°C	IR $\nu(NS)^+$ /cm^{-1}	^{31}P NMR δ/ppm
1.	$RuCl_3(PPh_3)_2S$ (A)	PPh_3	—	$Ru(NS)Cl_3(PPh_3)_2$ B 176	1316	13.3
2.	$RuCl_3(AsPh_3)_2S$ (A)	$AsPh_3$	—	$Ru(NS)Cl_3(AsPh_3)_2$ B >280	1310	—
3.	$RuCl_3(PPh_3)_2S$ (A)	$AsPh_3$	—	$Ru(NS)Cl_3(PPh_3)(AsPh_3)$ B 245—247	1305	13.2
4.	$RuCl_3(AsPh_3)_2S$ (A)	$SbPh_3$	—	$Ru(NS)Cl_3(AsPh_3)(SbPh_3)$ B 220	1300	—
5.	$Ru(NS)Cl_3(AsPh_3)(PPh_3)^{b)}$	$PPh_3{}^{a)}$	1	$Ru(NS)Cl_3(PPh_3)_2$ B 176	1316	13.3
6.	$Ru(NS)Cl_3(PPh_3)_2{}^{b)}$	$AsPh_3{}^{a)}$	8	$Ru(NS)Cl_3(PPh_3)(AsPh_3)$ B 245—247	1305	13.2
7.	$Ru(NS)Cl_3(AsPh_3)_2{}^{b)}$	$PPh_3{}^{a)}$	2	$Ru(NS)Cl_3(PPh_3)_2$ B 176	1316	13.3
8.	$Ru(NS)Cl_3(AsPh_3)(PPh_3)^{b)}$	$AsPh_3{}^{a)}$	48	$Ru(NS)Cl_3(AsPh_3)_2$ B >280	1310	—
9.	$Ru(NS)Cl_3(AsPh_3)(SbPh_3)^{b)}$	$AsPh_3{}^{a)}$	3	$Ru(NS)Cl_3(AsPh_3)_2$ B >280	1310	—
10.	$Ru(NS)Cl_3(AsPh_3)(SbPh_3)^{b)}$	$PPh_3{}^{a)}$	1	$Ru(NS)Cl_3(AsPh_3)(PPh_3)$ B 245—247	1305	13.2
11.	$Ru(NS)Cl_3(AsPh_3)(SbPh_3)^{b)}$	$SbPh_3{}^{a)}$	36	Mixture of products	—	
12.	$Ru(NS)Cl_3(PPh_3)_2{}^{b)}$	$SbPh_3{}^{a)}$	36	Mixture of products	—	
13.	$Ru(NS)Cl_3(PPh_3)_2$ (B, i)	Py	2	$Ru(NS)Cl_3(PPh_3)(Py)$ Y 128	1310	13.0
14.	$Ru(NS)Cl_3(PPh_3)_2$ (B, i)	γ-Pic	2	$Ru(NS)Cl_3(PPh_3)(\gamma\text{-Pic})$ Y 125	1310	—
15.	$Ru(NS)Cl_3(PPh_3)_2$ (B, ii)	Pz	3	$Ru(NS)Cl_3(PPh_3)(Pz)$ B 195	1310	25.5
16.	$Ru(NS)Cl_3(PPh_3)_2$ (B, i)	Pa	3	$Ru(NS)Cl_3(PPh_3)(Pa)$ Y 140	1310	23.3
17.	$Ru(NS)Cl_3(AsPh_3)_2$ (B, i)	Py	3	$Ru(NS)Cl_3(AsPh_3)(Py)$ Y 125—128	1310	—
18.	$Ru(NS)Cl_3(AsPh_3)_2$ (B, i)	γ-Pic	3	$Ru(NS)Cl_3(AsPh_3)(\gamma\text{-Pic})$ Y 125	1310	
19.	$Ru(NS)Cl_3(AsPh_3)_2$ (B, i)	Pz	12	$Ru(NS)Cl_3(AsPh_3)(Pz)$ Y 280	1320	
20.	$Ru(NS)Cl_3(AsPh_3)_2$ (B, ii)	Pa	6	$Ru(NS)Cl_3(AsPh_3)(Pa)^{c)}$ G 175—178	1310	
21.	$Ru(NS)Cl_3(AsPh_3)(SbPh_3)$ (B, ii)	Pa	5	$Ru(NS)Cl_3(SbPh_3)(Pa)$ G 145	1310	
22.	$Ru(NS)Cl_3(AsPh_3)(SbPh_3)$ (B, i)	Py	3	$Ru(NS)Cl_3(AsPh_3)(Py)$ Y 128—130	1310	
23.	$Ru(NS)Cl_3(AsPh_3)(SbPh_3)$ (B, i)	γ-Pic	3	$Ru(NS)Cl_3(AsPh_3)(\gamma\text{-Pic})$ Y 125	1310	
24.	$Ru(NS)Cl_3(AsPh_3)(PPh_3)$ (B, i)	Py	3	$Ru(NS)Cl_3(AsPh_3)(Py)$ Y 128	1310	
25.	$Ru(NS)Cl_3(AsPh_3)(PPh_3)$ (B, i)	γ-Pic	3	$Ru(NS)Cl_3(AsPh_3)(\gamma\text{-Pic})$ Y 125	1310	
26.	$Ru(NS)Cl_3(AsPh_3)(PPh_3)$ (B, i)	Pa	4	$Ru(NS)Cl_3(AsPh_3)(Pa)$ B 175	1310	

B=Brown, Y=Yellow, G=Green, S=DMSO, DMF, THF, CH_3CN, CH_3CHO, $(CH_3)_2CO$, CS_2. Py=pyridine, γ-Pic=γ-picoline, Pa=pyrazole, Pz=pyrazine.

a) Molar ratio of reactant and ligand=1 : 5. b) Prepared by known literature method.[11] c) Mass spectra (FD) found.

of these completes were also octahedral in nature.

These reactions appeared to be slightly complicated and perhaps undergo through an intermediate formation. All efforts to isolate the intermediate in the pure solid form were unsuccessful. Although the solutions, obtained after the initial $N_3S_3Cl_3$ reactions with ruthenium complexes yielded a precipitate with light petroleum ether but it became oily on purification through precipitation several times from different solvents. Possibly a coordinatively unsaturated Ru(III) complex is initially formed as an intermediate followed by its reduction with the formation of coordinatively saturated complex by linking with the ligand EPh_3 or $E'Ph_3$.



$$RuCl_3(EPh_3)_2S \xrightarrow{N_3S_3Cl} RuCl_3(EPh_3)NSCl + EPh_3 + S$$

$$RuCl_3(EPh_3)NSCl \xrightarrow{EPh_3} Ru(NS)Cl_3(EPh_3)_2 \qquad RuCl_3(EPh_3)NSCl \xrightarrow{E'Ph_3} Ru(NS)Cl_3(EPh_3)(E'Ph_3)$$

Interconversion reactions of $Ru(NS)Cl_3(EPh_3)_2$ or $Ru(NS)Cl_3(EPh_3)(E'Ph_3)$ with $E''Ph_3$ (E=P, As; E′=P, As, Sb; E″=P, As, Sb) led to the formation of $Ru(NS)Cl_3(EPh_3)(E''Ph_3)$, $Ru(NS)Cl_3(E'Ph_3)(E''Ph_3)$, or $Ru(NS)Cl_3(E''Ph_3)_2$ (cf. Table 1). These complexes exhibited similar analytical, spectral (IR, ^{31}P NMR etc.), chemical, and physical properties as those of the literature known complexes synthesized by photochemical process.[11] It suggested that these complexes are the substitution derivatives of $Ru(NS)Cl_3(EPh_3)_2$.

A chemically interesting feature of these interconversion reactions is the fact that the variation in the substitution reaction rates of $Ru(NS)Cl_3(EPh_3)(E'Ph_3)$ or $Ru(NS)Cl_3(EPh_3)_2$ with $E''Ph_3$ (E″=P, As, Sb) with respect to leaving ligand is in the order $PPh_3 < AsPh_3 < SbPh_3$. The reaction of $Ru(NS)Cl_3(PPh_3)_2$ with $AsPh_3$ resulted in the formation of $Ru(NS)Cl_3(AsPh_3)_2$ in 48 hours, on the other hand the reverse process, the formation of $Ru(NS)Cl_3(PPh_3)_2$ from $Ru(NS)Cl_3(AsPh_3)_2$ in presence of PPh_3 takes only two hours. $Ru(NS)Cl_3(AsPh_3)(SbPh_3)$ with $SbPh_3$ did not yield $Ru(NS)Cl_3(SbPh_3)_2$ even after a very long refluxing period. The reason for the variations in rates could be due to the differences in the σ-basic and π-acidic characters of the ligands ($PPh_3 > AsPh_3 > SbPh_3$). The kinetic and the thermodynamic stability of the complexes were in the order $PPh_3 > AsPh_3 > SbPh_3$ as reported elsewhere.[14] Owing to the weak σ-basic and π-acidic nature of $AsPh_3$ followed by that of $SbPh_3$, the Ru–As and Ru–Sb bonds should be relatively thermodynamically weaker than $Ru-PPh_3$ bond. Consequently the substitution rate with respect to leaving group should be $PPh_3 < AsPh_3 < SbPh_3$.

Substitution reactions of $Ru(NS)Cl_3(EPh_3)(E'Ph_3)$ with heterocyclic bases (L) viz. pyridine, γ-picoline, pyrazine, pyrazole led to the formation of $Ru(NS)Cl_3(EPh_3)L$ or $Ru(NS)Cl_3(E'Ph_3)L$. The IR spectra of these complexes exhibited characteristic bands due to vibrational modes of bases besides the bands due to $\nu(NS)^+$ around 1310 cm^{-1} and the characteristic bands of EPh_3. The moderately intense band around 320—290 cm^{-1} was assigned to ν(Ru–Cl).

The substitution reactions of $Ru(NS)Cl_3(EPh_3)(E'Ph_3)$ with bases like 2,2′-bipyridine and 1,10-phenanthroline failed. Inspite the change of solvents and the reaction periods, these reactions led to the formation of a mixture of products. Attempts to separate them were unsuccessful. The presence of different products were confirmed by ^{31}P NMR which displayed a number of bands. Efforts to synthesize bridged compounds with pyrazine were also unsuccessful and only monomers have been obtained.

The substitution of one PPh_3 molecule by heterocyclic base molecule depleted electron density at the ruthenium center through $d\pi$–$d\pi$ back bonding. As a consequence electron density available at ruthenium for $d\pi$–$d\pi$ back bonding towards the remaining PPh_3 molecule is reduced. This results in the reduction of net electron density at phosphorus causing a downfield shift of the ^{31}P NMR band (from δ 13 to δ 25), depending upon the nature of heterocyclic molecule attached to ruthenium. Triphenylphosphine molecules are trans to each other in $Ru(NS)Cl_3(PPh_3)_2$, replacement of one PPh_3 by heterocyclic base will lower the trans effect thereby strengthening the Ru–P bond by sigma bond formation. Thus formation of $P \rightarrow Ru$ σ bond and weaker $Ru \rightarrow P$ back bonding will result in the lower electron density at P and will cause the observed downfield shift.

The visible spectra of all the complexes exhibited a rather broad band around 450 nm. Since it is generally believed that (MLCT) transition in ruthenium +2 complexes occur under a broad band around 450—430 nm,[15] a similar band in the electronic spectra of our complexes suggested ruthenium in +2 oxidation state which was also confirmed by magnetic moment (diamagnetic). The electronic spectra of the starting complexes $RuCl_3(EPh_3)_2S$ showed bands in the region 620—350 nm.[16]

In conclusion, all the complexes found to be diamagnetic suggesting ruthenium in +2 oxidation state having (d^6) system.

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