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Thionitrosyl Complexes of Rhodium

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Reactions of trithiazyltrichloride with rhodium(I) carbonyl complexes gave carbonylthionitrosyl complexes, $[Rh(CO)(NS)Cl_2L]_2$ ($L = PPh_3$ or $AsPh_3$) which reacted with excess of triphenylphosphine and triphenylarsine to give $Rh(CO)(NS)Cl_2L_2$ and $Rh(CO)(NS)(PPh_3)_2$. Reactions of nitrosylhalides with these carbonylthionitrosyl complexes yielded carbonylnitrosyl complexes $[Rh(CO)(NO)ClXL_2]$ ($X = Cl, Br$; $L = PPh_3$ or $AsPh_3$). Their geometries have been proposed on the basis of the results of various physicochemical studies.

Introduction

In the past few years there has been a considerable upsurge in the study of transition metal thionitrosyl complexes [1–4]. Although the literature is replete with transition metal nitrosyl complexes, due to lack of reagents which can be utilized to introduce the thionitrosyl group on to a transition metal, analogous thionitrosyl complexes are less abundant. Only a few such complexes have been prepared by the reactions of elemental sulphur, propylene sulphide or disulfurdichloride with coordinated nitrido ligands [5–7] and by the reaction of trithiazyltrichloride with $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]$ [8] and $RuCl_3 \cdot xH_2O$, $OsCl_3$ in the presence of triphenylphosphine and triphenylarsine in tetrahydrofuran [9]. X-ray studies of $(\eta^5\text{-}C_5H_5)Cr(CO)_2NS$ [10, 11] and $Mo(NS)(S_2CNMe_2)_3$ [12] have indicated the mode of bonding of thionitrosyl group as terminal, linear with M–N–S angle 176.8(2)° and 172.0(7)° respectively. In a formal sense the thionitrosyl group can be considered to be bonded as NS^+. This paper describes the syntheses and characterizations of the carbonyl thionitrosyl complexes of rhodium. Their geometries have been proposed on the basis of the results of various physicochemical studies.

Experimental

All the reagents used were Analar or of chemically pure grade. The solvents were freshly distilled before use. Every reaction was carried out under pure, dry argon.

Carbonylchlorobis(triphenylphosphine)rhodium(I), carbonylchlorobis(triphenylarsine)rhodium(I), carbonyl hydrido tris(triphenylphosphine)rhodium(I), trithiazyltrichloride, nitrosyl chloride and nitrosylbromide were prepared according to the methods described in the literature [13–17].

Preparations of Complexes and Their Reactions

Preparation of Di-μ-chloro-bis(carbonylchlorothionitrosyl triphenylphosphine)rhodium(III) $[(Rh(CO)(NS)Cl_2(PPh_3)]_2$

(a) A solution of $(NSCl)_3$ in THF (20 ml) was slowly added with stirring to a solution of $Rh(CO)Cl(PPh_3)_2$ (0.2 g) in THF (10 ml) at room temperature. After the addition of $(NSCl)_3$ was complete (20 min), the mixture was further stirred for about an hour whereby the colour of the solution changed from brown to deep green. The solvent was removed completely under reduced pressure and the residue was extracted with benzene. On addition of petroleum ether (60–80°) to the extract, a green complex precipitated out which was washed several times with petroleum ether and water. It was dried in air and recrystallized with benzene–petroleum ether. A green complex $[Rh(CO)(NS)Cl_2(PPh_3)]_2$, thus obtained, was analysed (yield 24%).

On leaving the green reaction mixture, obtained after stirring for one hour in the above reaction at room temperature for four hours, the colour of the solution was changed from green to brown from which the complex $Rh(CO)(NS)Cl_2(PPh_3)_2$ was obtained by a similar procedure as given in (a).

b) A saturated solution of $(NSCl)_3$ in CCl_4 (15 ml) was slowly added with stirring to a solution of $RhH(CO)(PPh_3)_3$ (0.2 g) in chloroform (10 ml) at room temperature. After the addition of $(NSCl)_3$ was complete, the mixture was further stirred for about an hour whereby the colour of the solution changed from brown to deep green, from which the green complex was separated by a similar procedure as given in (a).

Preparation of Di-μ-chloro-bis(carbonyl-chlorothionitrosyltriphenylarsine rhodium(III) [Rh(CO)(NS)Cl$_2$(AsPh$_3$)]$_2$

A solution of $(NSCl)_3$ in THF (20 ml) was slowly added with stirring to a solution of Rh(CO)Cl(AsPh$_3$)$_2$ (0.2 g) in THF (10 ml) at room temperature. After the addition of $(NSCl)_3$ solution was complete, the mixture was further stirred for about 1.5 hours whereby the colour of solution changed from brown to yellowish green. The yellowish green complex [Rh(CO)(NS)Cl$_2$(AsPh$_3$)]$_2$ was obtained by a similar procedure as in (a). It was recrystallised from benzene–petroleum ether.

On leaving for twenty hours the yellowish-green mixture which was obtained after stirring for one and a half hours in the above reaction, the colour of the solution changed from yellowish green to red-brown from which a red-brown complex Rh(CO)(NS)Cl$_2$(AsPh$_3$)$_2$ was obtained by a similar procedure as given in (a).

Preparation of carbonyl dichloro thionitrosyl bis(triphenylphosphine)rhodium(III) Rh(CO)(NS)Cl$_2$(PPh$_3$)$_2$

Triphenylphosphine (0.5 g) was dissolved in 20 ml of a dichloromethane solution of [Rh(CO)(NS)Cl$_2$(PPh$_3$)]$_2$ (0.2 g). The resulting solution was stirred for 2 hours at room temperature whereby the colour of the solution changed from green to red-brown. On addition of diethyl ether, a brown complex Rh(CO)(NS)Cl$_2$(PPh$_3$)$_2$·0.5CH$_2$Cl$_2$ precipitated which was recrystallized from benzene–diethylether. The crystallized product analysed as Rh(CO)(NS)Cl$_2$(PPh$_3$)$_2$.

Preparation of carbonyl thionitrosyl bis(triphenylphosphine)rhodium(I) Rh(CO)(NS)(PPh$_3$)$_2$

Triphenylphosphine (0.5 g) was dissolved in 10 ml dichloromethane solution of [Rh(CO)(NS)Cl$_2$(PPh$_3$)]$_2$ (0.1 g). The resulting solution was refluxed for 50 min whereby the colour of the solution changed from green to red-brown. On addition of hot ethanol (10 ml) followed by reducing the volume of the solution to about 5 ml, red-brown shining crystals of Rh(CO)(NS)(PPh$_3$)$_2$ separated which were centrifuged, washed with diethylether and dried in air.

Preparation of carbonyl dichlorothionitrosyl-bis(triphenylarsine)rhodium(III) Rh(CO)(NS)Cl$_2$(AsPh$_3$)$_2$

Triphenylarsine (0.6 g) was added to a yellowish green solution prepared by dissolving 0.2 g of [Rh(CO)(NS)Cl$_2$(AsPh$_3$)]$_2$ in dichloromethane (20 ml). The solution was refluxed for 3 h whereby the colour of the solution became red-brown. On addition of diethyl ether, a red brown complex Rh(CO)(NS)Cl$_2$(AsPh$_3$)$_2$·0.5CH$_2$Cl$_2$ separated which was centrifuged, washed with ether and dried under vacuum. The recrystallization of Rh(CO)(NS)Cl$_2$(AsPh$_3$)$_2$·0.5CH$_2$Cl$_2$ from benzene–ether gave Rh(CO)(NS)Cl$_2$(AsPh$_3$)$_2$.

Rh(CO)(NS)Cl$_2$(AsPh$_3$)$_2$ was also obtained as a result of reaction of [Rh(CO)(NS)Cl$_2$(PPh$_3$)]$_2$ with triphenylarsine in dichloromethane.

Reaction of [Rh(CO)(NS)Cl$_2$L$_2$] (L = PPh$_3$ or AsPh$_3$) with nitrosylchloride

A saturated solution of nitrosyl chloride in dichloromethane (10 ml) was added dropwise to 20 ml of a stirred solution of [Rh(CO)(NS)Cl$_2$L$_2$] (L = PPh$_3$ or AsPh$_3$) (0.2 g) in dichloromethane. The reaction mixture was refluxed for 30 min followed by an addition of hot methanol (30 ml). Fine yellow crystals of Rh(CO)(NO)Cl$_2$L$_2$ separated which were centrifuged, washed with methanol, ether and dried under vacuum.

Reaction of [Rh(CO)(NS)Cl$_2$L$_2$] (L = PPh$_3$ or AsPh$_3$) with nitrosylbromide

2 ml solution of NOBr (*ca.* 2*M*) in dichloromethane was added dropwise to 20 ml of a dichloromethane solution of Rh(CO)(NS)Cl$_2$L$_2$ (0.2 g). The reaction mixture was refluxed for 30 min followed by an addition of hot methanol (50 ml). Orange crystals of Rh(CO)(NO)ClBrL$_2$ (L = PPh$_3$, AsPh$_3$) were separated out which were centrifuged, washed with methanol, ether and dried under vacuum.

Analyses

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

For the estimation of phosphorus and arsenic, samples were decomposed with sodium peroxide, sugar and sodium nitrate in ratio 20:1:3 in a Parr bomb crucible, extracting the melt with water. A few ml of concentrated H$_2$SO$_4$ was added to the water extract which was heated to sulfur trioxide fumes. It was diluted with water and filtered if necessary. In this solution phosphorus was estimated as phosphoammonium molybdate. For estimation of arsenic, the above solution was diluted to 100 ml and 25 ml of the solution was taken in a 250 ml conical flask. 40 ml water, 5 g sodium bicarbonate and 2 ml of starch solution were added. The solution was swirled until the sodium hydrogen carbonate has dissolved. It was titrated slowly with the standard iodine solution to the first blue colour.

In order to estimate rhodium [19], samples were decomposed with concentrated sulphuric acid and concentrated nitric acid. The solution was evaporated to dryness and extracted with water. Rhodium was estimated in the water extract as $[Co(NH_3)_6]^{3+}$-$[Rh(NO_2)_6]^{3-}$.

The percentage of sulphur in the samples were determined by first decomposing with KNO_3 and KOH (8 times and 64 times, respectively, of the amount of sample) in a nickel crucible for about 10 minutes and cooled. It was extracted with water and acidified with HCl. Sulphur was estimated as barium sulfate. Analytical data for the complexes is listed in Table I.

Spectra of the compounds were recorded with a Perkin-Elmer Model-580 Infrared Diffraction Grating Spectrophotometer in the 4000–200 cm^{-1} range. Samples were prepared as KBr pellets and CsI pellets. Conductivity measurements of the compounds were made on an Elico conductivity meter type CM-80 of Millimolar solutions in nitrobenzene. All the compounds are found to be non-conducting. The electronic spectra were recorded in chloroform solutions using a Cary Model-17 recording spectrophotometer. These measurements were made using a Gouy balance at room temperature (25 °C).

Results and Discussion

Trithiazyltrichloride reacts with carbonyl chlorobis(triphenylphosphine)rhodium(I) giving an air stable green solid of empirical formula $Rh(CO)(NS)Cl_2(PPh_3)$ which is also prepared by treating $RhH(CO)(PPh_3)_3$ with a solution of trithiazyltrichloride in THF.

$$Rh(CO)Cl(PPh_3)_2 + \frac{1}{3}(NSCl)_3 \xrightarrow{THF} \underset{\mathrm{I}}{Rh(CO)(NS)Cl_2(PPh_3)} + PPh_3$$

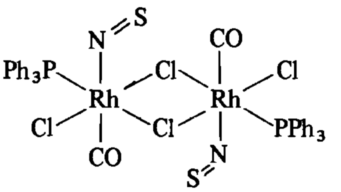
The IR spectra of the green complex $[Rh(CO)NSCl_2(PPh_3)]_2$ shows absorption bands at 2110 cm^{-1}, 1118 cm^{-1}, 340 cm^{-1} and 260 cm^{-1} besides the characteristic bands of triphenylphosphine [20]. The bands at 2110 cm^{-1} and 1118 cm^{-1} are characteristic stretching frequency of terminal carbonyl and thionitrosyl groups. The magnetic data show it to be diamagnetic suggesting rhodium in the complex to be present either in +1 $[Rh^{I}–NS^{+}]$ or +3 $[Rh^{III}–NS^{-}]$ oxidation state. The high frequency of $\nu_{(CO)}$ in this complex, as compared to its precursor ($\nu_{(CO)}$ = 1960 cm^{-1}) is reasonable for rhodium(III) system and is probably influenced by the strong, primarilly, σ-bonding *trans* effect of the *trans* NS^{-} group. The band at 340 cm^{-1} is typical of $\nu_{(Rh–Cl)}$ (Cl *trans* to Cl) while the band at 260 cm^{-1} could be due either to $\nu_{(Rh–Cl)}$ (Cl *trans* to P) or to bridging chlorine modes or to both [21]. The green complex I may, therefore, be dimeric in the solid state with mutually chlorine *trans* to chlorine, chlorine *trans* to phosphine; NS^{-} *trans* to CO, and bridging chlorines as in (I).

TABLE I. Analytical Data of the Complexes.

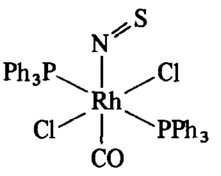
Compounds	Analyses													
	Calculated (%)							Found (%)						
	C	H	N	S	Cl/Br	P/As	Metal	C	H	N	S	Cl/Br	P/As	Metal
$[Rh(CO)(NS)Cl_2(PPh_3)]_2$	44.7	2.9	2.7	6.3	13.9	6.1	20.2	44.6	3.0	2.5	6.1	14.1	6.0	19.9
$Rh(CO)(NS)Cl_2(PPh_3)_2$	57.5	3.9	1.8	4.1	9.2	8.0	13.3	57.3	3.8	2.1	4.2	9.4	7.9	13.0
$[Rh(CO)(NS)Cl_2(AsPh_3)]_2$	41.2	2.7	2.5	5.8	12.8	13.5	18.6	41.2	3.0	2.8	5.7	13.0	13.6	18.4
$Rh(CO)(NS)Cl_2(AsPh_3)_2$	51.6	3.5	1.6	3.7	8.3	17.4	12.0	51.8	3.6	1.9	3.8	8.5	17.6	12.1
$Rh(CO)(NS)(PPh_3)_2$	63.3	4.3	2.0	4.6	–	8.8	14.7	63.1	4.5	2.3	4.8	–	8.6	14.8
$Rh(CO)(NO)Cl_2(PPh_3)_2$	58.7	4.0	1.9	–	9.4	8.2	13.6	58.5	4.2	2.4	–	9.6	8.0	13.4
$Rh(CO)(NO)ClBr(PPh_3)_2$	55.5	3.7	1.7	–	14.4	7.7	12.9	55.4	3.9	2.0	–	14.6	8.0	13.2
$Rh(CO)(NO)Cl_2(AsPh_3)_2$	52.6	3.5	1.7	–	8.4	17.8	12.2	52.8	3.5	2.0	–	8.7	17.6	12.0
$Rh(CO)(NO)ClBr(AsPh_3)_2$	50.0	3.4	1.6	–	13.0	16.9	11.6	50.1	3.4	1.8	–	13.2	17.0	11.4

TABLE II. Colour, Melting Point and Important Infrared Frequencies of the Complexes.

Compounds	Colour	M.P. (°C)	ν_{CO} (cm^{-1})	ν_{NO} (cm^{-1})	ν_{NS} (cm^{-1})	Other frequencies (cm^{-1})
$Rh(CO)(NS)Cl_2(PPh_3)_2$	Green	170	2110	–	1118	340, 260
$Rh(CO)(NS)Cl_2(PPh_3)_2$	Red-brown	165	2105	–	1120	335
$Rh(CO)(NS)Cl_2(AsPh_3)_2$	Yellowish green	176	2105	–	1118	340, 260
$Rh(CO)(NS)Cl_2(AsPh_3)_2$	Red-brown	170	2100	–	1120	335
$Rh(CO)(NS)(PPh_3)_2$	Red-brown	145	1970	–	1122	–
$Rh(CO)(NO)Cl_2(PPh_3)_2$	Yellow	205	2100	1630	–	340
$Rh(CO)(NO)ClBr(PPh_3)_2$	Yellow-orange	210	2095	1630	–	338
$Rh(CO)(NO)Cl_2(AsPh_3)_2$	Yellow	255	2090	1630	–	340
$Rh(CO)(NO)ClBr(AsPh_3)_2$	Yellowish orange	261	2090	1630	–	340



(I)



(II)

The reactions of $[Rh(CO)(NS)Cl_2(PPh_3)]_2$ with L (L = PPh_3, $AsPh_3$) give red brown complex $Rh(CO)(NS)Cl_2L_2$ (II) whose IR spectra show absorption bands $\nu_{(CO)}$, 2105 cm^{-1}, $\nu_{(NS)}$, 1120 cm^{-1}. The far IR spectra of these complexes show bands due to $\nu_{(Rh-Cl)}$ at 330 cm^{-1} (Cl *trans* to Cl). No band is observed in the range 230–280 cm^{-1} which rules out the possibility of chlorine *trans* to phosphorus and indicating that triphenylphosphines and arsines are mutually *trans* in $[Rh(CO)(NS)Cl_2L_2]$ (L = PPh_3, $AsPh_3$). Similarly the reaction of $(NSCl)(THF)_x$ with $Rh(CO)Cl(AsPh_3)_2$ gives yellowish green complex $[Rh(CO)(NS)Cl_2(AsPh_3)]_2$ which reacts with triphenylarsine to give $Rh(CO)(NS)Cl_2(AsPh_3)_2$. These complexes have similar structures as in I and II and are characterized by their IR spectra (Table II). On refluxing the green solution of $[Rh(CO)(NS)Cl_2(PPh_3)]_2$ in dichloromethane with triphenylphosphine brown crystals of $Rh(CO)(NS)(PPh_3)_2$ are obtained. The IR spectrum exhibits absorption bands at 1970 cm^{-1} due to $\nu_{(CO)}$ and at 1122 cm^{-1} due to $\nu_{(NS)}$.

Reaction of nitrosyl halides NOX (X = Cl, Br) with $Rh(CO)(NS)Cl_2L_2$ (L = PPh_3, $AsPh_3$) gives nitrosyl complexes of rhodium(III), $Rh(CO)(NO)ClXL_2$ (X = Cl, Br; L = PPh_3, $AsPh_3$) after displacing thionitrosyl ligand by nitrosyl. The mechanism of the reaction is not known. The carbonyl and nitrosyl stretching frequencies in these complexes $Rh(CO)(NO)ClXL_2$ are in the range observed for carbonyl-nitrosyl complexes of rhodium(III) [22]. A comparison of spectroscopic properties of the compounds $Rh(CO)(NO)Cl_2(PPh_3)_2$ ($\nu_{(CO)}$, 2100 cm^{-1}) and $Rh(CO)(NS)Cl_2(PPh_3)_2$ ($\nu_{(CO)}$, 2110 cm^{-1}) indicates that NS ligand is more effective in removing electron density from the central metal atom than is the NO ligand.

The electronic spectrum of $[Rh(CO)(NS)Cl_2(PPh_3)]_2$ showed bands at 15300 cm^{-1}, 21745 cm^{-1}, 27760 cm^{-1}. The spectra of the complexes $Rh(CO)(NX)Cl_2(PPh_3)_2$ (X = O, S) showed bands at 25000 cm^{-1}, 29410 cm^{-1} and 22220 cm^{-1}, 27200 cm^{-1} respectively. The very high intensity of these bands suggests that they should be charge transfer and not d–d transition bands. All d–d transitions are masked by intense charge transfer bands and hence no d–d bands appeared in any of the spectra of these complexes.

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