Notes

Thiazyl Chloride† Complexes of Ruthenium(II)

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The compound $(NSCl)_3$ reacts with ruthenium(II) complexes of type $[Ru(\eta^5-C_5H_5)X(PPh_3)_2]$ (X = Cl, Br, CN, SCN, or $SnCl_3$) and $[RuCl_2(PPh_3)_2(pip)_2]$ (pip = piperidine) to yield $[Ru(NSCl)_2X(X')(PPh_3)_2]$ (X = Cl; X′ = Cl, Br, CN, SCN, or $SnCl_3$) and $[Ru(NSCl)_2Cl_2(PPh_3)(pip)]$, respectively. The complexes have been characterized by elemental analyses, spectroscopic (i.r., ^1H n.m.r., u.v.–visible), magnetic susceptibility, and t.l.c. data.

Although the co-ordinating ability of thionitrosyl to transition-metal ions is well documented,[1–4] interest has been only partially focused on the synthetic and structural aspects of complexes with NSX (X = Cl or F) as coligands in the past few years.[5–9] We are presently engaged in a study of the reactions of $[Ru(\eta^5-C_5H_5)X(PPh_3)_2]$ with various donor molecules and NOX (X = Cl, Br, Br_3, or NO_2) which result in the substitution of the C_5H_5 group and the formation of octahedral ruthenium(II) nitrosyls. During these substitution reactions, possibly a co-ordinatively unsaturated reactive intermediate $[RuX(PPh_3)_2]^+$ with three vacant sites might initially be generated and subsequently react with the donor molecules and/or NOX to yield the final products.[10–12] We are also interested in the reactions of metal complexes with $(NSCl)_3$ where there also exists a possibility of co-ordinating NSCl as a coligand to the metal ion, *e.g.* in the reaction of $(NSCl)_3$ with $[Ru(\eta^5-C_5H_5)X(PPh_3)_2]$ in a medium containing no other Lewis base.

We report herein mixed-ligand ruthenium(II) complexes with two NSCl molecules co-ordinated as coligands. These have been characterized by elemental analyses, spectroscopic (i.r., u.v., visible, and n.m.r.), and magnetic moment data. The reaction has also been carried out using $[RuCl_2(PPh_3)_2(pip)_2]$ (pip = piperidine) as one of the reactants in place of $[Ru(\eta^5-C_5H_5)X(PPh_3)_2]$.

Experimental

All reagents were of AnalaR or chemically pure grade. The solvents were dried and distilled before use. The reactions were carried out under a nitrogen atmosphere. Thiazyl chloride, $(NSCl)_3$, $[Ru(\eta^5-C_5H_5)X(PPh_3)_2]$, and $[RuCl_2(PPh_3)_2(pip)_2]$ were prepared by the literature methods.[12,13–15]

Reactions of $(NSCl)_3$.—(*a*) *With* $[Ru(\eta^5-C_5H_5)Cl(PPh_3)_2]$. A solution of orange crystals of $[Ru(\eta^5-C_5H_5)Cl(PPh_3)_2]$ (100 mg, *ca.* 15 mmol) dissolved in dichloromethane (30 cm^3) was mixed with a solution of $(NSCl)_3$ (40 mg, *ca.* 1.5 mmol) in tetrahydrofuran (thf, 10 cm^3). The resulting solution was stirred for 4 h whereupon the colour had changed to dark reddish brown. A small amount of a precipitate which formed was centrifuged out. The centrifugate was concentrated to about 2 cm^3 on a water-bath and excess of light petroleum (b.p. 40—60 °C) was added, whereupon a green compound precipitated out. It was separated by centrifugation and recrystallized two or three times by dissolving it in CH_2Cl_2 and reprecipitating from light petroleum. The very fine micro-crystalline greenish precipitate was washed with light petroleum and dried under vacuum. Its analyses corresponded to the formula $[Ru(NSCl)_2Cl_2(PPh_3)_2]$ (yield > 50%).

(*b*) *With* $[Ru(\eta^5-C_5H_5)X(PPh_3)_2]$ (X = Br, CN, SCN, *or* $SnCl_3$). The reactions of $(NSCl)_3$ with $[Ru(\eta^5-C_5H_5)X(PPh_3)_2]$ were carried out similarly to that described above. Green to greenish yellow microcrystals of the complexes were obtained, separated by centrifugation, recrystallized, and dried in vacuum (yield *ca.* 50%). The formulae of the products corresponding to the respective microanalytical data are given in the Table.

(*c*) *With* $[RuCl_2(PPh_3)_2(pip)_2]$. Brown crystals of $[RuCl_2(PPh_3)_2(pip)_2]$ (50 mg, *ca.* 0.05 mmol) were dissolved in dry CH_2Cl_2 (25 cm^3) and a solution of $(NSCl)_3$ (25 mg, *ca.* 0.1 mmol) in thf (10 cm^3) was added. The resulting mixture was stirred for 3 h whereupon the colour changed to dark brown and a small amount of sulphur precipitated. The latter was removed by centrifugation and the centrifugate was concentrated on a water-bath to *ca.* 4 cm^3. Excess of light petroleum was added whereupon a dark brown complex was precipitated. It was separated by centrifugation, recrystallized by dissolving it in CH_2Cl_2 followed by precipitation with light petroleum, washed with light petroleum, and dried under vacuum. The analyses of the complex corresponded to the formula $[Ru(NSCl)_2Cl_2(PPh_3)(pip)]$ (yield > 50%).

Measurements.—The melting points of the complexes were determined on a Fisher-Johns apparatus. The electronic spectra (200—700 nm) of the complexes in dichloromethane solution were recorded on a Cary-17D spectrophotometer, i.r. spectra for KBr discs on a Shimadzu-420 spectrophotometer in the range 400—4 000 cm^{-1}. Magnetic moments were measured by the Gouy method using $Hg[Co(NCS)_4]$ as the calibrant. Carbon, hydrogen, and nitrogen analyses were made at the Kanpur microanalytical laboratory. Sulphur and halogens were estimated by standard methods,[16] phosphorus as described elsewhere.[17]

Results and Discussion

The reactions of $(NSCl)_3$ with $[Ru(\eta^5-C_5H_5)X(PPh_3)_2]$ (X = Cl, Br, CN, SCN, or $SnCl_3$) and with $[RuCl_2(PPh_3)_2(pip)_2]$ yielded light to dark green complexes whose microanalytical data suggested the formulae given in the Table. They are non-hygroscopic and soluble in halogenated organic solvents such as $CHCl_3$ and CH_2Cl_2 and insoluble in hydrocarbons like light petroleum. The purity of these compounds was tested with the help of t.l.c. which gave only one spot. All the complexes have a

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† 1,3,5-Trichlorocyclotri(aza-λ^4-thiene).

Table. Colours, melting points, analytical data and i.r. band positions of the complexes

Compound	Colour	M.p. (°C)	Analysis (%)[a]						I.r. bands (cm^{-1})[b]
			C	H	Cl	N	P	S	
$[Ru(NSCl)_2Cl_2(PPh_3)_2]$	Green	140	49.8	3.6	17.0	3.4	7.4	8.0	1 390, 1 295, 500
			(50.2)	(3.4)	(16.6)	(3.2)	(7.1)	(7.4)	
$[Ru(NSCl)_2Cl(Br)(PPh_3)_2]$	Green	170	46.9	3.0	20.9	3.4	6.9	6.8	1 390, 1 295, 495
			(47.7)	(3.3)	(20.7)	(3.1)	(6.7)	(7.0)	
$[Ru(NSCl)_2Cl(CN)(PPh_3)_2]$	Yellowish brown	186	53.0	4.0	12.4	4.8	7.5	7.8	1 395, 1 290, 500
			(52.8)	(3.5)	(12.7)	(5.0)	(7.2)	(7.6)	
$[Ru(NSCl)_2Cl(NCS)(PPh_3)_2]$	Brown	130	51.0	3.8	12.2	5.2	6.5	10.2	1 390, 1 290, 500
			(50.4)	(3.3)	(12.0)	(4.8)	(6.9)	(10.5)	
$[Ru(NSCl)_2(SnCl_3)_{0.5}Cl_{1.5}(PPh_3)_2]$	Yellowish green	186	45.0	2.7	20.2	3.6	6.6	6.4	1 388, 1 300, 500
			(45.1)	(3.1)	(19.9)	(3.0)	(6.4)	(6.6)	
$[Ru(NSCl)_2Cl_2(PPh_3)(pip)]$	Brown	135	41.1	4.0	20.9	6.4	4.3	9.9	1 388, 1 300, 500
			(40.6)	(3.9)	(20.8)	(6.1)	(4.5)	(9.7)	

[a] Calculated values in parentheses. [b] The band present at around 500 cm^{-1} is a doublet (maximum splitting 10 cm^{-1}).

tendency to decompose in methanol even on slight warming, giving a black compound insoluble in most organic and inorganic solvents. Analyses indicated it to contain sulphur and ruthenium. Since different samples gave different analytical data, no attempt was made to identify the compound. All the complexes are diamagnetic, suggesting the presence of ruthenium in oxidation state +2.

Although the ^1H n.m.r. spectra of all the reactant complexes except that of piperidine exhibited bands due to PPh_3 around δ 8.0 and that due to η^5-C_5H_5 around δ 4.0, the latter band was absent from the spectra of the product complexes. This suggested the replacement of C_5H_5 by other ligands. The spectra of the piperidine complexes showed characteristic bands between δ 2.5 and 2.8, indicating the presence of piperidine in the reactants as well as in the products.

The i.r. spectra of all the complexes exhibited an intense relatively broad band between 1 290 and 1 300 cm^{-1} and a medium intensity band around 1 380 cm^{-1} which in some complexes appeared as a shoulder to the phosphine band at 1 420 cm^{-1}. These spectra also showed another new intense band between 490 and 510 cm^{-1} which appeared as doublet. The bands at 1 380 and 1 290 cm^{-1} were assigned to ν_{asym}(SN) and ν_{sym}(SN), and the doublet around 500 cm^{-1} to ν(SCl). The positions of these bands conformed to those of known NSCl compounds.[5–9] The remaining bands were identified as those characteristic of the remaining coligands, *viz.* PPh_3 and piperidine. The positions of the ν(SN) and ν(SCl) bands were shifted towards high wavenumber compared to those of free NSCl, suggesting an increase in covalent bond strength for both SN and SCl. This shift could be explained by a reduction in the electronic charge on sulphur in the NSCl complexes. This would lead to a contraction and thereby a lowering in energy of the sulphur atomic orbitals and an enhancement of the covalent bond strength of SN and SCl because of the better matching of the sulphur atomic orbitals with those of nitrogen and chlorine.[18,19] In addition, the splitting of the bands due to ν(SN) and ν(SCl) indicated the presence of two *cis* NSCl groups with approximately C_{2v} symmetry on the metal centre. Because of their close proximity, the two groups may interact to yield i.r.-active bands due to ν_{sym}(SN), ν_{asym}(SN), ν_{sym}(SCl), and ν_{asym}(SCl). These types of band shifts and their splittings have also been observed in the spectra of analogous NSX complexes.[5–9]

The electronic spectra of all the complexes in the visible region showed a broad medium intensity band around 410 nm. Since octahedral ruthenium(II) complexes generally exhibit *d–d* or metal-to-ligand charge-transfer (m.l.c.t.) transitions which occur under a broad envelope centred around 420 nm,[20] a similar band observed for the present complexes suggested an octahedral geometry. Comparing their spectra with those of the parent complexes $[Ru(\eta^5\text{-}C_5H_5)X(PPh_3)_2]$ (*ca.* 550 nm),[12–15] there appeared to be a considerable shift towards higher energies. This blue shift could be due to the presence of a relatively larger number of donor groups capable of creating a stronger field around the metal ion in the product complexes. Although, because of the varying nature of X (Cl, Br, CN, SCN, *etc.*), there appeared to be a slight shift in the position of the band maximum for the different complexes, this shift was too small for any correlation to be made between the band maximum and the nature of the ligand, X. However, it appears that the position of the band is ligand-field dependent and. therefore, it is assigned to a m.l.c.t. The possibility of the band being due to a purely *d–d* transition is low because of the availability of low-lying empty π^* orbitals on the ligand X.[20–24]

The u.v. spectra of the complexes showed an intense absorption due to the presence of PPh_3, NSCl, NCS, CN, *etc.* bonded to ruthenium. It was possible to observe a few bands characteristic of phenyl only upon greatly diluting the solution. No attempt has, however, been made to interpret the u.v. spectra of the complexes.

The present work therefore suggests that the reactions of $[Ru(\eta^5\text{-}C_5H_5)X(PPh_3)_2]$ or $[RuCl_2(PPh_3)_2(pip)_2]$ with NSCl in thf yield octahedral diamagnetic ruthenium(II) complexes having two NSCl groups co-ordinated to the metal ion in *cis* position.

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