

Cyclopentadienyl Ruthenium Complexes. Part II.[‡] Reactivity of some η^5 -Cyclopentadienylbis(triphenylphosphine)- ruthenium(II) Complexes with Nitrosyl Chloride and Nitrosyl Bromide

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Abstract

NOCl and NOBr react with π -cyclopentadienyl ruthenium(II) complexes of the type $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{L}]^+\text{X}^-$ (where L = 2,2'-bipyridine or 1,10-phenanthroline, X = Cl or Br) or $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{L}(\text{X})]$ (where L = PPh₃, pyridine, 3-picoline, 4-picoline, 1/2(2,2'-bipyridine) or 1/2(1,10-phenanthroline), X = Cl, Br, I, CN, NCS, H or SnCl₃) to give (except where X = SnCl₃) mixed ligand ruthenium(II) nitrosyls, in which the NO seems to bind with the metal as NO⁺ with a terminal, linear M–N–O mode of bonding. In the case of trichlorostannate complexes, the conversion of NO to NO₂ has been observed, along with spectroscopic (IR & ¹H NMR) evidence supporting a π -interaction of one of the phenyl rings of the triphenylphosphine ligand, to the ruthenium center. All the complexes were characterised by spectroscopic (IR & ¹H NMR, UV-Vis), elemental analyses, magnetic measurements, conductivity and TLC data.

Introduction

Since ruthenium forms more nitrosyls than any other element [1], the work on ruthenium nitrosyls has been the central theme of research of nitrosyl chemistry during the past thirty years [2–6]. Many new synthetic routes to synthesize them have been reported [3–12]. Furthermore, as the η^5 -cyclopentadienyl group is formally equivalent to terdentate ligands [13], and the $[\text{M}(\text{PPh}_3)_2\text{Cl}]$ unit may formally be assumed to be equivalent to the M(Cp) unit, it may be interesting to examine the possibility of substituting one of the ligands bonded in π -cyclopentadienyl ruthenium complexes by NO, particularly in the light of current efforts to widen the range of available and potential platinum group complex catalysts. Although there is a reported attempt to nitrosylate the complex $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)$

$\text{PPh}_3)_2\text{Cl}]$ with diazald [14], the literature so far reveals no study concerning the reactions of η^5 -cyclopentadienyl ruthenium(II) complexes with nitrosyl chloride and nitrosyl bromide.

We report herein the results of the reactions of nitrosyl chloride and nitrosyl bromide with η^5 -cyclopentadienyl ruthenium(II) complexes of the type $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{L}]^+\text{X}^-$ (where L = 2,2'-bipy or 1,10-phen; X = Cl or Br) and $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{L})\text{X}]$ (where L = PPh₃, Py, 3-Pic, 4-Pic, 1/2(Bipy) or 1/2(o-Phen); X = Cl, Br, I, CN, NCS or SnCl₃). The products were characterised by spectroscopic and other physico-chemical methods.

Experimental

All the reagents used were of Analar grade. The solvents were distilled and dried before use. Nitrosyl chloride and nitrosyl bromide were prepared according to the methods described in the literature [15, 16]. The complex [14] $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{Cl}]$, complexes [17, 18] $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{Br}]$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{I}]$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{H})]$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{CN})]$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{NCS})]$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{SnCl}_3)]$, and the complexes [19], $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{Py})\text{Cl}]$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\beta\text{-Pic})\text{Cl}]$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\gamma\text{-Pic})\text{Cl}]$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{Bipy})]^+\text{Cl}^-$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(o\text{-phen})]^+\text{Cl}^-$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(o\text{-phen})]^+\text{Cl}^-$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{Py})\text{Br}]$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\beta\text{-Pic})\text{Br}]$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\gamma\text{-Pic})\text{Br}]$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{Bipy})]^+\text{Br}^-$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(o\text{-phen})]^+\text{Br}^-$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{Py})\text{I}]$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\beta\text{-Pic})\text{I}]$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\gamma\text{-Pic})\text{I}]$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{Bipy})]_{1/2}\text{I}$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(o\text{-phen})]_{1/2}\text{I}$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{Py})(\text{CN})]$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\beta\text{-Pic})(\text{CN})]$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\gamma\text{-Pic})(\text{CN})]$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{Bipy})]_{1/2}(\text{CN})]$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(o\text{-phen})]_{1/2}(\text{CN})]$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{Py})(\text{NCS})]$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\beta\text{-Pic})(\text{NCS})]$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\gamma\text{-Pic})(\text{NCS})]$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{Bipy})]_{1/2}(\text{NCS})]$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(o\text{-phen})]_{1/2}(\text{NCS})]$, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)$

[‡]Part I: ref. 19.

$(\text{PPh}_3)(\text{Py})(\text{SnCl}_3)$], $(\text{Ru}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)_3(\beta\text{-Pic})(\text{SnCl}_3))$], $[\text{Ru}(\eta\text{-C}_5\text{H}_5)(\beta\text{-Pic})(\text{SnCl}_3)]$, $[\text{Ru}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\gamma\text{-Pic})(\text{SnCl}_3)]$, $[\text{Ru}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{Bipy})_{1/2}(\text{SnCl}_3)]$ and $[\text{Ru}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(o\text{-phen})_{1/2}(\text{SnCl}_3)]$ were prepared as reported elsewhere.

All the reactions were carried out under dry and pure nitrogen.

Reaction of NOX' (X' = Cl or Br) with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{L}]^+\text{Cl}^-$ (where L = Bipy or 1,10-Phen) and $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{L})\text{Cl}]$ (where L = PPh₃, Py, 3-Pic or 4-Pic)

A saturated solution of NOX' in dichloromethane (~5 cm³) was slowly added with constant stirring to a solution of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{L}]^+\text{Cl}^-$ or $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{L})\text{Cl}]$ (~100 mg, ca. 0.16 mmol) in a mixed solvent containing 20 cm³ of dichloromethane and 40 cm³ of methanol at 30 °C. The reaction mixture was stirred vigorously for about 15 minutes whereupon shining orange yellow to orange brown crystals precipitated out. These were separated by filtration, washed with methanol and ether and dried under vacuum.

Reaction of NOX' (X' = Cl or Br) with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{L}]^+\text{Br}^-$ (where L = Bipy or o-Phen) and $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{L})\text{Br}]$ (where L = PPh₃, Py, 3-Pic, 4-Pic, 1/2(Bipy), 1/2(o-Phen))

To a solution of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{L}]^+\text{Br}^-$ (ca. 0.2 g; ca. 0.3 mmol), in dichloromethane (ca. 15 ml), a saturated solution of NOX' in dichloromethane (ca. 15 ml) was added. The mixture was stirred for 30 minutes and subsequently concentrated to about 10 cm³ under reduced pressure. The resulting solution was filtered, and the brown to reddish-brown coloured crystals were precipitated by the addition of about 25 cm³ of n-hexane to the filtrate. The products were filtered, washed several times with petroleum ether (40–60 °C) and dried under vacuum.

Reactions of NOX' (X' = Cl or Br) with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{L})\text{I}]$ (where L = PPh₃, Py, 3-Pic, 4-Pic, 1/2(Bipy) or 1/2(o-Phen))

The reactions were performed by a method similar to that described above, except that the complexes $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{L})\text{I}]$ were used in place of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{L})\text{Cl}]$. After the usual procedure triphenylphosphine was recovered from the solution, along with the major products of orange-brown to yellowish-brown nitrosyl complexes.

Reactions of NOX' (X' = Cl or Br) with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{L})\text{CN}]$ (where L = PPh₃, Py, 3-Pic, 4-Pic, 1/2(Bipy) or 1/2(1,10-Phen))

The cyano complexes (120 mg, ca. 0.2 mmol) were dissolved in 10 cm³ of dry dichloromethane and 25 cm³ of methanol was added, followed by

the addition of 2–3 cm³ of a saturated dichloromethane solution of NOX'. The reaction mixture was heated under reflux for about 30 minutes whereupon an oily liquid separated out from which it was difficult to obtain pure crystalline solid. In a few cases, however, the dissolution of the oil in CH₂Cl₂ or CHCl₃ and precipitation with petroleum ether gave a dark blackish green solid in rather low yield (~20%). It was filtered, washed with hexane and dried *in vacuo*. The product showed IR absorption bands characteristic of CN, NO and PPh₃ groups. The analytical data in a few cases fitted very well with the formula $[\text{Ru}(\text{NO})(\text{CN})\text{X}_2(\text{PPh}_3)_2\text{L}]$, but in the remaining ones, the values showed them to be random mixtures of $[\text{Ru}(\text{NO})(\text{CN})(\text{Cl}_2(\text{PPh}_3)_2\text{L})]$ and $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2\text{L}]$. Efforts to separate and purify the latter complexes failed.

It was, however, found that the addition of about 25 mg of triphenylphosphine into the reaction mixture, while under reflux, yielded shining orange-brown to orange-yellow crystals in very good yield (~85–90%). These were separated, washed with methanol and diethylether and dried *in vacuo*. The products were analysed for $[\text{Ru}(\text{NO})(\text{PPh}_3)_2(\text{L})\text{X}_3]$ (where X = Cl or Br).

Reactions of NOX' (X' = Cl or Br) with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{L})\text{NCS}]$ (where L = PPh₃, Py, β-Pic, γ-Pic, 1/2(Bipy) or 1/2(o-Phen))

A saturated dichloromethane solution of NOX' (5 cm³) was allowed to react with a chloroform solution (20 ml) of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{L})\text{NCS}]$ (~150 mg; ca. 0.28 mmol) by a method similar to that described above, whereupon dark brown crystals of the products were separated.

Reactions of NOX' (X' = Cl or Br) with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{L})\text{SnCl}_3]$ (where L = PPh₃, Py, 3-Pic, 4-Pic, 1/2(Bipy) or 1/2(1,10-Phen))

The bright yellow coloured $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{L})\text{SnCl}_3]$ (200 mg; ca. 0.28 mmol) in 20 cm³ of dichloromethane and 40 cm³ of methanol was refluxed with 5 cm³ of a saturated dichloromethane solution of NOX' for 20 minutes, whereupon orange-red shining microcrystals separated out. The products were filtered, washed with methanol, water, methanol and diethylether and finally dried under vacuum.

Reactions of NOX' (X' = Cl or Br) with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{H}]$

The bright yellow solids of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{H}]$ when dissolved in CH₂Cl₂ or CHCl₃ gave the chloro complex $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{Cl}]$ and in CHBr₃, the bromo complex $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{Br}]$. Subsequently, the reaction of the hydrido complex with NOX' by any of the above described methods, gave products identical to those obtained from the chloro, bromo or iodo complex, depending

on the haloform used for dissolving the hydrido complex prior to its reaction with NOX' .

The melting points of the complexes were found on a Fisher-Johns melting point apparatus.

The electronic spectra (210–700 nm) of the complexes in chloroform solution were recorded on a Cary 17-D model spectrophotometer.

The IR spectra were recorded as KBr discs on a Perkin-Elmer 580 spectrophotometer in the range 200–4000 cm^{-1} .

Magnetic moments were measured by the Gouy method using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the calibrant.

Carbon, hydrogen and nitrogen were estimated at the Microanalytical laboratory of the IIT, Kanpur.

Sulphur and halogen were estimated by standard methods [20]. The phosphorus in the complexes was estimated as described elsewhere [21].

Results and Discussion

Reactions of the yellow to orange coloured compounds $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{X}]$ with an excess of a saturated solution of NOX in dichloromethane or chloroform proceed with the formation of coloured micro crystals of the complexes (yield, 50–60%) whose microanalytical data fit well with the compositions given in Table I. They are air-stable, soluble in CH_2X_2 , CHX_3 and other analogous solvents to a large extent and relatively less soluble in most of the protonated solvents like alcohols and insoluble in ether and hydrocarbons like pentane, etc. The complexes having trichlorostannate as an anion were found to be relatively less soluble and this property has led us to carry out some detailed investigations on them.

Reactions of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{L})\text{SnCl}_3]$ ($\text{L} = \text{PPh}_3, \text{Py}, 3 \text{ Pic}, 4 \text{ Pic}, 1/2(2,2'\text{-bipyridine}), 1/2(1,10\text{-phenanthroline})$) with NOX' ($\text{X}' = \text{Cl}, \text{Br}$)

The reason for discussing the reactivities of these complexes with respect to NOX' under a separate heading stems from the difference in their behavioural pattern from that of the rest of the molecules. The following two significant differences in their reactivities towards NOX' have, rather surprisingly, been observed.

(1) The IR spectra did not show any band around 1850 cm^{-1} indicating that NOCl and NOBr could not nitrosylate these complexes. Instead, four new bands around 1340s cm^{-1} , 1320mw(sh), 840mw cm^{-1} and 300w cm^{-1} consistently appeared in all the spectra. There was no band present around 650 cm^{-1} . The positions of these bands suggested the presence of a NO_2^- group bonded to ruthenium [22]. Although it is not possible to differentiate with certainty the linkage mode of the NO_2^- ion

with the metal ion (as nitro or nitrito), it is however, observed that the nitrito complexes lack the wagging mode of vibration around 650 cm^{-1} [22]. Since there was no band present in the spectra around 650 cm^{-1} and unless it is masked by the intense band of phosphine at 590 cm^{-1} it has been tentatively concluded that the NO_2^- ion is linked as nitrito with the ruthenium ion.

(2) The second interesting aspect has been the presence of five bands in the region 1500 cm^{-1} –1350 cm^{-1} and three bands in the region 690–820 cm^{-1} . The group of five bands (1500–1350 cm^{-1}) has been suggested to be indicative of the presence of PPh_3 coordinated to the metal via one of its phenyl rings through a π bonded interaction [23–27]. Therefore, the bonding in the complexes may best be regarded as involving a η^6 -interaction using all the π -electrons of the phenyl ring in bonding to the metal. Furthermore, logically one should also expect a change in the position of the out-of-plane C–H bending mode in case one of the phenyl groups of PPh_3 is donating electron density to metal through π -bonding. Such a shift in the position of the C–H out-of-plane bending mode has been observed in π -complexes of cyclopentadiene and π -arene complexes. In the spectra of these complexes one extra band has been observed around 790–800 cm^{-1} which was not present in the spectra of those where PPh_3 is bonded to metal through phosphorus only. It has, therefore, been presumed that the new band around 800 cm^{-1} arises because of the out-of-plane (C–H) bending mode of the phenyl ring which is π -bonded to metal.

Most of the remaining IR bands (intense and moderately intense) of the spectra of the complexes can be assigned to the characteristic bands of the co-ligands bonded to the metal.

Because of the limited solubility of these complexes, their well-resolved ^1H NMR spectra could not be obtained, though a broad weak band around δ 7.2 was observed in every case. In one or two cases after repeated attempts, a very weak resonance around δ 5.4 assigned to the protons of the π -bonded phenyl ring of PPh_3 , besides the one present at δ 7.2, appeared in the spectra. Presuming these bands do not arise out of some impurities, the upfield shift of five protons out of the total number of hydrogen atoms present on the phenyl rings and on the co-ligand-N-heterocyclic rings, has been taken as definite evidence of the π -bonded interaction of one of the phenyl rings of PPh_3 .

Although an X-ray crystal structure determination is needed to give the structures of the SnCl_3 complexes, a tentative one can be put forward on the basis of the above data (Fig. 1) proposed on the same lines as that of the $[\text{RuH}(\text{PPh}_3)_3]^+$ ion [33]. The stability of the complex could also be explained by its being an eighteen electron system rather than

TABLE I. Reactions of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{L})\text{X}]$ with NOX' : Characterisation Data of Complexes^{a, b}.

No.	L	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{L})\text{X}]$	NOX'	Product *Colour, m.p. (°C)	a, b Analyses, Found (Calcd.) %						IR bands (cm ⁻¹) KBr discs	λ_{max} (nm) CHCl ₃ solvent
					C	H	X	N	P			
1	2	3	4	5	6	7	8	9	10	11	12	
1	PPh ₃	Cl	Cl	$[\text{Ru}(\text{NO})(\text{PPh}_3)_2\text{Cl}_3]$ OB, 240(d)	56.1 (56.7)	3.8 (3.9)	13.6 (14.0)	1.7 (1.8)	8.2 (8.1)	1868	430,375,335,295, 220	
2	Py	Cl	Cl	$[\text{Ru}(\text{NO})(\text{PPh}_3)(\text{Py})\text{Cl}_3]$ O, 245(d)	47.3 (47.7)	3.4 (3.5)	18.2 (18.4)	4.6 (4.8)	5.2 (5.4)	1860	435,370,335,295, 220	
3	3-Pic	Cl	Cl	$[\text{Ru}(\text{NO})(\text{PPh}_3)(3\text{-Pic})\text{Cl}_3]$ O, 230(d)	49.1 (48.6)	3.6 (3.7)	17.4 (18.0)	4.7 (4.7)	5.3 (5.2)	1864	435,370,335,295, 220	
4	4-Pic	Cl	Cl	$[\text{Ru}(\text{NO})(\text{PPh}_3)(4\text{-Pic})\text{Cl}_3]$ O, 235(d)	48.3 (48.6)	3.6 (3.7)	17.6 (18.0)	4.6 (4.7)	5.1 (5.2)	1868	430,370,335,290, 220	
*5	2,2'-Bipy	Cl	Cl	$[\text{Ru}(\text{NO})(\text{PPh}_3)(\text{Bipy})_{1/2}\text{Cl}_3]$ O, 270-72(d)	47.4 (47.8)	3.2 (3.3)	18.5 (18.4)	4.9 (4.8)	5.3 (5.4)	1868	565,415,280,220	
*6	1,10-Phen	Cl	Cl	$[\text{Ru}(\text{NO})(\text{PPh}_3)(o\text{-Phen})_{1/2}\text{Cl}_3]$ O, 220(d)	48.5 (48.9)	3.1 (3.2)	18.2 (18.1)	4.8 (4.7)	5.4 (5.3)	1865	430,345,310,270, 230	
7	PPh ₃	Cl	Br	$[\text{Ru}(\text{NO})(\text{PPh}_3)_2\text{ClBr}_2]$ YB, 242(d)	50.5 (50.8)	3.4 (3.5)	22.8 (23.0)	1.5 (1.6)	7.7 (7.3)	1862	430,340,310,270, 230	
8	Py	Cl	Br	$[\text{Ru}(\text{NO})(\text{PPh}_3)(\text{Py})\text{ClBr}_2]$ GY, 230(d)	40.9 (41.3)	2.9 (3.0)	28.9 (29.3)	4.1 (4.2)	4.4 (4.6)	1860	460,350,310,230	
9	3-Pic	Cl	Br	$[\text{Ru}(\text{NO})(\text{PPh}_3)(3\text{-Pic})\text{ClBr}_2]$ GB, 226(d)	42.0 (42.2)	3.2 (3.2)	28.5 (28.7)	4.3 (4.1)	4.4 (4.5)	1868	450,350,300,225	
10	4-Pic	Cl	Br	$[\text{Ru}(\text{NO})(\text{PPh}_3)(4\text{-Pic})\text{ClBr}_2]$ GB, 218(d)	41.9 (42.2)	3.1 (3.2)	28.4 (28.7)	4.3 (4.1)	4.3 (4.5)	1862	450,350,300,230	
*11	2,2'-Bipy	Cl	Br	$[\text{Ru}(\text{NO})(\text{PPh}_3)(\text{Bipy})_{1/2}\text{ClBr}_2]$ G, 209(d)	41.0 (41.4)	3.0 (2.9)	30.0 (29.3)	4.3 (4.2)	4.6 (4.7)	1860	545,425,395,300, 260,210	
*12	1,10-Phen	Cl	Br	$[\text{Ru}(\text{NO})(\text{PPh}_3)(o\text{-Phen})_{1/2}\text{ClBr}_2]$ DG, 225(d)	42.1 (42.4)	2.7 (2.8)	28.4 (28.8)	4.2 (4.1)	4.5 (4.6)	1870	550,420,400,300, 260,210	
13	PPh ₃	Br	Cl	$[\text{Ru}(\text{NO})(\text{PPh}_3)_2\text{Cl}_2\text{Br}]$ YB, 236(d)	53.3 (53.6)	3.8 (3.7)	18.2 (18.7)	1.6 (1.7)	7.9 (7.7)	1865	435,340,290,270, 230	
14	Py	Br	Cl	$[\text{Ru}(\text{NO})(\text{PPh}_3)(\text{Py})\text{Cl}_2\text{Br}]$ O, 230(d)	44.1 (44.3)	3.3 (3.2)	24.3 (24.2)	4.4 (4.5)	5.1 (5.0)	1864	430,350,280,270, 230	
15	3-Pic	Br	Cl	$[\text{Ru}(\text{NO})(\text{PPh}_3)(3\text{-Pic})\text{Cl}_2\text{Br}]$ B, 216(d)	45.0 (45.2)	3.4 (3.5)	23.9 (24.2)	4.5 (4.4)	4.4 (4.7)	1868	432,355,275,265, 230	
16	4-Pic	Br	Cl	$[\text{Ru}(\text{NO})(\text{PPh}_3)(4\text{-Pic})\text{Cl}_2\text{Br}]$ B, 212(d)	45.1 (45.2)	3.4 (3.5)	24.4 (24.2)	4.5 (4.4)	4.4 (4.7)	1868	430,355,275,265, 230	

*17	2,2'-Bipy	Br	Cl	[Ru(NO)(PPh ₃ (Bipy)) _{1/2} Cl ₂ Br] B, 202(d)	44.1 (44.4)	3.0 (3.1)	24.6 (24.4)	4.7 (4.5)	4.9 (5.0)	1865	430,355,275,265, 230
*18	1,10-Phen	Br	Cl	[Ru(NO)(PPh ₃ (<i>o</i> -Phen)) _{1/2} Cl ₂ Br] B, 201(d)	45.1 (45.4)	2.9 (3.0)	23.5 (23.8)	4.3 (4.4)	4.7 (4.9)	1870	580,400,330,260, 230
19	PPh ₃	Br	Br	[Ru(NO)(PPh ₃) ₂ Br ₃] YB, 239(d)	48.0 (48.3)	3.6 (3.4)	26.6 (26.8)	1.5 (1.6)	7.1 (6.9)	1864	465,350,300,230
20	Py	Br	Br	[Ru(NO)(PPh ₃ (Py))Br ₃] YB, 255(d)	36.9 (37.6)	2.6 (2.7)	34.8 (34.2)	3.6 (3.8)	4.3 (4.2)	1865	460,350,300,230
21	3-Pic	Br	Br	[Ru(NO)(PPh ₃ (3-Pic))Br ₃] OB, 285(d)	39.3 (39.7)	2.9 (3.0)	33.3 (33.1)	3.8 (3.9)	4.5 (4.3)	1868	460,315,235
22	4-Pic	Br	Br	[Ru(NO)(PPh ₃ (4-Pic))Br ₃] OB, 281(d)	39.4 (39.1)	2.9 (3.0)	34.3 (34.2)	3.7 (3.8)	4.3 (4.2)	1865	460,310,230
*23	2,2'-Bipy	Br	Br	[Ru(NO)(PPh ₃ (Bipy)) _{1/2} Br ₃] G, 168(d)	38.5 (38.8)	2.6 (2.7)	33.6 (33.8)	3.7 (3.9)	4.5 (4.4)	1870	460,310,225
*24	1,10-Phen	Br	Br	[Ru(NO)(PPh ₃ (<i>o</i> -Phen)) _{1/2} Br ₃] B, 215(d)	39.6 (39.8)	2.5 (2.6)	33.1 (33.2)	3.7 (3.9)	4.1 (4.3)	1868	680,460,310,225
25	PPh ₃	I	Cl	[Ru(NO)(PPh ₃) ₂ Cl ₂ I] YB, 240	50.2 (50.6)	3.7 (3.5)	23.1 (23.2)	1.5 (1.6)	7.5 (7.3)	1860	700,460,310,225
26	Py	I	Cl	[Ru(NO)(PPh ₃ (Py))Cl ₂ I] B, 243	40.9 (41.2)	2.9 (3.0)	21.9 (21.6)	4.1 (4.2)	4.3 (4.6)	1858	700,440,338,290, 270,225
27	3-Pic	I	Cl	[Ru(NO)(PPh ₃ (3-Pic))Cl ₃] O, 230	48.3 (48.6)	3.6 (3.7)	18.2 (17.9)	4.9 (4.7)	5.5 (5.2)	1864	410,335,325,230
28	4-Pic	I	Cl	[Ru(NO)(PPh ₃ (4-Pic))Cl ₃] O, 234	48.2 (48.6)	3.8 (3.7)	18.1 (17.9)	4.6 (4.7)	5.3 (5.2)	1868	430,335,325,230
29	1/2(2,2'-Bipy)	I	Cl	[Ru(NO)(PPh ₃ (Bipy)) _{1/2} Cl ₂ I] O, 225	41.1 (41.3)	2.9 (2.8)	29.8 (29.5)	4.4 (4.2)	4.5 (4.6)	1860	430,335,325,230
30	1/2(1,10-Phen)	I	Cl	[Ru(NO)(PPh ₃ (<i>o</i> -Phen)) _{1/2} Cl ₃] O, 220	49.1 (48.9)	3.1 (3.2)	18.0 (18.1)	4.5 (4.7)	5.2 (5.3)	1865	410,335,325,230
31	PPh ₃	I	Br	[Ru(NO)(PPh ₃) ₂ IBr ₂] YB, 245	46.1 (45.9)	3.4 (3.2)	33.6 (34.0)	1.6 (1.5)	6.4 (6.6)	1860	680,450,350,315, 230
32	Py	I	Br	[Ru(NO)(PPh ₃ (Py))IBr ₂] O, 238	36.9 (36.4)	2.7 (2.6)	37.6 (37.8)	3.9 (3.7)	4.0 (4.1)	1862	450,370,320,230
33	3-Pic	I	Br	[Ru(NO)(PPh ₃ (3-Pic))IBr ₂] YB, 241	37.4 (37.3)	2.7 (2.8)	37.3 (37.1)	3.7 (3.6)	4.2 (4.0)	1865	460,380,320,230
34	4-Pic	I	Br	[Ru(NO)(PPh ₃ (4-Pic))IBr ₂] YB, 236	37.5 (37.3)	2.9 (2.8)	37.4 (37.1)	3.8 (3.6)	4.2 (4.0)	1862	465,380,320,230
35	1/2(2,2'-Bipy)	I	Br	[Ru(NO)(PPh ₃ (Bipy)) _{1/2} IBr ₂] B, 238	35.6 (35.2)	2.6 (2.5)	39.8 (40.3)	3.4 (3.5)	3.7 (3.9)	1868	680,460,310,250, 215 (continued overleaf)

TABLE I (continued)

No.	[Ru(η^5 -C ₅ H ₅)(PPh ₃)(L) ₂ NOX] ⁺ X ⁻					a, b Analyses, Found (Calcd.) %										IR bands (cm ⁻¹) KBr discs	λ_{max} (nm) CHCl ₃ solvent
	L =	X =	X =	NOX ⁺	Product *Colour, m.p. (°C)	C	H	X	N	P	10	11					
1	2	3	4	5		6	7	8	9	10	11	12					
36	1/2(1,10-Phen)	I	Br		[Ru(NO)(PPh ₃)(<i>o</i> -Phen) _{1/2} Br ₃] O, 236	39.7 (39.8)	2.5 (2.6)	32.9 (33.2)	3.7 (3.9)	4.5 (4.3)	1865	430,335,325,230					
37	PPh ₃	CN	Cl		[Ru(NO)(CN)(PPh ₃)Cl ₂] ₂ YB, 228-30	46.7 (46.5)	3.0 (3.1)	14.6 (14.5)	5.9 (5.7)	6.5 (6.3)	1865,2040	432,335,325,230					
38	Py	CN	Cl		[Ru(NO)(PPh ₃)(Py)Cl ₃] O, 245(d)	47.8 (47.7)	3.7 (3.5)	18.2 (18.4)	4.7 (4.8)	5.7 (5.4)	1860	435,335,325,230					
39	3-Pic	CN	Cl		[Ru(NO)(PPh ₃)(3-Pic)Cl ₃] O, 230(d)	48.6 (48.6)	3.9 (3.7)	17.5 (18.0)	4.9 (4.7)	5.3 (5.2)	1864	438,335,325,230					
40	4-Pic	CN	Cl		[Ru(NO)(PPh ₃)(4-Pic)Cl ₃] O, 235(d)	48.7 (48.6)	3.8 (3.7)	17.6 (18.0)	4.8 (4.7)	5.4 (5.2)	1870	435,515,270,230					
41	1/2(2,2'-Bipy)	CN	Cl		[Ru(NO)(PPh ₃ (Bipy) _{1/2} Cl ₃] O, 270(d)	47.6 (47.8)	3.5 (3.3)	18.5 (18.4)	4.9 (4.8)	5.6 (5.4)	1868	565,415,280,220					
42	1/2(1,10-Phen)	CN	Cl		[Ru(NO)(PPh ₃)(<i>o</i> -Phen) _{1/2} Cl ₃] O, 220(d)	48.1 (48.9)	3.3 (3.2)	18.0 (18.1)	4.8 (4.7)	5.5 (5.3)	1864	430,345,310,270, 230					
43	PPh ₃	CN	Br		[Ru(NO)(CN)(PPh ₃) ₂ Br ₂] DB, 280	52.5 (52.8)	3.7 (3.6)	19.1 (19.0)	3.4 (3.3)	7.6 (7.4)	1870,2040	400,315,230					
44	Py	CN	Br		[Ru(NO)(CN)(PPh ₃)(Py)Br ₂] BY, 285	43.7 (43.8)	3.1 (3.0)	24.6 (24.3)	6.6 (6.4)	4.5 (4.7)	1865,2070	410,320,290,260, 220					
45	3-Pic	CN	Br		[Ru(NO)(CN)(PPh ₃)(3-Pic)Br ₂] B, 280	44.2 (44.6)	3.2 (3.3)	23.5 (23.8)	6.2 (6.3)	4.7 (4.6)	1865,2025	680,430,260,220					
46	4-Pic	CN	Br		[Ru(NO)(CN)(PPh ₃)(4-Pic)Br ₂] B, 280	44.3 (44.6)	3.1 (3.3)	23.4 (23.8)	6.5 (6.3)	4.5 (4.6)	1860,2020	560,460,340,280, 220					
47	1/2(2,2'-Bipy)	CN	Br		[Ru(NO)(CN)(PPh ₃)(Bipy) _{1/2} Br ₂] CB, 270(d)	40.2 (40.4)	2.9 (2.8)	31.4 (31.1)	5.6 (5.7)	4.1 (4.2)	1870,2050	610,440,310,220					
48	1/2(1,10-Phen)	CN	Br		[Ru(NO)(CN)(PPh ₃)(<i>o</i> -Phen) _{1/2} Br ₂] RB, 276(d)	44.6 (44.8)	2.7 (2.8)	23.6 (23.9)	6.4 (6.3)	4.4 (4.6)	1872,2040	580,440,310,220					
49	PPh ₃	NCS	Cl		[Ru(NO)(PPh ₃) ₂ Cl ₃] OB, 240	56.4 (56.7)	3.7 (3.9)	13.8 (14.0)	1.9 (1.8)	8.3 (8.1)	1868	460,300,215					
50	Py	NCS	Cl		[Ru(NO)(NCS)(PPh ₃)(Py)Cl ₂] DO, 240	47.3 (47.9)	3.4 (3.3)	11.9 (11.8)	6.9 (7.0)	5.1 (5.2)	1865,2150	500,450,310,220					
51	3-Pic	NCS	Cl		[Ru(NO)(PPh ₃)(3-Pic)Cl ₃] O, 232	48.2 (48.6)	3.9 (3.7)	18.3 (18.0)	4.8 (4.7)	5.3 (5.2)	1864	435,370,335,295, 220					

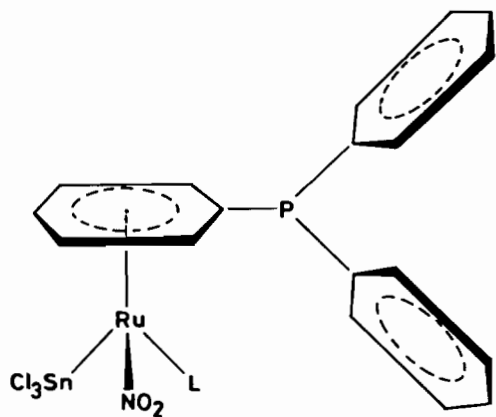
52	4-Pic	NCS	Cl	[Ru(NO)(PPh ₃)(4-Pic)Cl ₃] O, 234	48.5 (48.6)	3.5 (3.7)	18.1 (18.0)	4.9 (4.7)	5.4 (5.2)	1868	435,370,335,290, 215
53	1/2(2,2'-Bipy)	NCS	Cl	[Ru(NO)(PPh ₃ (Bipy)) _{1/2} Cl ₃] OY, 274	47.6 (47.8)	3.2 (3.3)	18.3 (18.5)	4.9 (4.8)	5.6 (5.4)	1868	500,430,340,280, 265,230
54	1/2(1,10-Phen)	NCS	Cl	[Ru(NO)(PPh ₃ (o-Phen)) _{1/2} Cl ₃]-1/2CH ₂ Cl ₂ DO, 230	46.1 (46.5)	3.1 (3.2)	22.3 (22.5)	4.3 (4.4)	4.7 (4.9)	1865	430,345,310,270, 230
55	PPh ₃	NCS	Br	[Ru(NO)(PPh ₃) ₂ Br ₃] YB, 239-40	47.9 (48.3)	3.5 (3.4)	27.1 (26.8)	1.5 (1.6)	7.0 (6.9)	1865	465,350,330,230
56	Py	NCS	Br	[Ru(NO)(NCS)(PPh ₃)(Py)Br ₂] O, 240	41.3 (41.7)	2.8 (2.9)	22.9 (23.2)	6.2 (6.1)	4.3 (4.5)	1870,2140	450,360,300,240
57	3-Pic	NCS	Br	[Ru(NO)(NCS)(PPh ₃)(3-Pic)Br ₂] B, 245	42.9 (42.6)	3.0 (3.1)	22.1 (22.7)	5.8 (6.0)	4.6 (4.4)	1872,2140	470,410,300,220
58	4-Pic	NCS	Br	[Ru(NO)(NCS)(PPh ₃)(4-Pic)Br ₂] B, 242	42.4 (42.6)	3.2 (3.1)	22.3 (22.7)	5.7 (6.0)	4.5 (4.4)	1872,2130	475,400,290,220
59	1/2(2,2'-Bipy)	NCS	Br	[Ru(NO)(PPh ₃ (Bipy)) _{1/2} Br ₃] Y, 241-43	38.5 (38.8)	2.6 (2.7)	33.6 (33.8)	3.7 (3.9)	4.5 (4.4)	1870	580,420,350,310, 280,220
60	1/2(1,10-Phen)	NCS	Br	[Ru(NO)(PPh ₃ (o-Phen)) _{1/2} Br ₃]-1/2CH ₂ Cl ₂ B, 228	38.0 (38.4)	2.5 (2.6)	35.8 (36.0)	3.6 (3.7)	4.2 (4.0)	1868	680,460,310,225
61	PPh ₃	SnCl ₃	Cl	[Ru(NO ₂)(SnCl ₃ (PPh ₃) ₂)-1/2CH ₂ Cl ₂ OR, 200	46.5 (46.6)	3.4 (3.3)	15.0 (15.1)	1.7 (1.5)	6.8 (6.6)	1500,1480,1430,1370, 1350,1340,1310,850, 230 800	550,350,320,275, 230
62	Py	SnCl ₃	Cl	[Ru(NO ₂)(SnCl ₃ (PPh ₃ (Py)))-CH ₂ Cl ₂ DR, 208	36.2 (36.1)	2.6 (2.8)	22.0 (22.2)	3.6 (3.5)	4.0 (3.9)	1500,1480,1430,1370, 1350,1340,1310,850, 230 800	560,440,320,290, 230
63	3-Pic	SnCl ₃	Cl	[Ru(NO ₂)(SnCl ₃ (PPh ₃)(3-Pic))-CH ₂ Cl ₂ OR, 209	36.7 (36.9)	2.9 (3.0)	21.7 (21.8)	3.5 (3.4)	3.9 (3.8)	1500,1485,1432,1372, 1350,1340,1310,850, 230 800	565,440,320,270, 230
64	4-Pic	SnCl ₃	Cl	[Ru(NO ₂)(SnCl ₃ (PPh ₃)(4-Pic))-1/2CH ₂ Cl ₂ OR, 208	38.4 (38.2)	2.9 (3.0)	18.3 (18.4)	3.4 (3.6)	4.1 (4.0)	1500,1486,1431,1373, 1348,1340,1310,850, 230 800	565,440,320,275, 230
65	1/2(2,2'-Bipy)	SnCl ₃	Cl	[Ru(NO ₂)(SnCl ₃ (PPh ₃ (Bipy)) _{1/2})-1/2CH ₂ Cl ₂ OR 205	37.7 (37.4)	2.5 (2.6)	20.7 (20.2)	3.6 (3.7)	4.0 (4.1)	1500,1480,1430,1370, 1350,1340,1310,850, 215 800	568,435,310,275, 215
66	1/2(1,10-Phen)	SnCl ₃	Cl	[Ru(NO ₂)(SnCl ₃ (PPh ₃ (o-Phen)) _{1/2})-1/2CH ₂ - Cl ₂ OR, 198	38.5 (38.3)	2.7 (2.6)	18.3 (18.5)	3.8 (3.7)	4.2 (4.0)	1500,1480,1432,1370, 1352,1340,1310,850, 215 798	568,435,310,375, 215
67	PPh ₃	SnCl ₃	Br	[Ru(NO ₂)(SnCl ₃ (PPh ₃) ₃)-1/2CH ₂ Cl ₂ OR, 198	46.8 (46.6)	3.2 (3.3)	15.3 (15.1)	1.4 (1.5)	6.8 (6.6)	1500,1480,1430,1370, 1350,1340,1310,850, 800	550,450,330,210

(continued overleaf)

TABLE I (continued)

No.	[Ru(η^5 -C ₅ H ₅)(PPh ₃)(L)X] NOX'		Product *Colour, m.p. (°C)	a, b Analyses, Found (Calcd.) %						IR bands (cm ⁻¹) KBr discs	λ_{max} (nm) CHCl ₃ solvent
	L =	X =		X'	C	H	X	N	P		
1	2	3	4	5	6	7	8	9	10	11	12
68	Py	SnCl ₃	Br	[Ru(NO ₂)(SnCl ₃)(PPh ₃ (Py)) _{1/2} CH ₂ Cl ₂] OR, 202	37.2 (37.3)	2.9 (2.8)	18.6 (18.8)	3.8 (3.7)	4.3 (4.1)	1500,1482,1432,1370, 1352,1340,1310,860, 800	520,450,340,300, 230
69	3-Pic	SnCl ₃	Br	[Ru(NO ₂)(SnCl ₃)(PPh ₃ (3-Pic)) _{1/2} CH ₂ Cl ₂] OR, 198	38.7 (38.9)	2.9 (3.0)	16.8 (16.6)	3.6 (3.7)	4.0 (4.1)	1500,1482,1432,1370, 1350,1340,1310,850, 800	545,440,290,240, 225
70	4-Pic	SnCl ₃	Br	[Ru(NO ₂)(SnCl ₃)(PPh ₃ (4-Pic)) _{1/2} CH ₂ Cl ₂] OR, 206	38.3 (38.2)	3.2 (3.0)	18.6 (18.4)	3.5 (3.6)	4.3 (4.0)	1500,1480,1430,1372, 1351,1342,1310,850, 800	550,450,320,280, 230
71	1/2(2,2'-Bipy)	SnCl ₃	Br	[Ru(NO ₂)(SnCl ₃)(PPh ₃ (Bipy)) _{1/2} CH ₂ Cl ₂] OR, 198	36.3 (36.1)	2.5 (2.6)	22.6 (22.2)	3.6 (3.5)	3.8 (3.9)	1500,1480,1430,1372, 1351,1342,1310,850, 800	540,455,320,275, 225,220
72	1/2(1,10-Phen)	SnCl ₃	Br	[Ru(NO ₂)(SnCl ₃)(PPh ₃ (o-Phen)) _{1/2} CH ₂ Cl ₂] Cl ₂ OR, 198	38.6 (38.3)	2.5 (2.6)	18.7 (18.5)	3.5 (3.7)	4.1 (4.0)	1500,1482,1432,1372, 1350,1340,1310,850, 798	530,440,390,330, 250,220

*Cationic complexes of composition [Ru(η^5 -C₅H₅)(PPh₃(L))⁺X⁻. †OB = Orange Brown, O = Orange, YB = Yellowish Brown, GY = Golden Yellow, GB = Golden Brown, G = Green, B = Black, DB = Dark Brown, CB = Chocolate Brown, RB = Reddish Brown, OR = Orange Red, DO = Deep Orange. ‡H NMR spectra showed broad multiplet resonance at δ 7.2 ppm due to phosphine and N-heterocyclic base protons. In addition complexes No. 61-72 showed multiplet absorption at δ 6.2 due to the π -bonded phenyl protons of the triphenylphosphine ligand. The picoline complexes exhibited in addition methyl resonance in the region δ 1.8-2.0. †Error limit \pm 1%. ‡The complexes having NCS as one of the anionic ligands analysed satisfactorily for sulfur.



[L = PPh₃, Pyridine, 3-Picoline, 4-Picoline, $\frac{1}{2}$ (2,2'-Bipyridine) or $\frac{1}{2}$ (1,10-Phenanthroline)]

Fig. 1. Tentative structure for the complexes.

sixteen. Its red colour also confirms the conclusion [31].

The problem of differential behaviour of the bonded SnCl₃⁻ complexes is interesting. It not only allows π -interaction of one of the phenyl rings of PPh₃, but also catalyzes NO to NO₂. The only difference one could visualize between SnCl₃⁻ and other anions is that the former is a very strong π -acceptor compared to others besides offering some steric hindrance. At this stage it will, however, be difficult to assign a particular reason for the unique behaviour of SnCl₃⁻.

The geometry of the ligands around the metal atom in the SnCl₃ complexes may be considered either as distorted octahedral or tetrahedral depending upon whether the C₆H₆ ring is assumed to occupy three positions or one position, respectively. We prefer the former description based on the interpretation of the electronic spectral data which are similar to those of the other complexes of Ru(II) in which the SnCl₃⁻ ion has been replaced by other anions.

Reactions of [Ru(η^5 -C₅H₅)(PPh₃)(L)X] (X = NCS or CN); L = PPh₃, pyridine, 3-picoline, 4-picoline, 1/2(2,2'-bipyridine), 1/2(1,10-phenanthroline) with NOX' (X' = Cl, Br)

The examination of the composition of the remaining complexes (Table I) invariably reveals the bonding of NO with ruthenium in each of the product complexes. It has been further supported by the presence of a band due to $\nu(\text{NO})$ around 1860 cm⁻¹ in their IR spectra besides the other characteristic bands of the co-ligands.

Interestingly, one observes the substitution of CN⁻ and SCN⁻ anions in their respective complexes

by chloride or the bromide of NOX'. Further, during the course of the reactions it has been observed that the initial product formed as a result of the reactions of cyanide complexes with NOX' invariably yielded an oil. In a few cases solid products with CN as co-ligand were obtained by repeated dissolution of the oil in CH₂Cl₂ or CHCl₃ and reprecipitation by dry petroleum ether (40–60 °C), but in all cases addition of a small amount of PPh₃ in the refluxing reaction mixture afforded in good yield very pure products in which CN⁻ had invariably been replaced by Cl⁻ or Br⁻. Similar observations have also been noted for the thiocyanato complexes. In the latter cases the presence of the sulfate ion has also been detected in the reaction products. The IR spectra of the latter complexes showed the presence of four characteristic bands of the bridged sulfato group (1200 cm⁻¹, 1050 cm⁻¹, 850 cm⁻¹, 600 cm⁻¹) [38] besides those due to other co-ligands. Generally, the NCS⁻ ion is very susceptible to oxidation to SO₄²⁻ or SO₃²⁻ by an oxidising agent. NOX' in that respect is quite powerful and therefore the presence of SO₄²⁻ in thiocyanate complexes is not unexpected. What role PPh₃ plays in these crystallization processes is difficult to surmise at the present stage.

¹H NMR spectra of all the complexes showed more or less identical features, a poorly resolved broad multiplet of the protons of the phenyl and N-heteronuclear groups in the region around δ 7.0. In the case of the picolines an additional band around δ 2.0 was also present, showing the presence of the methyl group. The evidence supporting the absence of the cyclopentadienyl group in the complexes is increased by the absence of a band in the region δ 4.0 and δ 5.5 [18].

Reactions of [Ru(η^5 -C₅H₅)(PPh₃)L]⁺X⁻ (where L = 2,2'-bipyridine or 1,10-phenanthroline; X = Cl or Br and [Ru(η^5 -C₅H₅)(PPh₃)(L)X] (where L = pyridine, 2-picoline, 4-picoline, 1/2(2,2'-bipyridine) or 1/2(1,10-phenanthroline), X = I and L = pyridine, 3-picoline, 4-picoline when X = Cl or Br with NOX' (X' = Cl or Br)

All the complexes have similar infrared patterns in the region 4000–350 cm⁻¹. The spectra showed a medium intense band in the 1840–1880 cm⁻¹ range, which suggested the presence of a NO⁺ group bonded to the ruthenium ion [39, 40]. The characteristic bands of the other co-ligands like PPh₃, Py, picolines, bipyridyl or 1,10-phenanthroline have also been exhibited in their spectra [41–44]. Variations in these positions were very small as expected. In addition, no band in the 850 cm⁻¹ region was present in the spectra of the complexes suggesting the absence of the C₅H₅ group in them [18].

The ^1H NMR spectra of the complexes were identical to those of the complexes categorized in this section (*vide infra*).

Magnetic and UV and Visible Spectral Data

All the complexes were diamagnetic in the solid state. This is consistent with an octahedral d^6 system in a strong ligand field causing a low-spin configuration.

The positions of the absorption bands of their electronic spectra taken in chloroform solution are listed in Table I.

All the complexes showed rather a broad medium intense absorption band around 450 nm. Generally $d-d$ or MLCT bands in ruthenium(II) octahedral complexes occur under a broad envelope around 450 nm [45]. It is, therefore, suggested that the presence of a broad band around 450 nm should also imply an octahedral geometry of ligands around the Ru(II) ion. It should be noted that the position of the band in the complexes has been found to be shifted considerably towards higher energy in comparison to those in the spectra of the parent complexes [19] $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{L})\text{X}]$, indicating a strong average ligand field effect of the donor group. In addition, because of the presence of a number of π -acceptor ligands like phosphine, pyridine, picolines, 2,2'-bipyridine or 1,10-phenanthroline, NO_2^- , NO , SCN^- and CN^- , a number of $\pi-\pi^*$ and $n-\pi^*$ transition bands were present in the UV region, resulting in a practically continuous absorption beyond 350 nm.

Conclusions

In conclusion, we wish to point out that NOCl and NOBr provide an efficient source of nitrosylation for various η^5 -cyclopentadienylruthenium(II) complexes, and in all cases except that of the trichlorostannate complexes, the nitrosyl products were isolated without difficulty. NO binds with the metal as NO^+ , with the linear $\text{M}-\text{N}-\text{O}$ mode of bonding, as shown by the high $\nu(\text{NO})$ values ($\sim 1870\text{ cm}^{-1}$). In all the reactions the η^5 -cyclopentadienyl moiety is lost from the coordination sphere upon nitrosylation. In trichlorostannate complexes NO is oxidized to NO_2^- resulting in the formation of nitrito complexes. These also show evidence for the π -interaction of one of the phenyl rings of the triphenylphosphine ligand to the ruthenium center.

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