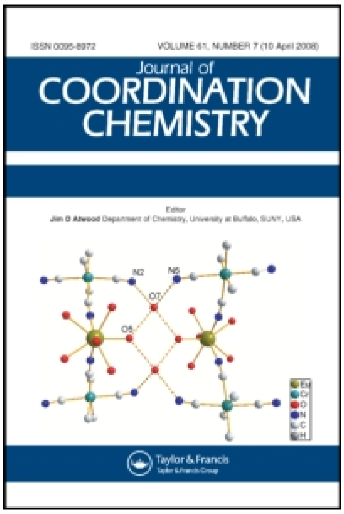

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Bipul C. Paul[a]; Shekhar C. Sarker[a]; Raj K. Poddar[a]
[a] Department of Chemistry, North-Eastern Hill University, Shillong, India

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CONVENIENT SYNTHESIS AND REACTIVITY OF DINITROSYLBIS (TRIPHENYLPHOSPHINE) RUTHENIUM

BIPUL C. PAUL, SHEKHAR C. SARKER and RAJ K. PODDAR*

Department of Chemistry, North-Eastern Hill University, Bijni Complex, Shillong 793003, India

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$[Ru(NO)_2(PPh_3)_2]$ has been synthsized by three convenient methods. Its reactivity has been studied with HX (X = Cl, Br or I) and with neutral mono- and bidentate nitrogen ligands. The products obtained have the compositions $[RuX_3(NO)(PPh_3)_2]$ (X = Cl, Br, or I) and $[Ru(NO)(NO_2)(OH)_2L]$ (L = py, bipy or phen), respectively.

KEY WORDS: Ruthenium, phosphines, nitrosyl, complexes, synthesis.

INTRODUCTION

$[Ru(NO)_2(PPh_3)_2]$ was first reported by Levison and Robinson[1,2] and subsequently by others.[3-7] Various methods[1-7] used in the synthesis of the compound involves (i) a reaction of a ruthenium(II) hydrido complex containing PPh_3 with NO or a nitrosylating agent such as *N*-methyl-*N*-nitrosotoluene-4-sulphonamide, (ii) decomposition of a ruthenium(II) complex containing PPh_3 and NO_2^-, or (iii) a reaction of $RuCl_3$ and PPh_3 or $[RuCl_2(PPh_3)_3]$ with NO or *N*-methyl-*N*-nitrosotoluene-4-sulphonamide in the presence of a strong base, *viz* $NaBH_4$, NEt_3 or NaOEt. In all the above reactions NO or *N*-methyl-*N*-nitrosotoluene-4-sulphonamide has been used as the nitrosyl source. We report here some novel methods of synthesis of $[Ru(NO)_2(PPh_3)_2]$ using HNO_3 or $AgNO_3$ as the nitrosylating agent.

Known reactions of $[Ru(NO)_2(PPh_3)_2]$ with CO, O_2, X_2 (X = Cl, Br or I), $PhCH_2Br$, R_FCOOH ($R_F = CF_3$ or C_2F_5) and $[RuCl_2(PPh_3)_3]$[4,5,8-10] reveal that ruthenium in the reaction products is either in the O or +2 oxidation state. Reactions of $[Ru(NO)_2(PPh_3)_2]$ with neutral nitrogen donor ligands such as pyridine, 2,2,-bipyridine and 1,10-phenanthroline were carried out in inert (nitrogen) and in oxygen atmosphere. The products isolated in oxygen atmosphere were characrerized as $[Ru(NO)(NO_2)(OH_2)(L)]$ (L = py, bipy or phen) whereas no productd could be isolated in case of reaction under nitrogen. Reactions of $[Ru(NO)_2(PPh_3)_2]$ and $[Ru(NO)(NO_2)(OH_2)(L)]$ (L = py, bipy or phen() with HX (X = Cl, Br or I) in oxygen

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* Author for correspondence.

atmosphere resulted in the formation of $[RuX_3(NO)(PPh_3)_2]$ (X = Cl, Br or I) and $[RuX_3(NO)(L)]$ (X = Cl, Br or I; L = py, bipy or phen), respectively.

EXPERIMENTAL

Ruthenium trichloride trihydrate was obtained from Arora Matthey Ltd., Calcutta. $HRu(SO_4)_2(H_2O)_6$ was prepared accprding to the reported method.[11] Analyses for chloride, bromide and iodide were carried out by standard method.[12] Carbon, hydrogen and nitrogen analyses were obtained from the Microanalytical Section of the Department of Chemistry, NEHU, Shillong (Table 1) infrared spectra were recorded on a Perkin-Elmer 983 IR spectrophotometer in the range 4000-200cm^{-1}. Electronic spectra were recorded in acetonitrile on a Hitachi-330 spectrophotometer in the range 800 to 250nm. ^1H NMR spectra were recorded on a Varian EM-390 90MHz spectrometer in CD_3CN. Thermogravimetric analyses were performed on a Perkin-Elmer TGS-2 instrument.

$[Ru(NO)_2(PPh_3)_2]$

Method 1

To a solution of hydrated ruthenium trichloride (0.2g) in ethanol (20cm^3), an ethanolic solution of sodium hydroxide (2 molar) was added dropwise with constant stirring until precipitation of $Ru(OH)_3$ was complete. The hydroxide was washed thrice with

Table 1 Analytical data for the ruthenium complexes

Compound	Colour	Melting point (°C)	Found (calcd)% C	H	N	X
$[Ru(NO)_2(PPh_3)_2]$	red	148	63.00	4.40	4.20	
			663.06)	(4.36)	(4.08)	
$[Ru(NO)(NO_2)(OH)_2(phen)]$	dark brown	280^d	36.10	2.8	14.00	
			(36.82)	(2.55)	(14.32)	
$[Ru(NO)(NO_2)(OH)_2(bipy)]$	dark brown	260^d	32.02	2.60	14.98	
			(32.69)	(2.72)	(15.25)	
$[Ru(NO)(NO_2)(OH)_2(py)]$	light brown	>300	20.21	2.40	14.22	
			(20.68)	(2.41)	(14.48)	
$[RuCl_3(NO)(PPh_3)_2]$	yellow	248	57.20	3.77	2.35	13.08
			(56.73)	(3.93)	(1.83)	(13.98)
$[RuBr_3(NO)(PPh_3)_2]$	orange	230	48.85	3.50	2.02	25.90
			(48.26)	(3.35)	(1.56)	(26.81)
$[RuI_3(NO)(PPh_3)_2]$	dark brown	280	42.34	3.60	1.51	35.95
			(41.69)	(2.89)	(1.35)	(36.77)
$[RuCl_3(NO)(bipy)]$	light brown	310^d	30.03	2.00	10.28	27.12
			(30.53)	(2.03)	(10.68)	(27.09)
$[RuCl_3(NO)(phen)]$	brown	315^d	34.16	2.45	9.91	25.44
			(34.53)	(2.39)	(10.07)	(25.50)
$[RuBr_3(NO)(bipy)]$	dark brown	245	22.71	1.60	7.95	45.02
			(22.77)	(1.51)	(7.96)	(45.54)
$[RuBr_3(NO)(phen)]$	dark brown	265	25.90	1.50	7.49	42.64
			(26.13)	(1.45)	(7.62)	(43.55)

^{d}Decomposes; X = Cl, Br or I.

ethanol and dissolved in the minimum quantity of conc. HNO_3 (~ $0.5cm^3$) by warming on a water-bath. The solution was diluted with ethanol (~ $20cm^{-3}$), triphenylphosphine (2.5g) was added and the mixture refluxed on a water bath for 20 mins when a red crystalline compound separated out. It was centrifuged and washed several times with ethanol and dried in *in vacuo*. Yield, 0.4g (76.3%).

Method 2

To a solution of $HRu(SO_4)_2(H_2O)_6$ (0.3g) in ethanol ($20cm^3$), conc. HNO_3 (~ $0.25cm^3$) was added and the mixture was refluxed for 15 min. To the clear solution triphenylphosphine was added and the mixture further refluxed for 1 hour when the red crystalline compound separated out. Yield, 0.3g (58%).

Method 3

To a solution of hydrated ruthenium trichloride (0.2g) in ethanol ($20cm^3$), silver nitrate (0.45g) (molar ratio 2:7) was added and the mixture refluxed for 3h. It was cooled, AgCl removed and the mother liquor evaporated to dryness on a water bath. The residue was dissolved in ethanol ($15cm^3$) and centrifuged to give a clear red solution. To the solution triphenylphosphine (2g) was added and the mixture refluxed for another 2h, when the red crystalline compound separated out. Yield, 0.32g (61%).

Reactions of $[Ru(NO)_2(PPh_3)_2]$

(*i*) *With nitrogen donor ligands*

A solution of the ligand, L (L = py, bipy or phen) in benzene ($5cm^3$) was added to a benzene solution ($10cm^3$) of $[Ru(NO)_2(PPh_3)_2]$ (0.2g) (molar ratio L: compound = 2:1). The mixture was stirred at room temperature for 2h or refluxed on a water bath (15 mins in case of bipy and phen, 1h in case of py). The compounds separated out, and were centrifuged, washed with benzene and dried *in vacuo*. The compounds obtained analysed satisfactorily for $[Ru(NO)(NO_2)(OH_2)(L)]$ (L = py, bipy or phen). Yield, 50–60%.

(*ii*) *With HX* (*X* = *Cl, Br or I*)

To a suspension of $[Ru(NO)_2(PPh_3)_2]$ (0.5g) in ethanol ($20cm^3$) conc. HX (X = Cl, Br or I) ($0.5cm^3$) was added, when a clear solution was obtained. This was refluxed on a water bath for 45 mins. The complexes separated out, and were centrifuged, washed with ethanol and dried *in vacuo*. The compounds obtained analysed for $[RuX_3(NO)(PPh_3)_2]$ (X = Cl, Br or I). Yield, 70–80%.

Reactions of $[Ru(NO)(NO_2)(OH)_2(L)]$ (*L* = *py, bipy or phen*) *with HX* (*X* = *Cl, Br or I*)

To a solution of $[Ru(NO)(NO_2)(OH)_2(L)]$, (0.2g‘ in water ($10cm^3$) conc. HX ($0.5cm^3$) was added and the mixture warmed on a water bath for 10 min to precipitate the complexes. They were centrifuged, washed with acetone and dried *in vacuo*. The compounds obtained analysed for $[RuX_3(NO)(L)]$ (X = Cl, Br or I; L = py, bipy or phen).

RESULTS AND DISCUSSION

Reported methods of preparation of $[Ru(NO)_2(PPh_3)_2]$ generally involve the use of NO gas or *N*-methyl-*N*-nitrosotoluene-4-sulphonamide as the nitrosylating agent.[1-4,6,7] Grundy *et al.*[5] prepared the compound from $[Ru(CO)_2(NO_2)_2(PPh_3)_2]$, where coordinated NO_2^- transferred one oxygen atom to CO or PPh_3. We report here the preparation of $[Ru(NO)_2(PPh_3)_2]$ using NO_3^- as a source of nitrosylation. Nitrate ion is obtained either from conc. HNO_3 or from $AgNO_3$. The ruthenium source in these synthesis is ruthenium trichloride, freed from chloride by various chemical reactions, *viz* (i) in *method 1*, freshly prepared ruthenium hydroxide is reated with conc. HNO_3, (ii) in *method 2*, $HRu(SO_4)_2(H_2O)_6$ (obtained from $RuCl_3$ and Ag_2SO_4) is treated with conc. HNO_3, (iii) in *method 3*, $RuCl_3.3H_2O$ is treated with $AgNO_3$ to quantitatively precipitate chloride as AgCl. Presence of chloride leads to the formation of $[RuCl_3(NO)(PPh_3)_2]$ as an impurity.[2] The compound is characterized by its elemental analyses, melting point and IR spectrum. The IR spectrum is superimposable on that of the compound obtained by the reported method.[2] Characteristic absorptions (in KBr) due to ν_{NO} are at 1660 and $1616 cm^{-1}$.

Reactions of the compound with conc. HX (X = Cl, Br or I) lead to the formation of $[RuX_3(NO)(PPh_3)_2]$ (X = Cl, Br or I). IR spectra showed a strong, sharp band due to ν_{NO} at 1875, 1870 and $1861 cm^{-1}$, for X = Cl, Br and I, respectively (reported[13-15] at 1876 and $1871 cm^{-1}$ for X = Cl and Br, respectively). The modes $\nu_{Ru\text{-}X}$ (X = Cl and Br) were observed at 323 and $213 cm^{-1}$, respectively. The formation of Ru(II) complexes, *viz* $[RuX_3(NO)(PPh_3)_2]$ (X = Cl, Br or I) from $[Ru(NO)_2(PPh_3)_2]$ was reported by oxidation with halogens.[5]

Reactions of $[Ru(NO)_2(PPh_3)_2]$ with neutral nitrogen donor ligands, *viz* pyridine, 2,2′-bipyridine and 1,10-phenanthroline under aerobic conditions, resulted in the formation of $[Ru(NO)(NO_2)(OH)_2(L)]$ (L = py, bipy or phen), whereas reactions under nitrogen atmosphere gave no compound which could be isolated. The absence of PPh_3 and presence of the *N*-heterocycle in the complexes was confirmed by IR and ^1H NMR studies. The IR showed strong absorptions at 3420 and $1833 cm^{-1}$ (at $1825 cm^{-1}$ for L = py) due to ν_{OH} and ν_{NO} respectively. Further, the presence of bands at 1383 and $1312 cm^{-1}$ in all the complexes could be assigned to $\nu_{asy(NO)}$ and $\nu_{sym(NO)}$ modes of vibration of the nitro group.[16-17]

Thermogravimetric analyses of $[Ru(NO)(NO_2)(OH)_2(L)]$ (L = bipy or py) under nitrogen were similar. In the case of the bipyridine complex weight loss corresponding to one H_2O molecule was observed between 110 and 207°C, weight loss corresponding to NO and NO_2 was observed from 207 to 328°C, and weight loss corresponding to one bipyridine molecule was between 328 and 445°C. The loss of one H_2O molecular is due to the two hydroxo groups coordinated to the metal. In the case of $[Ru(NO)(NO_2)(OH)_2(py)]$, a gradual weight loss up to 160°C corresponding to one H_2O molecule, between 160 and 290°C corresponding to NO and NO_2 groups, and a sharp loss from 290 to 330°C corresponding to one pyridine molecule was observed.

The electronic absorption spectra of $[Ru(NO)(NO_2)(OH)_2(L)]$ (L = bipy or phen) in MeCN showed one band at 440 nm. The molar extension coefficient for the phen complex was $870 M\ cm^{-1}$, as for the bipy complex it was about ten times greater (8200). The absorption in the former case could be assigned to a combination of $^1A_{1g} \rightarrow {}^1T_{1g}$ and Ru(II)→phen charge transfer transitions, whereas in the latter case, it could be mostly due to Ru(II)→bipy charge transfer transition.

Reactions of $[Ru(NO)(NO_2)(OH)_2(L)]$ (L = bipy or phen) with HX (X = Cl, Br or

I) lead to the formation of $(RuX_3(NO)L]$, whose IR spectra had the following characteristic features: ν_{NO} was observed in the range 1880 to 1860cm^{-1}, as reported.[13] Bands at 3420 and 1383cm^{-1} due to ν_{OH} and ν_{NO} (NO_2^- group) respectively of $[Ru(NO)(NO_2)(OH)_2(L)]$ were not observed. In the case of $[RuCl_3(NO)L]$, two medium intensity bands at 335 and 298cm^{-1} were observed, and which may be assigned to $\nu_{Ru\text{-}Cl}$. Reactions of $[Ru(NO)(NO_2)(OH)_2(L)]$ (L = py, bipy or phen) with HX (X = Cl, Br or I) indicate that the nitro and hydroxo ligands are completely substituted by halides.

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