Pergamon

0277-5387(94)00454-4

Polyhedron Vol. 14, No. 13–14, pp. 1987–1991, 1995

0277–5387/95 $9.50+0.00

ORGANOMETALLIC THIONITROSYL AND NITROSYL COMPLEXES OF RUTHENIUM

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(*Received* 28 *April* 1994; *accepted* 20 *October* 1994)

Abstract—Trithiazyltrichloride, $(NSCl)_3$, reacted with $[Ru(\eta\text{-}C_5H_5)_2]$, $[\{Ru(cod)Cl_2\}_x]$ (cod = *cis-cis*-1,5-cyclooctadiene), $[Ru(cht)Cl_2]_2$ (cht = 1,3,5-cycloheptatriene) and $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ to give thionitrosyl complexes $[(\eta^5\text{-}C_5H_5)Ru(NS)Cl_2]$, $[Ru(NS)Cl_2(cod)]Cl$, $[Ru(NS)Cl_2(cht)]Cl$ and $[(\eta^6\text{-}C_6H_6)Ru(NS)Cl_2]Cl$, respectively. Reaction of nitrosyl chloride with $[Ru(\eta^5\text{-}C_5H_5)_2]$, $[\{Ru(cod)Cl_2\}_x]$, $[Ru(cht)Cl_2]_2$ and $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ yielded corresponding nitrosyl complexes $[(\eta^5\text{-}C_5H_5)Ru(NO)Cl_2]$, $[Ru(NO)Cl_2(cod)]Cl$, $[Ru(NO)Cl_2(cht)]Cl$ and $[(\eta^6\text{-}C_6H_6)Ru(NO)Cl_2]Cl$. The complex $[(\eta^5\text{-}C_5H_5)Ru(NO)Cl_2]$ was also prepared by the reaction of $Ru(NO)Cl_3$ with C_5H_6. In the presence of zinc dust, reaction of $Ru(NO)Cl_3$ with C_5H_6 gave a paramagnetic complex $[\{(\eta^5\text{-}C_5H_5)Ru(NO)\}_2(\mu\text{-}Cl)_2]$.

Despite the absence of requisite precursors and the inconvenience of handling sulphur nitrogen compounds, a number of transition metal thionitrosyl complexes have been studied.[1–5] The thionitrosyl radical with one unpaired electron has only a transient existence. So far there is no report of an organometallic thionitrosyl ruthenium complex and relatively few organometallic nitrosyl complexes have been reported.[6–9] Herein we wish to report the isolation of organometallic thionitrosyl and nitrosyl complexes. $[(\eta^5\text{-}C_5H_5)Ru(NS)Cl_2]$ and $[Ru(NS)Cl_2(L)]Cl$ [L = *cis-cis*-1,5,-cyclooctadiene (cod), 1,3,5-cycloheptatriene (cht), $\eta^6-C_6H_6$] are useful starting materials and excellent precursors for synthesizing organometallic thionitrosyl complexes.

EXPERIMENTAL

All the reagents used were of AnalaR grade or of chemically pure grade. Solvents were dried over appropriate drying agents, purged with nitrogen and distilled before use. Reactions of $(NSCl)_3$ were performed under pure, dry nitrogen. $[Ru(\eta^5\text{-}C_5H_5)_2]$, $[\{Ru(cod)Cl_2\}_x]$, $[Ru(cht)Cl_2]_2$, $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$, $Ru(NO)Cl_3$, trithiazyltrichloride and nitrosyl chloride were prepared by literature methods.[10–16]

Analysis

Carbon, hydrogen and nitrogen analysis were performed by the microanalytical section of the Central Drug Research Institute, Lucknow, India. For the determination of chloride, the samples were decomposed with $NaNO_3$ and NaOH in the ratio 8:64 in a nickel crucible for about 20 min and allowed to cool. The chloride was extracted with distilled water and acidified with HNO_3 and was estimated as AgCl. For the determination of sulphur, the samples were decomposed with HCl and HNO_3 and from the solution, sulphur was estimated as $BaSO_4$. The IR spectra of the samples were recorded with the Shimadzu model 460 spectrophotometer. Samples were prepared as KBr pellets. The magnetic measurement was made on a Gouy balance at room temperature (25°C) and mercury tetrathiocyanatocobaltate(II) was used as calibrant. The proton NMR spectra were recorded on a Varian

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CFT-20 at 300 MHz in $CDCl_3$ or DMSO-d_6 using tetramethylsilane as an internal reference. ESR spectrum was recorded on a Varian Associates E-line EPR Century Series model E-104 A spectrophotometer. Analytical data and important frequencies of the complexes are given in Tables 1 and 2.

(a) *Preparation of* $[(\eta^5\text{-}C_5H_5)Ru(NS)Cl_2]$

A solution of trithiazyltrichloride (0.09 g, 0.37 mmol) in tetrahydrofuran (25 cm^3) was added dropwise to a stirred solution of ruthenocene (0.2 g, 0.86 mmol) in tetrahydrofuran (30 cm^3) at -5°C. The reaction mixture was then stirred for 2 h. The resulting solution was evaporated to 5 cm^3 under reduced pressure. On addition of n-hexane (50 cm^3), a green complex $[(\eta^5\text{-}C_5H_5)Ru(NS)Cl_2]$ separated, which was collected, recrystallized from dichloromethane–hexane and dried *in vacuo* (yield 0.14 g, 57%).

(b) *Preparation of* $[Ru(NS)Cl_2(cod)]Cl$

A solution of trithiazyltrichloride (0.09 g, 0.39 mmol) in tetrahydrofuran (25 cm^3) was added dropwise to a stirred suspension of $[\{Ru(cod)Cl_2\}_x]$ (0.2 g, 0.72 mmol) in tetrahydrofuran (40 cm^3) at room temperature. The reaction mixture was stirred for 20 h. It was reduced to dryness under reduced pressure. A red brown complex $[Ru(NS)Cl_2(cod)]Cl$

Table 1. Elemental analysis of the complexes

	Found (calc.) (%)				
Complex	C	H	N	S	Cl
$[(\eta^5\text{-}C_5H_5)Ru(NS)Cl_2]$	21.1	1.8	4.9	11.5	25.1
	(21.2)	(1.7)	(4.9)	(11.3)	(25.0)
$[Ru(NS)Cl_2(cod)Cl$	26.6	3.2	3.9	8.7	28.8
	(26.5)	(3.3)	(3.8)	(8.8)	(29.4)
$[Ru(NS)Cl_2(cht)]Cl$	24.4	2.3	4.1	9.1	30.6
	(24.3)	(2.3)	(4.0)	(9.2)	(30.8)
$[(\eta^6\text{-}C_6H_6)Ru(NS)Cl_2]Cl$	21.6	2.3	4.3	9.6	31.6
	(21.7)	(1.8)	(4.2)	(9.6)	(32.1)
$[(\eta^5\text{-}C_5H_5)Ru(NO)Cl_2]$	22.6	1.8	5.1	—	26.7
	(22.4)	(1.8)	(5.2)	—	(26.5)
$[Ru(NO)Cl_2(cod)]Cl$	27.6	3.5	4.1	—	30.7
	(27.7)	(3.4)	(4.0)	—	(30.8)
$[Ru(NO)Cl_2(cht)]Cl$	25.5	2.3	4.2	—	32.2
	(25.4)	(2.4)	(4.2)	—	(32.3)
$[(\eta^6\text{-}C_6H_6)Ru(NO)Cl_2]Cl$	22.7	2.5	4.3	—	33.6
	(22.8)	(1.9)	(4.4)	—	(33.7)
$[\{(\eta^5\text{-}C_5H_5)Ru(NO)\}_2(\mu\text{-}Cl)_2]$	25.7	2.5	3.1	—	15.2
	(25.9)	(2.5)	(3.0)	—	(15.3)

Table 2. Colour, m.p. and important IR frequencies of the complexes

Complex	Colour	m.p. (°C)	ν(NS) (cm^{-1})	ν(NO) (cm^{-1})
$[(\eta^5\text{-}C_5H_5)Ru(NS)Cl_2]$	Green	Dec. 195–97	1270	—
$[Ru(NS)Cl_2(cod)]Cl$	Reddish-brown	>250	1332	—
$[Ru(NS)Cl_2(cht)]Cl$	Brown	>250	1325	—
$[(\eta^6\text{-}C_6H_6)Ru(NS)Cl_2]Cl$	Brown	>250	1322	—
$[(\eta^5\text{-}C_5H_5)Ru(NO)Cl_2]$	Green	230	—	1810
$[Ru(NO)Cl_2(cod)]Cl$	Red–brown	>250	—	1890
$[Ru(NO)Cl_2(cht)]Cl$	Brown	>250	—	1891
$[(\eta^6\text{-}C_6H_6)Ru(NO)Cl_2]Cl$	Orange–brown	>250	—	1895
$[\{(\eta^5\text{-}C_5H_5)Ru(NO)\}_2(\mu\text{-}Cl)_2]$	Brown	Dec. 198	—	1880

was isolated, washed with cold water, ethanol, ether and dried *in vacuo* (yield 0.19 g, 73%).

(c) *Preparation of* [Ru(NS)Cl$_2$(cht)]Cl

A solution of trithiazyltrichloride (0.07 g, 0.31 mmol) in tetrahydrofuran (25 cm^3) was added dropwise to a stirred suspension of [Ru(cht)Cl$_2$]$_2$ (0.2 g, 0.76 mmol) in tetrahydrofuran (40 cm^3) at room temperature. The reaction mixture was stirred for 20 h. A brown complex [Ru(NS)Cl$_2$(cht)]Cl was isolated by the same procedure as given in (b) (yield 0.18 g, 69%).

(d) *Preparation of* [(η^6-C$_6$H$_6$)Ru(NS)Cl$_2$]Cl

A solution of trithiazyltrichloride (0.08 g, 0.33 mmol) in tetrahydrofuran (30 cm^3) was added dropwise to a stirred suspension of [(η^6-C$_6$H$_6$)RuCl$_2$]$_2$ (0.2 g, 0.79 mmol) in tetrahydrofuran (40 cm^3) at room temperature. The reaction mixture was stirred for 20 h. A brown complex [(η^6-C$_6$H$_6$)Ru (NS)Cl$_2$]Cl was isolated by the same procedure as given in (b) (yield 0.18 g, 70%).

(e) *Preparation of* [(η^5-C$_5$H$_5$)Ru(NO)Cl$_2$]

Method I. A saturated solution of NOCl (20 cm^3) in dichloromethane was added dropwise to a stirred solution of ruthenocene (0.2 g, 0.86 mmol) in dichloromethane (20 cm^3) at room temperature. The reaction mixture was stirred for 5 min. It was evaporated to 10 cm^3 under reduced pressure. On addition of n-hexane (50 cm^3), a green complex [(η^5-C$_5$H$_5$)Ru(NO)Cl$_2$] separated out which was filtered, washed with n-hexane and dried *in vacuo*. It was recrystallized with dichloromethane–n-hexane (yield 0.14 g, 62%).

Method II. Freshly distilled cyclopentadienyl (2 cm^3) was added to a stirred solution of Ru(NO)Cl$_3$ (0.3 g, 1.26 mmol) in tetrahydrofuran (30 cm^3) at room temperature. The reaction mixture was stirred for 24 h. It was reduced to 5 cm^3 under reduced pressure. On addition of n-hexane (40 cm^3), a green complex [(η^5-C$_5$H$_5$)Ru(NO)Cl$_2$] separated out, which was filtered, washed with n-hexane. It was recrystallized with dichloromethane–n-hexane and dried *in vacuo* (yield 0.19 g, 41%).

(f) *Preparation of* [Ru(NO)Cl$_2$(cod)]Cl

A saturated solution of NOCl (20 cm^3) in dichloromethane was added dropwise to a stirred suspension of [{Ru(cod)Cl$_2$}$_x$] (0.2 g, 0.72 mmol) in dichloromethane (40 cm^3) at room temperature. The reaction mixture was stirred for 20 h and then filtered. A red–brown residue [Ru(NO)Cl$_2$(cod)]Cl was washed with n-hexane and dried *in vacuo* (yield 0.17 g, 67%).

(g) *Preparation of* [Ru(NO)Cl$_2$(cht)]Cl

A saturated solution of NOCl (20 cm^3) in dichloromethane was added dropwise to a stirred suspension of [Ru(cht)Cl$_2$]$_2$ (0.2 g, 0.76 mmol) in dichloromethane (40 cm^3) at room temperature. The reaction mixture was stirred for 20 h. A brown complex [Ru(NO)Cl$_2$(cht)]Cl was isolated by a similar procedure as given in (f) (yield 0.19 g, 72%).

(h) *Preparation of* [(η^6-C$_6$H$_6$)Ru(NO)Cl$_2$)]Cl

A saturated solution of NOCl (20 cm^3) in dichloromethane was added dropwise to a stirred suspension of [(η^6-C$_6$H$_6$)RuCl$_2$]$_2$ (0.2 g, 0.79 mmol) in dichloromethane (40 cm^3) at room temperature. The reaction mixture was stirred for 20 h. An orange–brown complex [(η^6-C$_6$H$_6$)Ru(NO)Cl$_2$]Cl was isolated by a similar procedure as given in (f) (yield 0.19 g, 73%).

(i) *Preparation of* [{(η^5-C$_5$H$_5$)Ru(NO)}$_2$(μ-Cl)$_2$]

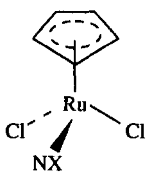
Freshly distilled cyclopentadienyl (2 cm^3) and zinc dust (0.5 g) were added to a stirred solution of Ru(NO)Cl$_3$ (0.3 g, 1.26 mmol) in tetrahydrofuran (30 cm^3) at room temperature. The reaction mixture was stirred for 24 h. It was filtered and reduced to 5 cm^3 under reduced pressure. On addition of n-hexane a brown complex [{(η^5-C$_5$H$_5$)Ru(NO)}$_2$(μ-Cl)$_2$] was isolated, which was filtered, washed with n-hexane and dried *in vacuo* (yield 0.13 g, 44%).

RESULTS AND DISCUSSION

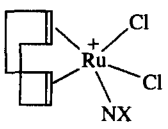
Reaction of [Ru(η^5-C$_5$H$_5$)$_2$] with trithiazyltrichloride in tetrahydrofuran resulted in the formation of the thionitrosyl complex [(η^5-C$_5$H$_5$)Ru(NS)Cl$_2$] (**1**). The IR spectrum of **1** showed a sharp band at 1270 cm^{-1} due to thionitrosyl stretching vibration, besides the bands due to cyclopentadienyl. Complex is air and moisture sensitive.

Reaction of trithiazyltrichloride with [{Ru(cod) Cl$_2$}$_x$], [Ru(cht)Cl$_2$]$_2$ and [(η^6-C$_6$H$_6$)RuCl$_2$]$_2$ in tetrahydrofuran resulted in the formation of cationic thionitrosyl complexes [Ru(NS)Cl$_2$(cod)Cl (**2**), [Ru(NS)Cl$_2$(cht)]Cl (**3**) and [(η^6-C$_6$H$_6$)Ru(NS) Cl$_2$]Cl (**4**), respectively. The IR spectra of these complexes exhibited bands at 1332, 1325 and 1322 cm^{-1} due to ν(NS), respectively.

The proton NMR spectrum of **2** shows multiplets



(1)



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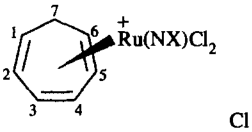

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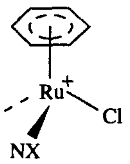

(4)

(X=S or O)

at δ 5.47 and δ 2.25 ppm due to the olefinic and methylenic protons, respectively. The proton NMR spectrum of **3** exhibits multiplets due to H-2, H-3, H-4 and H-5 protons at the lowest field (δ 6.16 ppm); due to terminal protons H-1 and H-6 at δ 5.36 and δ 2.17 ppm due to H-7 protons. The proton NMR spectrum of $[(\eta^6\text{-}C_6H_6)Ru(NS)Cl_2]Cl$ shows the presence of only one benzene resonance at δ 5.97 ppm. This is assigned to **4**.

Reaction of ruthenocene with nitrosyl chloride in dichloromethane resulted in the formation of a green complex $[(\eta^5\text{-}C_5H_5)Ru(NO)Cl_2]$, which was also prepared by the reaction of $[Ru(NO)Cl_3]$ with C_5H_6. The complex $[(\eta^5\text{-}C_5H_5)Ru(NO)Cl_2]$ was previously prepared (a) by the reaction of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2Cl]$ with NO under UV radiation[17] and (b) by the reaction of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2Cl]$ with NOCl.[18] The IR spectrum of the complex $[(\eta^5\text{-}C_5H_5)Ru(NO)Cl_2]$ exhibited a band at 1810 cm^{-1} due to ν(NO). ^1H NMR spectrum of complex $[(\eta^5\text{-}C_5H_5)Ru(NO)Cl_2]$ showed a singlet at δ 6.30 due to the C_5H_5 group.

Reaction of nitrosyl chloride with $[\{Ru(cod)Cl_2\}_x]$, $[Ru(cht)Cl_2]_2$ and $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ in dichloromethane yielded cationic nitrosyl complexes $[Ru(NO)Cl_2(cod)]Cl$, $[Ru(NO)Cl_2(cht)]Cl$ and $[(\eta^6\text{-}C_6H_6)Ru(NO)Cl_2]Cl$, respectively. The IR spectra of the complexes $[Ru(NO)Cl_2(cod)]Cl$, $[Ru(NO)Cl_2(cht)]Cl$ and $[(\eta^6\text{-}C_6H_6)Ru(NO)Cl_2]Cl$ exhibited bands at 1890, 1891 and 1895 cm^{-1} due to ν(NO), respectively. The proton NMR spectrum $[Ru(NO)Cl_2(cod)]Cl$ exhibits resonances at δ 5.50 ppm for the olefinic protons and at δ 2.30 ppm for the methylene protons. The proton NMR spectrum of $[Ru(NO)Cl_2(cht)]Cl$ exhibits multiplets due to H-2, H-3, H-4 and H-5 protons at lowest field (δ 6.18 ppm); due to terminal protons H-1 and H-6 at δ 5.33 and δ 2.17 ppm due to H-7 protons. The proton NMR spectrum of $[(\eta^6\text{-}C_6H_6)Ru(NO)Cl_2]Cl$ shows the presence of only one benzene resonance at δ 5.96 ppm.

In the presence of zinc dust, the reaction of $Ru(NO)Cl_3$ with cyclopentadiene, C_5H_6 yielded the $[\{(\eta^5\text{-}C_5H_5)Ru(NO)\}_2(\mu\text{-}Cl)_2]$ complex. The IR spectrum of the complex $[\{(\eta^5\text{-}C_5H_5)Ru(NO)\}_2(\mu\text{-}Cl)_2]$ exhibited a band at 1880 cm^{-1} due to ν(NO) suggesting the presence of linear nitrosyl group. This complex can be regarded as involving ruthenium(I) and NO^+. Coordination compounds of ruthenium(I) have as yet attracted less attention than those of ruthenium(II) and ruthenium(III).[19] The complex $[\{(\eta^5\text{-}C_5H_5)Ru(NO)\}_2(\mu\text{-}Cl)_2]$ is paramagnetic with a magnetic moment $\mu = 1.61$ B.M. at 298 K. The first derivative X-band ESR powder spectrum of the complex $[\{(\eta^5\text{-}C_5H_5)Ru(NO)\}_2(\mu\text{-}Cl)_2]$ showed a broad band with $g_{av} = 2.12$.

Acknowledgements—We thank Council of Scientific & Industrial Research, New Delhi for Senior Research fellowship (to H.G.) and Department of Science and Technology, New Delhi for financial support of this work. We also thank RSIC, Indian Institute of Bombay for recording NMR spectra.

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