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Ligating properties of thionitrosoamines

IV *. Cationic complexes of rhodium(I), rhodium(III), and ruthenium(II) containing *N*-thionitrosodimethylamine

Giuseppe Tresoldi*, Sergio Sergi, Sandra Lo Schiavo and Pasquale Piraino
Dipartimento di Chimica Inorganica e Struttura Molecolare dell'Università, 98100 Messina (Italy)

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Abstract

The solvento species obtained by treatment of the complexes [Rh(1,5-cyclooctadiene)Cl]$_2$, [Rh(norbornadiene)Cl]$_2$, [Rh(CO)$_2$Cl]$_2$, $C_5H_5Rh(CO)I_2$, [$C_5Me_5RhCl_2$]$_2$, and [Ru(C_6H_6)Cl_2]$_2$ with $AgPF_6$ in acetone or acetonitrile react with a large excess of Me_2NNS to give the compounds [Rh(1,5-C_8H_{12})($SNNMe_2$)$_2$]PF_6 (**1a**), [Rh(C_7H_8)($SNNMe_2$)$_2$]PF_6 (**1b**), [Rh(CO)$_2$($SNNMe_2$)$_2$]PF_6 (**2**), [C_5H_5Rh($SNNMe_2$)$_3$](PF_6)$_2$ (**3**), [C_5Me_5Rh($SNNMe_2$)$_3$](PF_6)$_2$ (**4**), and [Ru(C_6H_6)($SNNMe_2$)$_3$](PF_6)$_2$ (**5**). If the thionitroso ligand is not present in large excess decomposition often occurs. The use of $AgClO_4$ allows isolation of the perchlorate salts of **1a**, **1b**, **2**, **4**, and **5**, and the complexes [C_5H_5Rh($SNNMe_2$)$_2$(ClO_4)]ClO_4 (**6**) and Rh(1,5-C_8H_{12})($SNNMe_2$)(ClO_4) (**7**). In the H^1 NMR spectra the methyl protons of Me_2NNS are observed as two quadruplets, in the range δ 3.75–4.25 (^4J(HH) ca. 0.7 Hz) because of restricted rotation around the N–N bond. The rhodium(I) complexes (**1a**, **1b**, and **2**) reacts with PPh_3 or *p*-tolylPPh$_2$ to give labile products, and only [Rh(1,5-C_8H_{12})($SNNMe_2$)(PPh_3)]ClO_4 (**8**) and [Rh(1,5-C_8H_{12})($SNNMe_2$)(*p*-tolylPPh$_2$)]ClO_4 (**9**) were isolated and characterized.

Introduction

Neutral complexes of palladium(II), platinum(II), rhodium(I), rhodium(III), and chromium(0) containing thionitrosoamines have been reported previously [1–4]. In all those complexes the ligand is *S*-coordinated and there is a $\sigma + \pi$ synergistic interaction of the metal with Me_2NNS ligand.

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We reported only two cationic species $[Pd(SNNMe_2)_4]^{2+}$ and $[Pt(SNNMe_2)_4]^{2+}$, the salts of which are less stable [2]. It seems clear that the dipolar form, which contributes to the over-all electronic structure of Me_2NNS [5], plays an important role in determining the strength of the metal–sulfur bond and the stability of the cationic complexes. It was therefore of interest to obtain more information, and we have now extended our studies to the synthesis and characterization of the cationic complexes of rhodium(I), rhodium(III), and ruthenium(II) containing *N*-thionitrosodimethylamine.

Results and discussion

The route used for the preparation of cationic *N*-thionitrosodimethylamine-rhodium(I), -rhodium(III), and -ruthenium(II) complexes involves the in situ formation of solvento species from dimeric chloro-bridged complexes and displacement of the coordinated solvent by Me_2NNS. The reactions occur rapidly at room temperature and high yields of the products can be obtained if a large excess of Me_2NNS is used. Thus treatment of acetone or acetonitrile solutions of $[Rh(diene)Cl]_2$, $[Rh(CO)_2Cl]_2$, $[C_5Me_5RhCl_2]_2$ and $[Ru(C_6H_6)Cl_2]_2$ with AgX ($X = ClO_4$, PF_6) gives solutions of the solvento species, which are filtered into diethyl ether solutions of Me_2NNS to give the complexes $[Rh(diene)(SNNMe_2)_2]X$ (diene = 1,5-cyclooctadiene (**1a**), norbornadiene (**1b**), $[Rh(CO)_2(SNNMe_2)_2]X$ (**2**), $[C_5Me_5Rh(SNNMe_2)_3]X_2$ (**4**) or $[Ru(C_6H_6)(SNNMe_2)_3]X_2$ (**5**). Complex **2** can also be obtained by bubbling CO through an acetone solution of **1a** or **1b** [3]. The solvents species obtained from $C_5H_5Rh(CO)I_2$ and $AgPF_6$ also reacts with an excess of Me_2NNS to give $[C_5H_5Rh(SNNMe_2)_3](PF_6)_2$ (**3**).

Complexes **1a**, **1b**, **3**, **4**, and **5** are orange solids stable for several weeks, whereas **2** is stable only for a few days. Disappearance of the ν(CO) stretches at 2015s and 2080s cm^{-1} and the appearance of a ν(CO) band at 2040 cm^{-1} shows that complex **2** loses CO to give a monocarbonyl compound, but we were unable to obtain it pure. These complexes are soluble in acetone, acetonitrile, and dimethylsulfoxide, although $[Ru(C_6H_6)(SNNMe_2)_3](ClO_4)_2$ is quite insoluble in acetone and acetonitrile and **2** decomposes rapidly in solution.

Conductivity measurements for a 5×10^{-4} *M* acetone solution of these complexes indicate that **1a**, **1b** and **2** are uni-univalent electrolytes (Λ_M is in the range 160–170 $ohm^{-1}\,cm^2\,mol^{-1}$) while **3**, **4** and **5** are bi-univalent electrolytes (Λ_M is in the range 210–220 $ohm^{-1}\,cm^2\,mol^{-1}$).

The IR spectra of all the compounds show the ν(N–S) of the Me_2NNS moiety at about 780 cm^{-1}, consistent with the *S*-coordination of the thionitroso ligand to the metal [1–4]. The ν(N–N) stretches of these cationic compounds are found at about 1135 cm^{-1}; the same bands in the neutral rhodium(I) and rhodium(III) complexes appear at about 1120s and 1130s cm^{-1}, respectively [3]. The shift to higher wavenumbers indicates a greater double bond character of the N–N bond when the ligand is coordinated to the cationic complexes, and suggests that in this case the dipolar character of the ligand is the main factor which stabilizes the sulfur–metal bond.

The ^1H NMR spectra show the resonance of the $N–CH_3$ protons as two quadruplets (^4J(HH) ca. 0.7 Hz) in the range δ 3.75–4.25. In order to confirm the spin–spin coupling of the protons of the two methyl groups we carried out a homodecoupling experiment on **1a**; irradiation of the signal at δ 4.15 enabled observation of the signal at δ 3.87 as a singlet.

The course of the reactions of the solvento species with Me_2NNS is dependent on the ratio of the reagents. If Me_2NNS is not present in large excess the products are different from those described above, and are often unstable. When a diethyl ether solution of Me_2NNS is slowly added to an acetone solution of the solvento species obtained from $C_5H_5Rh(CO)I_2$ and $AgClO_4$ an orange compound which analyzes as $C_5H_5Rh(SNNMe_2)_2(ClO_4)_2$ is formed. The same reaction with $AgPF_6$ leads to the formation of the decomposition product. Its ^1H NMR spectrum is similar to that of **3** although the signals of the cyclopentadienyl (δ 5.9, *J*(RhH) 0.5 Hz) and of $N-CH_3$ (δ 3.9 and 4.18, ^4J 0.65 Hz) protons are slightly shifted and the integrated cyclopentadienyl and $N-CH_3$ signals are in a 5/12 ratio. Conductivity measurements in acetone solution for this compound indicate that it is bi-univalent electrolyte (Λ_M 200 ohm^{-1} cm^2 mol^{-1} for a 5×10^{-4} *M* solution). Unfortunately its insolubility prevented measurements in apolar solvents. The bands of the Me_2NNS moiety at 1135s and 1025m cm^{-1} in the IR spectrum prevent definite confirmation of the presence of coordinated perchlorate [6].

Table 1

Analytical and characteristic ^1H NMR data

Complex	Analyses (Found (calc) (%))			^1H NMR (δ, ppm; *J*, Hz) (acetone-d_6)
	C	H	N	δ($N-CH_3$)
$[Rh(1,5\text{-}C_8H_{12})(SNNMe_2)_2]ClO_4$ [a]	29.30	4.88	11.50	3.87q ^4J(HH) 0.66
(**1a**)	(29.36)	(4.93)	(11.41)	4.15q
$[Rh(C_7H_8)(SNNMe_2)_2]ClO_4$ [a]	27.78	4.20	11.76	3.80q *J*(HH) 0.66
(**1b**)	(27.82)	(4.24)	(11.80)	4.16q
cis-$[Rh(CO)_2(SNNMe_2)_2]ClO_4$ [a]	16.50	2.71	12.80	
(**2**)	(16.43)	(2.76)	(12.77)	
$[C_5H_5Rh(SNNMe_2)_3](PF_6)_2$	18.20	3.17	11.58	4.00q ^4J(HH) 0.70
(**3**)	(18.14)	(3.18)	(11.54)	4.20q
				6.15d [b] *J*(RhH) 0.48
$[C_5Me_5Rh(SNNMe_2)_3](ClO_4)_2$ [a]	27.16	4.74	11.92	3.85q ^4J(HH) 0.68
(**4**)	(27.16)	(4.70)	(11.88)	4.08
				1.70s [c]
$[Ru(C_6H_6)(SNNMe_2)_3](ClO_4)_2$ [a]	22.26	3.71	13.00	4.00q [d] ^4J(HH) 0.70
(**5**)	(22.22)	(3.73)	(12.96)	4.25q [d]
				6.40s [d,e]
$[C_5H_5Rh(SNNMe_2)_2(ClO_4)]ClO_4$	19.78	3.14	10.18	3.90q ^4J(HH) 0.65
(**6**)	(19.75)	(3.13)	(10.24)	4.18q
				5.90d [b] *J*(RhH) 0.50
$[Rh(1,5\text{-}C_8H_{12})(SNNMe_2)(ClO_4)]$	29.80	4.60	7.00	
(**7**)	(29.97)	(4.53)	(6.99)	
$[Rh(1,5\text{-}C_8H_{12})(SNNMe_2)(PPh_3)]ClO_4$	50.67	4.80	4.23	3.55q ^4J(HH) 0.66
(**8**)	(50.73)	(5.03)	(4.23)	3.90q
$[Rh(1,5\text{-}C_8H_{12})(SNNMe_2)(p\text{-tolylPPh}_2)]$	51.37	5.18	4.14	3.54q ^4J(HH) 0.68
ClO_4 (**9**)	(51.45)	(5.21)	(4.14)	3.92q
				2.40s [f]

[a] The data for the analogous hexafluorophosphate salts are omitted. [b] Protons of C_5H_5. [c] Protons of C_5Me_5. [d] ^1H NMR data for $[Ru(C_6H_6)(SNNMe_2)_3](PF_6)_2$ soluble in acetone-d_6. [e] Protons of C_6H_6. [f] Protons of the methyl of the tolyl group.

In view of the data collected we suggest that the compound in the solid state can be formulated as $[C_5H_5Rh(SNNMe_2)_2(ClO_4)]ClO_4$ (**6**), whereas in solution it exists as $[C_5H_5Rh(SNNMe_2)_2(solvent)](ClO_4)_2$.

The solvento species obtained from $[Rh(1,5\text{-}C_8H_{12})Cl]_2$ and $AgClO_4$ also reacts with a diethyl ether solution of Me_2NNS (added slowly) to give a dark orange solid which analyses as $Rh(1,5\text{-}C_8H_{12})(SNNMe_2)(ClO_4)$. This product loses the diene (slowly in the solid state, rapidly in solution) to give an unidentified solid containing Me_2NNS and ClO_4.

It can be formulated as $Rh(1,5\text{-}C_8H_{12})(SNNMe_2)(ClO_4)$ (**7**) analogous to complex **6**. In accordance with this formulation, **7** is formed by reaction of $Rh(1,5\text{-}C_8H_{12})(SNNMe_2)Cl$ [3] with $AgClO_4$.

The attempts to prepare analogous complexes by reaction of the solvento species $[Rh(C_7H_8)(acetone)_2]ClO_4$ or $[Rh(CO)_2(acetone)_2]ClO_4$ with Me_2NNS (added slowly) failed because of the instability of the products. Reactions of $[C_5Me_5Rh(acetone)_3](ClO_4)_2$ or $[Ru(C_6H_6)(acetone)_3](ClO_4)_2$ with Me_2NNS always give **4** or **5** respectively.

We examined the reactions of PPh_3 and p-tolylPPh_2 with the thionitroso complexes **1a**, **1b**, **2**, **3**, **4**, **5**. The rhodium(III) and ruthenium(II) complexes did not react (decomposition of Me_2NNS prevents the use of drastic conditions), but **1a** reacted with PPh_3 or p-tolylPPh_2 (ratio 1/1) to give the products $[Rh(1,5\text{-}C_8H_{12})(SNNMe_2)(PPh_3)]ClO_4$ (**8**) and $[Rh(1,5\text{-}C_8H_{12})(SNNMe_2)(p\text{-tolyl-}PPh_2)]ClO_4$ (**9**). These products lose the $1,5\text{-}C_8H_{12}$ to give unidentified compounds. The same reactions with **1b** and **2** gave products too labile for characteritation.

The ^1H NMR spectrum of complexes **8** and **9** show, in addition to the signals associated with the phenyl and diene groups, two quadruplets in the range δ 3.5–3.95 (Table 1) assigned to $N\text{–}CH_3$ protons. Complex **9** also exhibits a singlet at δ 7.4 characteristic of the tolyl methyl groups.

Experimental

The complexes $[Rh(CO)Cl]_2$ [7], $[Rh(1,5\text{-}C_8H_{12})Cl]_2$ [8], $[Rh(C_7H_8)Cl]_2$ [9], $C_5H_5Rh(CO)_2$ [10], $[C_5Me_5RhCl_2]_2$, [11], $[Ru(C_6H_6)Cl_2]_2$ [12] and Me_2NNS [5] were prepared by published methods.

For preparation of $C_5H_5Rh(CO)I_2$ a hexane solution of $C_5H_5Rh(CO)_2$ was treated with a solution of I_2 in the same solvent. The brown precipitate obtained was separated, washed several times with light petroleum and dried.

All the other reagents and solvents were used as supplied. Elemental analyses were carried by the Microanalytical Laboratory of the Organic Chemistry Institute of Milan. Conductance measurements were performed with acetone solutions at 20 °C using a WTW LBR conductivity meter. Infrared spectra were recorded with Perkin–Elmer 783 spectrometer, using CsI plates and a polystyrene film for calibration. A Bruker Sy 80 spectrometer was used to record the ^1H NMR spectra.

Analytical and characteristic ^1H NMR data are reported in Table 1.

Preparation of $[Rh(1,5\text{-}C_8H_{12})(SNNMe_2)_2]X$ (1a), $[Rh(C_7H_8)(SNNMe_2)_2]X$ (1b), $[Rh(CO)_2(SNNMe)_2]X$ (2), $[C_5Me_5Rh(SNNMe_2)_3]X_2$ (4) and $[Ru(C_6H_6)(SNNMe_2)_3]X_2$ (5) ($X = PF_6$, ClO_4)

0.5 mmol of chloride-bridged complex was dissolved in acetone (10 ml) and 1 mmol (for preparation of **1a**, **1b**, and **2**) or 2 mmol (for **4** and **5**) of AgX were added.

The solution of the solvento species thus obtained filtered into a diethyl ether solution (ca. 50 ml) of Me_2NNS (360 mg, 4 mmol). The orange solid obtained was separated, washed with diethyl ether and dissolved in acetone (10 ml), the solution was filtered into diethyl ether. The pure product which separated was dried over P_2O_5 (Yields ca. 80% (**1a**, **4**, and **5**) and ca. 50% (**1b** and **2**)).

Complex **2** was also made by bubbling CO through an acetone solution (10 ml) of **1a** or **1b** (0.5 mmol). Addition of hexane (ca. 50 ml) gave an orange solid, which was separated, washed with diethyl ether, and dried (Yield ca. 50%).

Preparation of $[C_5H_5Rh(SNNMe_2)_3](PF_6)_2$ (3)

To an acetone solution (10 ml) of $C_5H_5Rh(CO)I_2$ (225 mg, 0.5 mmol) was added $AgPF_6$ (253 mg, 1 mmol). The solution was filtered into a diethyl ether solution of an excess of Me_2NNS. The orange solid which separated was purified in the usual way (Yields ca. 60%).

Preparation of $[C_5H_5Rh(SNNMe_2)_2(ClO_4)]ClO_4$ (6) and Rh(1,5-cyclooctadiene)-$(SNNMe_2)(ClO_4)$ (7)

A diethyl ether solution of Me_2NNS was added slowly to an acetone solution (10 ml) of solvento species (0.5 mmol) (obtained in the usual way) until the orange compound **6** or the dark orange compound **7** was completely precipitated. These compounds were separated, washed with diethyl ether, and dried (Yields ca. 60%).

Preparation of $[Rh(1,5\text{-cyclooctadiene})(SNNMe_2)(PPh_3)]ClO_4$ (8) and $[Rh(1,5\text{-cyclooctadiene})(SNNMe_2)(p\text{-tolylPPh}_2)]ClO_4$ (9)

An acetone solution (20 ml) of **1a** (245.5 mg, 0.5 mmol) was added to a stirred diethyl ether solution (40 ml) of phosphine (0.5 mmol) and Me_2NNS (180 mg, 2 mmol). After 5 min diethyl ether was added until **8** or **9** separated completely as orange solid, which was filtered off washed with diethyl ether, and dried (Yields ca. 60%).

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