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# Dithionitronium Hexachloroantimonate: A Thionitrosylating Reagent

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## Abstract

The reaction of $Ru(CO)_3(PPh_3)_2$ with $(NS_2)(SbCl_6)$ in acetonitrile results in the formation of $[Ru(CO)_2(NS_2)(PPh_3)_2](SbCl_6)$ which reacts with $PPh_3$ to give the thionitrosyl complex $[Ru(CO)_2(NS)(PPh_3)_2](SbCl_6)$. The $NS_2$-complex in $CH_2Cl_2$ gives $Ru(CO)_2Cl_2(PPh_3)_2$.

## Introduction

The stabilization of unstable small inorganic ligands such as thionitrosyl [1], thiazate [2], thionitro [3] and sulfurmonoxide [4] is a topic of much current interest. As yet, there is no general synthetic route to metal thionitrosyl complexes. Therefore, they have been prepared by (a) reactions of nitrido-complexes with sulfur [5], sulfur halides [5] or potassium thiocyanate [6], (b) reactions of trithiazyltrichloride with transition metal complexes [7, 8], (c) elimination of fluoride form NSF metal complexes [9] and (d) reactions of $NS^+$ salts [10]. Herein I report for the first time the synthesis of a dithionitro-complex $[Ru(CO)_2(NS_2)(PPh_3)_2](SbCl_6)$ and a synthetic route to metal thionitrosyl complexes.

## Experimental

All reactions were performed in a Schlenk apparatus under dry nitrogen. Solvents were dried, distilled and deaerated just prior to use. $(NS_2)(SbCl_6)$ and $Ru(CO)_3(PPh_3)_2$ were prepared as described in the literature [11, 12]. IR spectra were recorded on a Perkin Elmer Model 735B spectrophotometer as nujol mulls. Elemental analyses were performed by Beller of the Microanalytical Laboratory, Göttingen, F.R.G.

### *Preparation of $[Ru(CO)_2(NS_2)(PPh_3)_2](SbCl_6)$*

A mixture of $Ru(CO)_3(PPh_3)_2$ (0.248 g, 3.5 mmol) and $(NS_2)(SbCl_6)$ (0.165 g, 4 mmol) was stirred for 4 h in acetonitrile (30 ml). The reaction mixture turned from yellow to brown. After filtration, it was concentrated under reduced pressure to 5 ml. The suspension was then diluted with 20 ml of n-hexane and filtered. The brown complex $[Ru(CO)_2(NS_2)(PPh_3)_2](SbCl_6)$ was washed with hexane and dried under vacuum. The yield was 0.218 g (57%). *Anal.* Calcd. for $C_{38}H_{30}NO_2P_2S_2Cl_6SbRu$: C, 41.69; H, 2.74; N, 1.28; S, 5.85; Cl, 19.47. Found: C, 41.7; H, 2.9; N, 1.2; S, 5.7; Cl, 19.7%.

### *Preparation of $[Ru(CO)_2(NS)(PPh_3)_2](SbCl_6)$*

A solution of triphenylphosphine (0.04 g in 10 ml of acetonitrile) was added to a solution of $[Ru(CO)_2(NS_2)(PPh_3)_2](SbCl_6)$ (0.16 g in 20 ml of acetonitrile) and the reaction mixture was stirred for 1 h. It was concentrated under reduced pressure to 5 ml and slow addition of 40 ml of hexane precipitated a yellow complex $[Ru(CO)_2(NS)(PPh_3)_2](SbCl_6)$ which was filtered, washed with hexane and dried under vacuum. The yield was 0.14 g (91%). $SPPh_3$ was recovered from the washings and analysed. *Anal.* Calcd. for $C_{38}H_{30}NO_2P_2SCl_6SbRu$: C, 42.94; H, 2.82; N, 1.31; S, 3.01; Cl, 20.06. Found: C, 42.8; H, 2.8; N, 1.2; S, 2.9; Cl, 20.1%.

### *Preparation of $Ru(CO)_2Cl_2(PPh_3)_2$*

A suspension of $[Ru(CO)_2(NS_2)(PPh_3)_2](SbCl_6)$ (0.2 g in 20 ml of dichloromethane) was stirred for 2 h and filtered. The filtrate was diluted with 80 ml of hot methanol. The pale yellow crystals of $Ru(CO)_2Cl_2(PPh_3)_2$ were collected by filtration, washed with methanol, diethyl ether and dried under vacuum. The yield was 0.1 g (74%). *Anal.* Calcd. for $C_{38}H_{30}O_2P_2Cl_2Ru$: C, 60.64; H, 3.99; Cl, 9.44. Found: C, 60.6; H, 4.0; Cl, 9.6%. IR: $\nu$(CO), 1980, 2060 $cm^{-1}$

## Results and Discussion

$(NS_2)(SbCl_6)$ reacts with $Ru(CO)_3(PPh_3)_2$ to give dithionitronium complex $[Ru(CO)_2(NS_2)(PPh_3)_2](SbCl_6)$ and CO (eqn. 1):

$$Ru(CO)_3(PPh_3)_2 + (NS_2)(SbCl_6) \longrightarrow [Ru(CO)_2(NS_2)(PPh_3)_2](SbCl_6) + CO \quad (1)$$

The dithionitronium complex is an air-sensitive brown solid. It exhibits IR absorption bands at 2080, 2020 $cm^{-1}$ due to $\nu$(CO); 1125 $cm^{-1}$ due to $\nu$(N=S);

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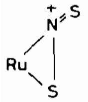
815 $cm^{-1}$ due to $\nu$(N–S) (which may be assigned due to $\nu$(RuNS), and bands due to triphenylphosphine. It is presumed that the ligand $NS_2^+$ in this complex is bonded as:



The $NS_2$ complex reacts with 1 equivalent of $PPh_3$ to give the thionitrosyl complex $[Ru(CO)_2(NS)(PPh_3)_2]$-$(SbCl_6)$ and $SPPh_3$ (eqn. 2). It decomposes in dichloromethane to afford $Ru(CO)_2Cl_2(PPh_3)_2$ [13].

$$[Ru(CO)_2(NS_2)(PPh_3)]^+ + PPh_3 \longrightarrow [Ru(CO)_2(NS)(PPh_3)_2]^+ + SPPh_3 \quad (2)$$

The thionitrosyl complex exhibits IR absorption bands at 2060, 1960 $cm^{-1}$ due to $\nu$(CO); 1266 $cm^{-1}$ due to $\nu$(NS) and the bands due to triphenylphosphine.

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