

# Rhodium(I) carbonyl complexes with sulphur and nitrogen donor ligands

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## Summary

Rhodium(I) carbonyl complexes, namely  $[\text{Rh}(\text{CO})_2\text{CIL}]$  where L = thiourea (Tu), 1,3-diphenyl-2-thiourea (DTu), dithizone (Dtz), indole (Id), 3-chloropyridine (Clpy), 3-hydroxypyridine (HOpy), 3-methylpyridine (Mepy), 2,5-dimethylpyridine ( $\text{Me}_2\text{py}$ ) or 2,5-dichloropyridine ( $\text{Cl}_2\text{py}$ )] were prepared.  $[\text{Rh}(\text{CO})_2\text{Cl}(\text{Clpy})_2]$  has also been isolated. In the (Tu) complex,  $\nu(\text{C}-\text{S})$  occurs at ca.  $710\text{ cm}^{-1}$ , indicating the presence of a metal-sulphur bond. The carbonyl stretching frequencies in  $[\text{Rh}(\text{CO})_2\text{CIL}]$  and  $[\text{Rh}(\text{CO})_2\text{CIL}_2]$  occur at ca. 2100 1990 and 1830–1800  $\text{cm}^{-1}$ , respectively.  $\text{PPh}_3$  reacts with the complexes to form *trans*- $[\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ . The complexes were characterized by elemental analyses, conductivity measurements and by their i.r. spectra.

## Introduction

Rhodium(I) complexes have gained much importance because of their applications in catalysis and biological activity. A limited number of rhodium(I) complexes with sulphur donor ligands are known. Most of the reported<sup>(1–6)</sup> rhodium(I) carbonyl complexes having metal-sulphur bonds containing alkyl/aryl, sulphoxide/sulphide ligands. So far no attempt has been made to prepare these complexes with ligands such as thiourea. Bridge splitting of  $[(\text{OC})_2\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{CO})_2]$  with a considerable number of heterocyclic nitrogen ligands have been reported<sup>(1,7–9)</sup>, but a systematic study with some mono- and di-substituted heterocyclic nitrogen ligands has not been made hitherto. In this study, we report the synthesis and characterization of rhodium(I) carbonyl complexes containing thiourea (Tu), 1,3-diphenyl-2-thiourea (DTu), dithizone (Dtz), indole (Id), 3-chloropyridine (Clpy), 3-hydroxypyridine (HOpy), 3-methylpyridine (Mepy), 2,5-dimethylpyridine ( $\text{Me}_2\text{py}$ ) or 2,5-dichloropyridine ( $\text{Cl}_2\text{py}$ ) ligands.

## Experimental

$\text{RhCl}_3 \cdot x\text{H}_2\text{O}$  was obtained from Johnson Matthey. Analytically pure Tu, DTu, Dtz, Id, py and substituted pyridines (Aldrich) were used directly without further purification. All solvents were purified by standard methods before use. I.r. spectra were recorded on a Specord 75 IR spectrophotometer ( $4000\text{--}400\text{ cm}^{-1}$ ). Conductivity measurements were carried out with the help of a Systronics type 303 conductivity meter. Carbon and hydrogen elemental analyses were performed by CSIRO, Australia. Rhodium analysis was done by a standard gravimetric method<sup>(10)</sup>.

All the complexes were prepared from  $[(\text{OC})_2\text{Rh}(\mu\text{-}$

$\text{Cl})_2\text{Rh}(\text{CO})_2]$ , which was in turn prepared<sup>(11)</sup> by passing dry CO gas over  $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$  at ca.  $100^\circ\text{C}$ .

### $[\text{Rh}(\text{CO})_2\text{Cl}(\text{Tu})]$

$[(\text{OC})_2\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{CO})_2]$  (0.3 g) was dissolved in  $\text{Me}_2\text{CO}$  (ca.  $20\text{ cm}^3$ ) and Tu (0.125 g) was then added very slowly with constant stirring. On removal of the solvent by evaporation under vacuum, a brown compound separated. It was washed with  $\text{Me}_2\text{CO}$  and dried over fused  $\text{CaCl}_2$  in a desiccator.

### $[\text{Rh}(\text{CO})_2\text{CIL}]$ (L = DTu or Dtz)

$[(\text{OC})_2\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{CO})_2]$  (0.2 g) in benzene ( $15\text{ cm}^3$ ) was treated with DTu (0.24 g) or Dtz (0.28 g). The mixture was stirred thoroughly and evaporated under vacuum. The complexes thus obtained were washed with benzene and finally dried over fused  $\text{CaCl}_2$  in a desiccator.

### $[\text{Rh}(\text{CO})_2\text{CIL}]$ (where L = Id, py, Clpy, HOpy, Mepy, $\text{Me}_2\text{py}$ and $\text{Cl}_2\text{py}$ )

$[(\text{OC})_2\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{CO})_2]$  (0.2 g) in benzene ( $15\text{ cm}^3$ ) was treated with a stoichiometric amount of the respective ligand with constant stirring. The solution was evaporated *in vacuo* and the solid mass was washed with benzene. The complexes thus obtained were dried over fused  $\text{CaCl}_2$  in a desiccator.

### $[\text{Rh}(\text{CO})_2\text{Cl}(\text{Clpy})_2]$

$[(\text{OC})_2\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{CO})_2]$  (0.2 g) in benzene ( $20\text{ cm}^3$ ) was treated with about a four-fold excess (0.95 g) of Clpy under constant stirring. The solution was evaporated under vacuum and washed with benzene. The solid complex was dried over fused  $\text{CaCl}_2$  in a desiccator.

## Results and discussion

It was reported<sup>(12–20)</sup> that the bivalent sulphur atoms in thioureas can act as donor atoms with a degree of  $\pi$ -acceptor property. Such a molecule therefore contains both sulphur and nitrogen donor atoms. It is well known that thiourea may coordinate in either of the following modes:



Coordination through the nitrogen atom gives rise to structure (1), resulting in a relatively high C—S bond order<sup>(13)</sup>. On the other hand, coordination through the

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