

A ruthenium(II) complex of *bis*(1-pyrazolyl) borate

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Abstract. A new neutral ruthenium(II) complex of dihydro-*bis*(1-pyrazolyl) borate is synthesised by the reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with the ligand in methanol and is characterised on the basis of IR and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra.

Keywords. Pyrazolyl borate complex; ruthenium(II); uninegative chelating agents.

1. Introduction

The polypyrazolylborates are uninegative chelating agents in which the number of pyrazolyl groups attached to boron primarily determine the bonding modes of polypyrazolylborates to the metal ion. Chelates of Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} with pyrazolylborates were reported earlier (Trofimenko 1966, 1967a, b). As polypyrazolylborates exhibit remarkable hydrolytic and oxidative stability in their complexes it was considered important to prepare a ruthenium(II) complex in order to test its catalytic activity (Taqui Khan and Martell 1974). In this note we report the synthesis, characterization and structure of *bis*-(1-pyrazolyl)borate-*bis*-triphenylphosphineruthenium(II). The complex was characterised on the basis of elemental analysis, IR and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra.

2. Experimental

Potassium dihydrobis-pyrazolylborate was used as received from Alfa Chemicals. $\text{RuCl}_2(\text{PPh}_3)_3$ was prepared by reacting $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ and triphenylphosphine by a reported procedure (Stephenson and Wilkinson 1966). The IR and far-IR spectra of the complex were recorded on a Beckman IR-Model-12 and Nicolet 200SX spectrometer, respectively. The conductivity was taken on a Digisun electronic conductivity meter. The elemental analysis was performed at the Australian Micro-analytical Service (AMDEL), Australia. The $^{31}\text{P}\{^1\text{H}\}$ spectrum was recorded on a Jeol FX-100 FT-NMR spectrometer operating at 40.27 MHz in a 10 mm tube with a capillary of D_2O for the lock signal, while 85% H_3PO_4 was used as an external reference.

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A solution of $\text{RuCl}_2(\text{PPh}_3)_3$ (0.496 gm, 1 mM) in methanol was treated with potassium dihydrogenpyrazolylborate (0.372 gm, 2 mM). The mixture was refluxed for two hours till the yellow precipitate settled down. The yellow precipitate was filtered and washed with methanol and finally with an ethanol-water mixture. The complex was recrystallized with dichloromethane and dried in vacuum. Yield 0.39 gm (43%). Analytical data: found C = 62.58, H = 5.09 and N = 11.86%; calculated C = 63.50, H = 5.07 and N = 11.34%. The complex decomposes at 80°C.

3. Results and discussion

The complex is water insoluble and air stable. The conductivity data of the complex in CH_2Cl_2 shows that it is neutral. The far-IR spectrum of the complex shows a strong band at 620 cm^{-1} which is assigned to $\nu(\text{Ru-N})$ stretching frequency. It also shows two bands at 528 and 550 cm^{-1} which can be assigned to $\nu(\text{Ru-P})$ stretching frequencies, indicating a *cis*-disposition of the two triphenyl phosphine groups. Absence of bands around $300\text{--}350\text{ cm}^{-1}$ indicates the displacement of all the chloride groups from the coordination sphere of the metal ion.

The proton decoupled phosphorus-31 NMR spectrum gives two doublet centred at 78.201 and 74.174 ppm with $J(\text{P}_a\text{-P}_b)$ coupling constant equal to 20 Hz due to the two magnetically inequivalent phosphorus atoms of the two PPh_3 group. The doublet centred at 78.201 ppm can be assigned to the phosphorus atom P_a of PPh_3 which is at an equatorial position and the other doublet centred at 74.174 ppm can be assigned to P_b which is at an axial position. The larger downfield shift, $\delta(\text{complex}) - \delta(\text{free ligand})$ corresponds to the equatorial phosphorus which is closer to the metal ion than the axial

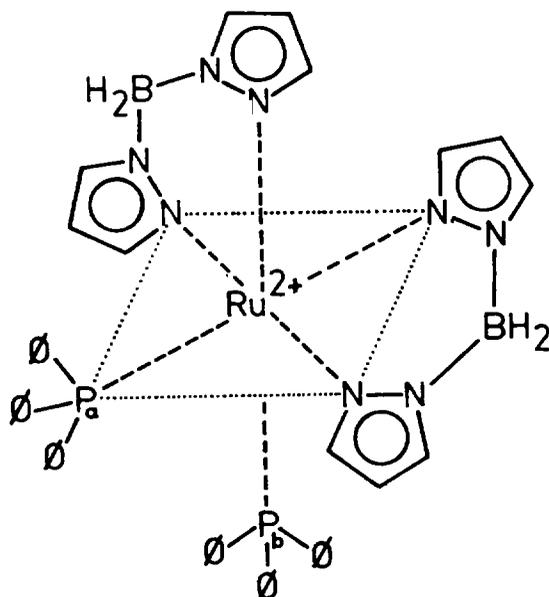


Figure 1. Structure of *bis*-dihydro-*bis*(1-pyrazolyl)-borate-*bis*-triphenylphosphine-ruthenium(II).

one (Bertrand and Plymale 1966). The low $J(\text{P-P})$ coupling constant of 20 Hz is typical for ruthenium complexes with a *cis*-disposition of phosphorus groups (Briggs *et al* 1984; Gill *et al* 1973). On the basis of the above physicochemical and spectral data a distorted octahedral structure can be proposed for the complex where two PPh_3 groups are *cis* to each other. The structure of the complex is shown in figure 1.

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