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Article

# Syntheses and NMR Characterisation of Novel Ruthenium(II) Complexes Containing Dioxaphospholane

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A síntese de alguns complexos de rutênio(II) contendo os ligantes 2-cloro-1,3,2-dioxafosfolano e 2-cloro-4,5-benzo-1,3,2-dioxafosfolano são apresentadas pela primeira vez. As reações do dicloro-tris(trifenilfosfino)rutênio(II) com os ligantes em questão produziram sempre um complexo contendo duas moléculas de dioxafosfolano, independente da estequiometria empregada. Já os complexos derivados do cloro(ciclopentadienil)bis(trifenilfosfino)rutênio(II) têm apenas um ligante em sua estrutura. Os complexos foram caracterizados por RMN de $^{31}P\{^{1}H\}$ e $^{1}H$.

Syntheses of some ruthenium(II) complexes containing 2-chloro-1,3,2-dioxaphospholane and 2-chloro-4,5-benzo-1,3,2-dioxaphospholane are reported for the first time. The reaction of dichloro-tris(triphenylphosphane)ruthenium(II) with these ligands always leads to formation of a product containing two molecules of dioxaphospholane, independently of the stoichiometric proportion employed. On the other hand, complexes derived from chloro(cyclopentadienyl) bis (triphenylphosphane)ruthenium(II) have only one ligand in their structure. The complexes were characterized by $^{31}P\{^{1}H\}$ and $^{1}H$-NMR spectroscopy.

**Keywords:** *ruthenium, dioxaphospholane, $^{31}P\{^{1}H\}$ NMR spectroscopy*

## Introduction

Metal complexes containing phosphorus ligands have always been in evidence, due to their possible catalytic activity, and a variety of them have already been reported. It has always been our interest to investigate the chemical properties of some new metal complexes containing unusual phosphorus ligands and how these properties are related to the NMR spectroscopic data. Dioxaphospholane derivatives had been in evidence before and their reactivity behaviour with several organic compounds is well documented[1]. Now this class of compound is in evidence again and as a result of those studies, some new compounds derived from dioxaphospholanes have been used in the development of specific imunoassays for the detection of pesticides[2]. Since few reports dealing with the complexation of dioxaphospholanes have appeared in the literature and following the recent reports of the new facile preparation methods of dioxaphospholane derivatives[3] and their platinum(0), platinum(II) and palladium(II) complexes[4], we are prompted to report some new complexes of ruthenium(II) with 2-chloro-1,3,2-dioxaphospholane (**1**) and 2-chloro-4,5-benzo-1,3,2-dioxaphospholane (**2**).

Two ruthenium(II) starting materials, $[Ru(\eta^5\text{-}C_5H_5)Cl(PPh_3)_2]$ (**3**) and $[RuCl_2(PPh_3)_3]$ (**4**), have been used herein and they were prepared as described in the literature[5,6].

## Results and Discussion

### *Reactions with $[Ru(\eta^5\text{-}C_5H_5)Cl(PPh_3)_2]$ (3)*

Treatment of (**1**) and (**2**) with the ruthenium(II) complex (**3**), at room temperature in dichloromethane, leads to the formation of (**5**) and (**6**), respectively.

$^{31}P\{^{1}H\}$NMR spectroscopy shows that complex (**5**) is formed as a mixture of two conformers along with a side product, which unfortunately could not be isolated by the usual methods of separation. The $^{31}P\{^{1}H\}$NMR spectrum of this mixture consists of a pattern of lines corresponding to [AB] + [AB] + [$AB_2$] spin systems. At δ170 and δ165, two doublets are seen and they can be attributed to a $P^A$ of each of the conformers and the two doublets found at δ50

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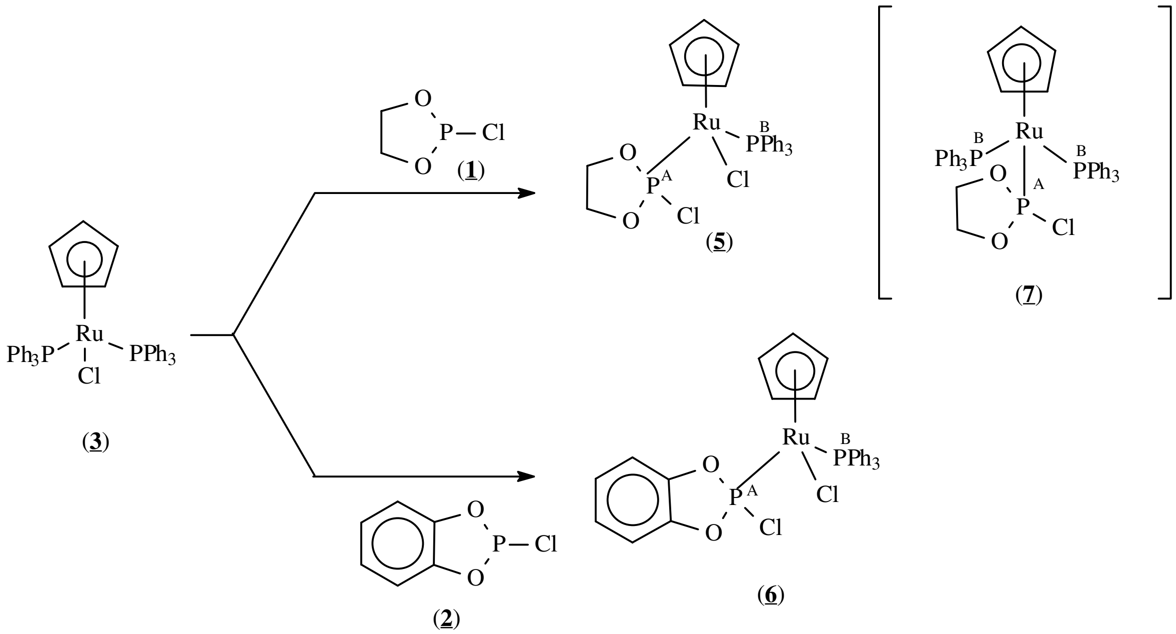
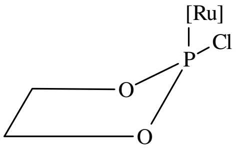
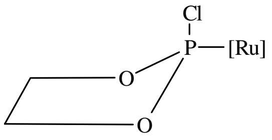


and δ53 can be assigned to $P^B$. The proximity of both chemical shifts and $^2J_{PAPB}$ coupling constants (76 and 73 Hz) for each of the conformers suggests little difference between them. One would say that this is a consequence of the fact that the dioxaphospholane (**1**) exists as a pair of two conformers, in which the lone pair in the phosphorus is in an axial or in an equatorial position, due to a free rotation of the chloro atom leading to an inversion of the phosphorus[7,8]. Thus, the $[Ru(\eta^5\text{-}C_5H_5)Cl]$ fragment can be found bonded through the phosphorus in an axial or equatorial position (**5a**) or (**5b**), respectively.



(**5a**)



(**5b**)

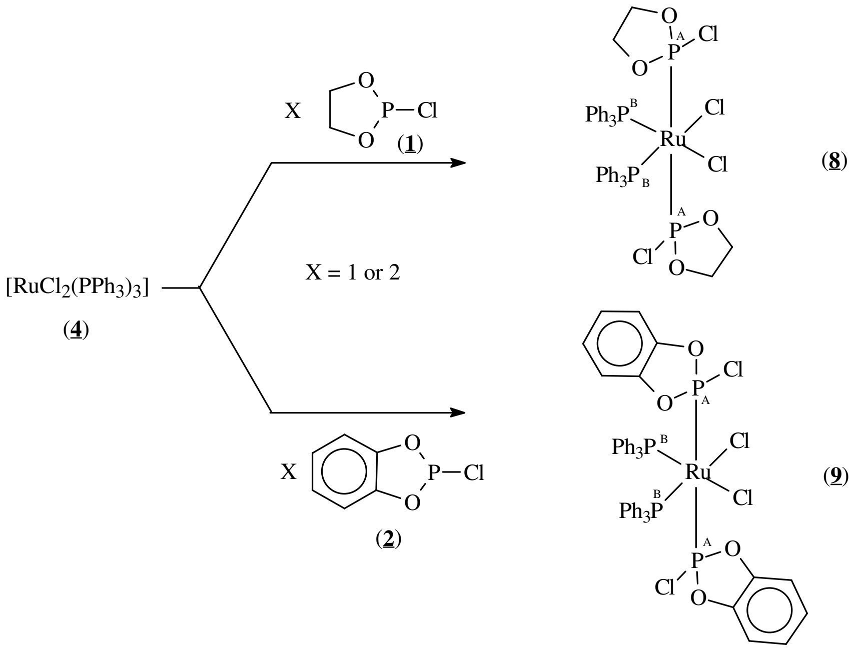
A similar conclusion has been drawn for platinum(II) complexes[4]. The chemical shifts of $P^A$ are in accordance with those found for platinum and palladium complexes[4]. In all cases a deshielding is observed upon coordination. The $^2J_{PAPB}$ coupling constants (~76 Hz) are within the range of those found for complexes of this type[9]. The other lines that are observed in the spectrum are a triplet at δ159 and a doublet at δ44. Due to the proximity of the chemical shifts found for (**5**), one would expect the first to be attributed to $P^A$ and the latter to $P^B$. Thus, the complex has to be formulated as having two $PPh_3$ and one molecule of 2-chloro-1,3,2-dioxaphospholane. Based on this, an ionic structure (**7**) has been proposed for the side product. However, further studies must be carried out in order to clarify this, since it could not be separated.

Unlike complex (**5**), (**6**) is not formed as a mixture of conformers and it might be due to the fact that 2-chloro-4,5-benzo-1,3,2-dioxaphospholane is more rigid than its analogue 2-chloro-1,3,2-dioxaphospholane. The $^{31}P\{^1H\}$NMR spectrum of (**6**) shows two doublets at δ156 and δ58 corresponding to $P^A$ and $P^B$, respectively. The $^{31}P\{^1H\}$NMR data of the complex are listed in Table 1.

### *Reactions with $[RuCl_2(PPh_3)_3]$ (**4**)*

The coordinatively unsaturated 16e$^-$ ruthenium(II) complex (**4**) is a well known catalyst, or at least the precursor of an important catalytic species, $[RuHCl(PPh_3)_3]$, for a variety of processes. In particular, complex (**4**) is probably the most effective and important hydrogenation catalyst yet discovered[8,9]. Upon dissolution, (**4**) readily loses triphenylphosphane and gives rise to the dimeric species $[Ru_2Cl_4(PPh_3)_4]$, which contains two chloride ligands bridging the ruthenium nuclei. The approach of a ligand leads to bridge-cleavage of the dimer, generating an extremely reactive fragment $[RuCl_2(PPh_3)_2]$, which contains two vacant coordination sites, allowing two molecules of the ligand to bond to the ruthenium. In order to avoid the coordination of two molecules of dioxaphospholane ligands, the reactions have been carried out at ice temperature. However, even with this care, treatment of (**4**) with ligands (**1**) and (**2**), in dichloromethane, leads to the formation of a complex containing two dioxaphospholane either when one or two equivalents of the ligands are employed, *viz.*

Thus, in order to avoid the inconvenience of having an excess of the ligand by the end of the reaction, one equiva-



lent of the ruthenium(II) complex (**4**) was treated with two equivalents of the ligands (**1**) or (**2**). The resulting products were characterized by $^{31}P\{^1H\}$NMR and $^1H$-NMR spectroscopy.

The $^{31}P\{^1H\}$NMR spectra of (**8**) and (**9**) are very similar and they consist of a pattern of lines corresponding to an $[A_2B_2]$ spin system. A triplet on the region corresponding to $P^A$ - δ145 (**8**) and δ155 (**9**) – and another on the triphenylphosphane region - δ41 (**8**) and δ59 (**9**) – are observed. The values for the $^2J_{PAPB}$ coupling constants are 39 Hz for (**8**) and 33 Hz for (**9**). These values are small and suggest that $P_A$ and $P_B$ are in a *cis* position[13,14]. The $^{31}P\{^1H\}$NMR data are shown in Table 1.

## Conclusions

Although the change of the group bonded through the oxygen on the dioxaphospholane ligand from $-CH_2CH_2-$ to $–C_6H_4-$ seems to increase the reactivity of the ligand, it does not affect to a great extent the phosphorus-phosphorus coupling constants, as the results found in this work show. However, we believe that further work, especially those using fluoro ligands derived from (**1**) and (**2**), shold give us good relations between P-P coupling constants and the electronic nature of the ligands.

**Table 1.** $^{31}P\{^1H\}$NMR data for ligands and their complexes.

| Complexes | | δ$_{PA}$ | δ$_{PB}$ | $^2J_{PAPB}$ (Hz) |
|---|---|---|---|---|
| $PPh_3$ | | -8 (s) | --- | --- |
| (**1**) | | 167 (s) | --- | --- |
| (**2**) | | 173 (s) | --- | --- |
| (**5**) | **a** | 170 (d) | 50 (d) | 76 |
| | **b** | 165 (d) | 53 (d) | 73 |
| (**6**) | | 156 (d) | 58 (d) | 56 |
| (**8**) | | 145 (t) | 41 (t) | 39 |
| (**9**) | | 155 (t) | 59 (t) | 33 |

## Experimental

All reactions were carried out either under dry dinitrogen in Schlenk tubes or by use of high-vacuum techniques. Glassware was flame-dried in vacuum, and solvents were dried, freshly distilled under dinitrogen, and degassed prior to use. The NMR spectra were recorded on a Bruker DRX400 spectrometer. Chemical shift data were recorded at ambient temperatures and are quoted in ppm, with positive values to low field of the indicated reference (85% $H_3PO_4$ solution) and corrected with respect to the appropriate deuterium frequency. Coupling constants are quoted in Hertz.

2-Chloro-1,3,2-dioxaphospholane (**1**) and 2-chloro-4,5-benzo-1,3,2-dioxaphospholane (**2**) have been prepared from the corresponding diol with $PCl_3$, following a recent modified method[3]. The $[Ru(\eta^5-C_5H_5)Cl(PPh_3)_2]$[3] (**3**) and $[RuCl_2(PPh_3)_3]$[6] (**4**) were prepared by the published methods.

### *Preparation of (η⁵-cyclopentadienyl)chloro(2-chloro-1,3,2-dioxaphospholane) (triphenylphosphane)ruthenium(II) (**5**)*

To a solution of (**1**) (0.07g; 0.56 mmol) in dichloromethane (10 mL) was added, dropwise, a solution of $[Ru(\eta^5-C_5H_5)Cl(PPh_3)_2]$ (**3**) (0.41 g; 0.56 mmol), also in dichloromethane (10 mL), at room temperature. The mixture was kept under magnetic stirring for a further 24 h. The solvent was pumped off till dry and the oil obtained was washed with hexane (8 x 6 mL) and a yellow powder was obtained.

$^{1}$H-NMR data (400.13 MHz; $CDCl_3$, 25 °C)

δ3.97 (s,4H,$2CH_2$); δ4.84 (s,5H, $C_5H_5$); δ7.05-7.24 (m, 15H, $PPh_3$)

$^{31}$P{$^{1}$H}NMR data (161.98 MHz; $CDCl_3$, 25 °C)

conformer a: $\delta_{PA}$170 (d); $\delta_{PB}$50 (d); $^{2}J_{PAPB}$ = 76 Hz

conformer b : $\delta_{PA}$165 (d); $\delta_{PB}$53 (d); $^{2}J_{PAPB}$ = 73 Hz

### *Preparation of ($\eta^5$-cyclopentadienyl)chloro(2-chloro-4,5-benzo-1,3,2-dioxaphospholane)(triphenylphosphane) ruthenium(II) (**6**)*

A solution of [Ru($\eta^5$-$C_5H_5$)Cl($PPh_3$)$_2$] (**3**) (0.31 g; 0.42 mmol) in dichloromethane (20 mL) was added to a solution of (**2**) (0.07 g; 0.42 mmol), also in dichloromethane (10 mL). After 24 h, the solvent was pumped off and an oil was obtained, which was washed with hexane (8 x 6 mL) to afford a yellow powder (0.17 g).

$^{1}$H-NMR data (400.13 MHz; $CDCl_3$, 25 °C)

δ4.80 (s,5H, $C_5H_5$); δ 6,84-6,96 (m, 4H, $C_6H_4$); δ7.05-7.24 (m, 15H, $PPh_3$)

$^{31}$P{$^{1}$H}NMR data (161.98 MHz; $CDCl_3$, 25 °C)

$\delta_{PA}$156 (d); $\delta_{PB}$58 (d); $^{2}J_{PAPB}$ = 56 Hz

### *Preparation of dichlorobis(2-chloro-1,3,2-dioxaphospholane)bis (triphenylphosphane)ruthenium(II) (**8**)*

A solution of [$RuCl_2(PPh_3)_3$] (**4**) (0.49 g; 0.56 mmol) in dichloromethane (20 mL) was added, at ice temperature, to a solution of (**1**) (0.14 g; 1.12 mmol) in dichloromethane (10 mL) and magnetically stirred for 24 h. The mixture was dried and the oil obtained was washed with hexane (6 x 8 mL) to yield the title brown complex (0.25 g).

$^{1}$H-NMR data (400.13 MHz; $CDCl_3$, 25 °C)

δ3.74 (s,8H, $4CH_2$); δ7.29-7.40 (m, 30H, $2PPh_3$)

$^{31}$P{$^{1}$H}NMR data (161.98 MHz; $CDCl_3$, 25 °C)

$\delta_{PA}$145 (t); $\delta_{PB}$41 (t); $^{2}J_{PAPB}$ = 39 Hz

### *Preparation of dichlorobis(2-chloro-4,5-benzo-1,3,2-dioxaphospholane)bis (triphenylphosphane)ruthenium(II) (**9**)*

To a solution of (**2**) (1.15 g; 0.84 mmol), in dichloromethane (10 mL), a solution of [$RuCl_2(PPh_3)_3$] (**4**) (0.11 g; 0.42 mmol), in dichloromethane (20 mL), was added dropwise under magnetic stirring, at ice temperature. The solvent was pumped off till dryness and an oil was obtained, which was washed with hexane (6 x 8 mL) to yield a brown powder of (**9**) (0.18 g).

$^{1}$H-NMR data (400.13 MHz; $CDCl_3$, 25 °C)

δ6.77-6.87 (m,8H, $C_6H_4$); δ7.40-7.63 (m, 30H, $2PPh_3$)

$^{31}$P{$^{1}$H}NMR data (161.98 MHz; $CDCl_3$, 25 °C)

$\delta_{PA}$155 (t); $\delta_{PB}$59 (t); $^{2}J_{PAPB}$ = 33 Hz

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## References

1. Corbridge, D.E.C.; *Phosphorus – An outline of its chemistry, biochemistry and technology,* Amsterdam, 1990, p. 643.
2. tem Hoeve,W.; Wynberg, H.; Jones, W.T.; Harvey, D.; Ryan, G.B.; Reynolds, P.H.S. *Bioconjugate Chemistry* **1997**, *8*, 257.
3. Matos, R.M.; da Costa, R.F.F.; Trigo Passos, B.F. *Química Nova* **1998**, *21*, 484.
4. Matos, R.M.; da Costa, R.F.F.; Knupp, V.F.; Trigo Passos, B.F. In preparation; da Costa, R.F.F., Dissertação de mestrado, DQ-UFMG; Belo Horizonte, 1996.
5. Bruce, M.I.; Hameister, C.; Swincer, A.G.; Wallis, R.C.; Ittel, S.D. *Inorg. Synt.* **1982**, *21*, 78.
6. Hallman, P. S.; Stephensen, T. A ; Wilkinson, C.; *Inorg. Synt.* **1970**, 12, 237.
7. Ggnaire, D.; Robert, J.B.; Verrier, J. Wolf, R.; *Bull. Soc. Chim. France* **1966**, 3719.
8. Mikolajczyk, M.; GrazyK. P. P. *In Phosphorus-31 NMR spectral properties in compound characterization and structural analysis;* Quin, L.D.; Verkade, J.G., eds.; VCH; Weinheim, 1994, p. 17.
8. Nixon, J.F.; Pidcock, A. *Annual Review of NMR Spectroscopy* **1969**, *2*, 459.
10. Schröder, M.; Stephenson, T.A. *In Comprehensive Coordination Chemistry*; Wilkinson, G.; Gillard, R.G.; McCleverty, J.A., eds.; Pergamon Press; Oxford, 1987, v. 4, p. 463.
11. Jardine, F.H. *Prog. Inorg. Chem.* **1984**, *31*, 265 and references therein.
12. Hitchcock, P.B.; Nixon, J.F.; Matos, R.M. *J. Organomet. Chem.* **1995**, *490*, 155.
13. PanKowski, M.; Chadkiewicz, W.; Simonin, M. *Inorg. Chem.* **1985**, *24*, 533.
14. Nelson, J.H. *In Phosphorus-31 NMR spectral properties in compound characterization and structural analysis;* Quin, L.D.; Verkade, J.G., eds.; VCH; Weinheim, 1994, p.203.

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