Polyhedron 30 (2011) 41–46

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

The *mer*-[$RuCl_3$(dppb)(H_2O)] complex: A versatile tool for synthesis of Ru^{II} compounds

Marilia I.F. Barbosa [a], Edjane R. dos Santos [a], Angelica E. Graminha [a], André L. Bogado [b], Leticia R. Teixeira [c], Heloisa Beraldo [c], Maria Teresa S. Trevisan [d], Javier Ellena [e], Eduardo E. Castellano [e], Bernardo L. Rodrigues [e], Márcio P. de Araujo [f,*], Alzir A. Batista [a,*]

[a] Departamento de Química, Universidade Federal de São Carlos, CP 676, CEP 13565-905, São Carlos (SP), Brazil
[b] Faculdade de Ciências Integradas do Pontal, Universidade Federal de Uberlândia, CEP 38302-000, Ituiutaba (MG), Brazil
[c] Departamento de Química, Universidade Federal de Minas Gerais, CEP 31270-901, Belo Horizonte (MG), Brazil
[d] Departamento de Química Orgânica e Inorgânica, Universidade Federal do Ceará, CP 12200 60451-970 Fortaleza, Ceará, Brazil
[e] Instituto de Física, Universidade de São Paulo, CEP 13560-970, São Carlos (SP), Brazil
[f] Departamento de Química, Universidade Federal do Paraná, Centro Politécnico, CP 19081, CEP 81531-980, Curitiba (PR), Brazil

ARTICLE INFO

Article history:
Received 13 August 2010
Accepted 22 September 2010
Available online 29 September 2010

Keywords:
Ruthenium complexes
Mangiferin
N(4)-meta-tolyl-2-acetylpyridine thiosemicarbazone
X-ray structures

ABSTRACT

The complex *mer*-[$RuCl_3$(dppb)(H_2O)] [dppb = 1,4-bis(diphenylphosphino)butane] was used as a precursor in the synthesis of the complexes *tc*-[$RuCl_2(CO)_2$(dppb)], *ct*-[$RuCl_2(CO)_2$(dppb)], *cis*-[$RuCl_2$(dppb)(Cl-bipy)], [RuCl(2Ac4mT)(dppb)] (2Ac4mT = N(4)-*meta*-tolyl-2-acetylpyridine thiosemicarbazone ion) and *trans*-[$RuCl_2$(dppb)(mang)] (mang = mangiferin or 1,3,6,7-tetrahydroxyxanthone-C2-β-D-glucoside) complexes. For the synthesis of Ru^{II} complexes, the Ru^{III} atom in *mer*-[$RuCl_3$(dppb)(H_2O)] may be reduced by H_2(g), forming the intermediate [Ru_2Cl_4(dppb)$_2$], or by a ligand (such as H2Ac4mT or mangiferin). The X-ray structures of the *cis*-[$RuCl_2$(dppb)(Cl-bipy)], *tc*-[$RuCl_2(CO)_2$(dppb)] and [RuCl(2Ac4mT)(dppb)] complexes were determined.

1. Introduction

The "Ru(P–P)" containing complexes represent an attractive class of compounds on account of their catalytic activities, and in this laboratory an ongoing research involves synthesizing new complexes with this unit [1–9]. The Ru^{III} complex *mer*-[$RuCl_3$(dppb)(H_2O)] [dppb = 1,4-bis(diphenylphosphino)butane] was synthesized for the first time by our research group at about ten years ago, and since then it has been used by us in different kinds of reactions [10–13]. The coordinated water can easily be replaced by monodentate ligands, e.g. N-heterocyclic, forming derivatives with the general formula [$RuCl_3$(dppb)(L)] [11]. Thus, we have recently shown that the aqua complex can be used for dehydrogenation of diamine leading to the formation of Ru^{II} diimine complexes [11,14]. Certainly, this is possible due to the special characteristics of the aqua-diphosphine complex, which is irreversibly reduced at low potential (*ca.* 0.0 V *versus* Ag/AgCl) to form a mixed-valence complex [10,11].

In this study, we made use of the remarkably versatile aqua-complex *mer*-[$RuCl_3$(dppb)(H_2O)] as the precursor in the synthesis of Ru^{II} complexes, in which the reducing agents were an external mediator or the ligand itself, which was, in some cases, coordinated to the metal center in its reduced form. N(4)-*meta*-tolyl-2-acetylpyridine thiosemicarbazone and mangiferin were selected as ligands because of their known potential pharmaceutical properties [15]. Mangiferin is probably the best studied natural product extracted from plants of the Anacardiaceae family, the interest in this compound arises from its pharmacological effects as an antitumor, antiviral and antidiabetic agent. Our main interest in the preparation of the *tc*-[$RuCl_2(CO)_2$(dppb)], *ct*-[$RuCl_2(CO)_2$(dppb)] and *cis*-[$RuCl_2$(dppb)(Cl-bipy)] complexes is to use them as catalysts in the hydrogenation of unsaturated organic substrates, while the mangiferin complex was selected for its pharmacological properties.

2. Experimental

2.1. Materials for synthesis

The synthetic reactions had to be carried out under an inert atmosphere (Ar). Solvents were purified by standard methods.

* Corresponding authors.
E-mail addresses: mparaujo@ufpr.br (M.P. de Araujo), daab@ufscar.br (A.A. Batista).

0277-5387/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2010.09.025

The chemicals employed were of reagent grade quality (Aldrich). The precursors *cis*-[$RuCl_2$(P–P)(N–N)] [16], [Ru_2Cl_4(dppb)$_3$] [17], [$Ru_2Cl_4(CO)_2$(dppb)$_3$] [17], [Ru_2Cl_4(dppb)$_2$] [12], *mer*-[$RuCl_3$(dppb)(H_2O)] [10] and the N(4)-*meta*-tolyl-2-acetylpyridine thiosemicarbazone [15] ligand were prepared by the literature methods. Mangiferin (1,3,6,7-tetrahydroxyxanthone-C2-β-D-glucoside) was extracted from the mango fruit (*Mangifera indica L.*) in an ethanolic solution and purified as described in the literature [18].

The purity of the mangiferin was checked by elemental analyses (%C and %H) and UV–Vis spectrum analysis in ethanol solution (λ_{max} at 366, 316, 260 and 242 nm) [19].

2.2. Instrumentation

All the NMR spectra were recorded at 293 K, in a BRUKER 9.4 T spectrometer (400 MHz for hydrogen frequency) at 161.98 MHz, with CH_2Cl_2 as solvent (external reference 85% H_3PO_4), with a capillary containing D_2O. Cyclic voltammetry experiments were carried out in CH_2Cl_2 solutions containing 0.10 mol L^{-1}, Bu_4NClO_4 (TBAP) (Fluka Purum), with a Bioanalytical Systems Inc. BAS-100B/W electrochemical analyzer; the working and auxiliary electrodes were stationary Pt foils, and the reference electrode was Ag/AgCl in a Luggin capillary probe. Under these conditions, ferrocene is oxidized at 0.43 V (Fc+/Fc).

The elemental analyses were performed using a FISONS CHNS, EA 1108 micro analyzer of the Microanalytical Laboratory at Universidade Federal de São Carlos, São Carlos (SP).

2.3. X-ray crystallography

Crystals of the complexes were grown by slow evaporation of dichloromethane/diethyl ether solution. The crystals were mounted on an Enraf–Nonius Kappa-CCD diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. The final unit cell parameters were based on all reflections. Data were collected with the COLLECT program [20]; integration and scaling of the reflections were performed with the HKL DENZO-SCALEPACK system of programs [21]. Absorption corrections were carried out by the Gaussian method [22]. The structure was solved by direct methods with SHELXS-97 [23]. The model was refined by full-matrix least squares on F^2 by means of SHELXL-97 [24]. All hydrogen atoms were stereochemically positioned and refined with the riding model. The ORTEP diagrams were prepared with ORTEP-3 for windows [25]. Hydrogen atoms on the aromatic rings were isotropically set, with a thermal parameter 20% greater than the equivalent isotropic displacement parameter of the atom to which they are bonded. The data collected and some experimental details are summarized in Table 1.

2.4. Syntheses

In this paper, the first letter of the prefixes *tc* and *ct* in the dicarbonyl complexes formulae refers to the position (*cis* or *trans*) of the chlorines to each other, and the second letter refers to the position of the carbonyls to each other. For non-carbonyl complexes, the *cis* and *trans* refer to the positions of the chlorines to each other.

2.4.1. tc-[$RuCl_2(CO)_2$(dppb)]

tc-[$RuCl_2(CO)_2$(dppb)] was derived from [Ru_2Cl_4(dppb)$_2$] (100 mg, 0.0835 mmol) dissolved in benzene (5 mL) and exposed to CO gas (1 atm). The mixture was stirred at room temperature, and after 24 h, the yellow solid formed was filtered off, washed with diethyl ether and dried under vacuum. Yield: 83.1 mg; 76%. This complex can also be derived directly from [$RuCl_3$(dppb)(H_2O)], using MeOH/CH_2Cl_2 as the solvent and an atmosphere of H_2(g), as described previously [12]. In this case, the solution should be exposed to CO(g) and after about 4 h of reaction with hydrogen gas. Yield: 84.0 mg, 83%. *Anal.* Calc. (%) for $C_{30}H_{28}Cl_2O_2P_2Ru$: C, 55.66; H, 4.31. Found: C, 55.88; H, 4.74%.

2.4.2. ct-[$RuCl_2(CO)_2$(dppb)]

ct-[$RuCl_2(CO)_2$(dppb)] was synthesized from the precursor *mer*-[$RuCl_3$(dppb)(H_2O)] (100 mg, 0.153 mmol) dissolved in benzene (5 mL). The red suspension was exposed to CO gas (1 atm) forming a blue suspension. The mixture was stirred at room temperature, and after 20 min, the yellow solid formed was filtered off, washed with diethyl ether and dried under vacuum. Yield: 93.0 mg; 92%. *Anal.* Calc. (%) for $C_{30}H_{28}Cl_2O_2P_2Ru{\cdot}H_2O$: C, 53.58; H, 4.50. Found: C, 53.47; H, 4.60%.

2.4.3. cis-[$RuCl_2$(dppb)(Cl-bipy)]

cis-[$RuCl_2$(dppb)(Cl-bipy)] was prepared by allowing *mer*-[$RuCl_3$(dppb)(H_2O)] (100 mg, 0.153 mmol), dissolved in a mixture of CH_2Cl_2 (16 mL) and methanol (4 mL), to react with H_2(g), at

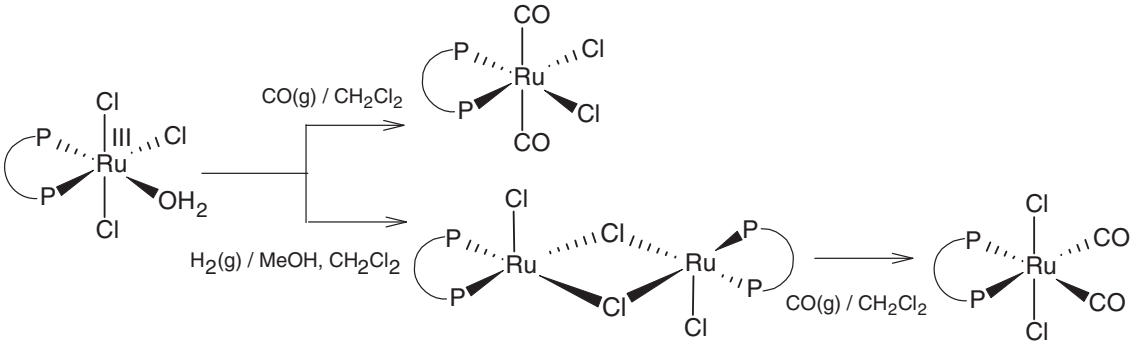
Table 1
Crystallographic data and refinement details for the complexes *cis*-[$RuCl_2$(dppb)(Cl-bipy)] (**1**), *tc*-[$RuCl_2(CO)_2$(dppb)] (**2**) and [RuCl(2Ac4mT)(dppb)] (**3**).

	1	**2**	**3**
Formula	$C_{38}H_{34}Cl_4N_2P_2Ru$	$C_{30}H_{28}Cl_2O_2P_2Ru$	$C_{43}H_{44}Cl_2N_4P_2{\cdot}RuS{\cdot}0.5H_2O$
Formula weight	823.48	654.43	891.80
T (K)	293(2)	293(2)	293(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a (Å)	18.7170(8)	15.2296(3)	13.9780(4)
b (Å)	10.4900(6)	9.8707(2)	20.3360(7)
c (Å)	20.6890(10)	19.5489(4)	16.5990(5)
β (°)	113.318(2)	94.8560(10)	105.095(2)
V (Å^3)	3730.3(3)	2928.18(10)	4555.6(2)
Z, ρ_{calc} (mg m^{-3})	4; 1.466	4; 1.484	4; 1.300
Index ranges	$-22 \le h \le 22$	$-19 \le h \le 19$	$-16 \le h \le 16$
	$-11 \le k \le 12$	$-12 \le k \le 12$	$-24 \le k \le 22$
	$-24 \le l \le 24$	$-22 \le l \le 24$	$-19 \le l \le 19$
Reflections collected	11326	19409	20865
Unique reflections/R_{int}	6573 [R_{int} = 0.0682]	8356 [R_{int} = 0.06601]	8084 [R_{int} = 0.0622]
Completeness to θ	25.0° (99.8%)	26.59° (99.7%)	25.23° (97.7%)
Final R indices [$I > 2\sigma(I)$][a,b]	R_1 = 0.0468	R_1 = 0.0431	R_1 = 0.0584
	wR_2 = .0868	wR_2 = 0.1068	wR_2 = 0.1627
R indices (all data)	R_1 = 0.1248	R_1 = 0.0589	R_1 = 0.0787
Goodness-of-fit (GOF)	wR_2 = 0.1018	wR_2 = 0.1192	wR_2 = 0.1838
S	0.901	1.018	1.051

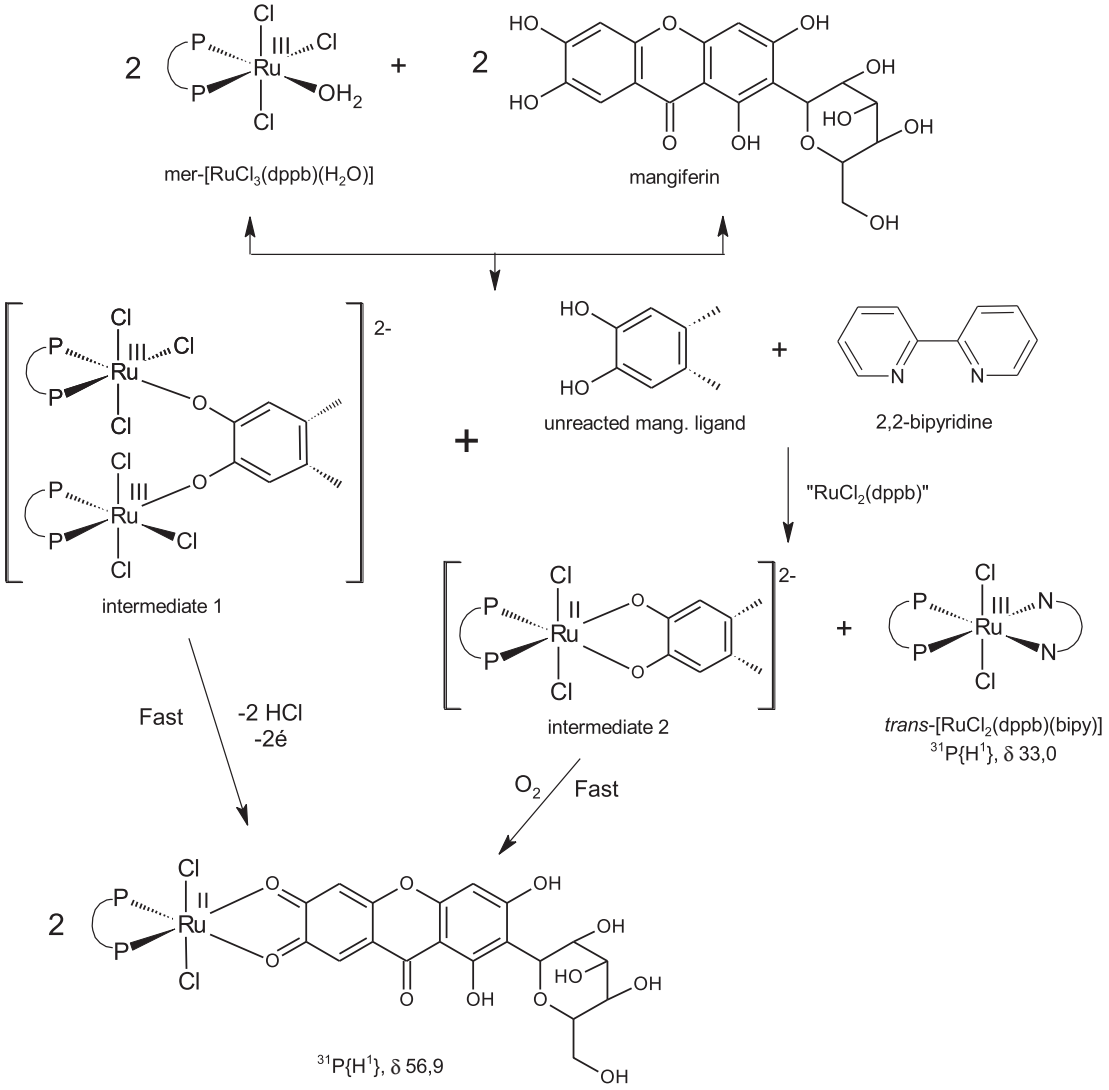
1 atm, in a Schlenk flask. The mixture was stirred at room temperature, and after 12 h of reaction, the ligand 4,4′-dichloro-2,2′-bipyridine (34.4 mg, 0.153 mmol) was added and the mixture refluxed for 36 h. The volume of the solution was then reduced to *ca.* 2 mL and hexane was added. The solid formed was filtered off and washed well with diethyl ether. This complex was also prepared as described in the literature, from the precursor $[Ru_2Cl_4(dppb)_3]$ [26]. Yield: 111 mg; 90%. *Anal.* Calc. (%) for $C_{38}H_{34}Cl_4N_2P_2Ru$: C, 57.35; N, 3.48; H, 4.81. Found: C, 56.99; N, 3.20; H, 4.93%.

2.4.4. [RuCl(2Ac4mT)(dppb)]

The ligand H2Ac4mT (74.0 mg, 0.260 mmol) was added to the suspension of *mer*-$[RuCl_3(dppb)(H_2O)]$ (85.0 mg, 0.130 mmol) in CH_2Cl_2 (20 mL) and the mixture was stirred for 2 h at room temperature. The volume of the solution was reduced to *ca.* 2 mL and



Scheme 1. Route for synthesis of carbonyl complexes from the precursor the *mer*-$[RuCl_3(dppb)(H_2O)]$.



Scheme 2. Metal-assisted oxidative dehydrogenation of mangiferin.

diethyl ether was added. The solid formed was filtered off, washed with diethyl ether and vacuum dried. Yield: Yield: 0.103 g; 89%. *Anal.* Calc. (%) for $(C_{42}H_{40}ClN_4P_2RuS)\cdot 1.5CH_2Cl_2$: C, 54.33; H, 4.82; N, 5.83; S, 3.33. Found: C, 54.72; H, 4.55; N, 6.29; S, 3.03%.

The mother liquor was dried, and its infrared spectrum showed a ν_{SO} band at 1080 cm^{-1}.

This reaction was also attempted with an equimolar mixture of precursor and ligand and in this case the yield fell to about 45%. The complex [RuCl(2Ac4mT)(dppb)] was also obtained from $[RuCl_2(dppb)(PPh_3)]$, using a 1:1 M ratio of complex:ligand. The yield obtained by this method was equal to that in the first method, 89%.

2.4.5. trans-[RuCl$_2$(dppb)(mang)]

The complex *trans*-$[RuCl_2(dppb)(mang)]$ was obtained by allowing *mer*-$[RuCl_3(dppb)(H_2O)]$ (100 mg, 0.154 mmol), dissolved in methanol (50 mL), to react with mangiferin (650 mg, 0.154 mmol). After 6 h, the solid obtained was filtered off, washed with methanol and vacuum dried. Yield: 0.110 g; 71%. *Anal.* Calc. (%) for $C_{47}H_{44}Cl_2O_{11}P_2Ru$: C, 55.41; H, 4.35. Found: C, 55.53; H, 4.41%.

3. Results and discussion

The synthetic routes used here to obtain the carbonyl complexes can be seen in Scheme 1.

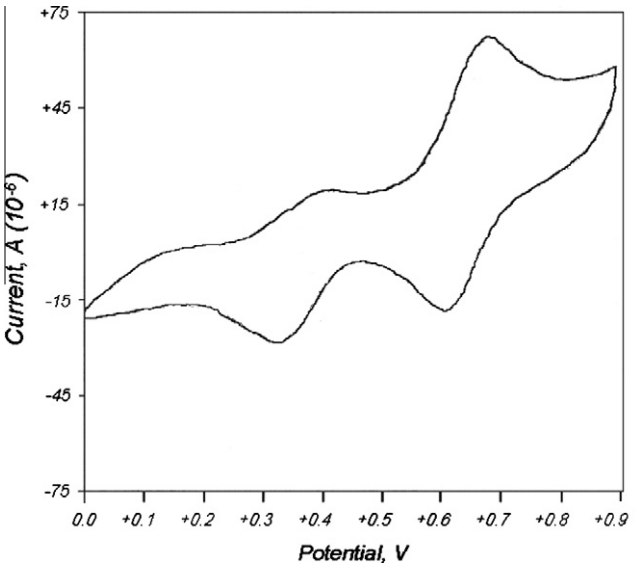


Fig. 1. Cyclic voltammogram of products of the reaction of the *mer*-$[RuCl_3(dppb)H_2O]$ complex with mangiferin in presence of 2,2′-bipyridine (1:1), in CH_2Cl_2 (Pt *versus* AgCl, 0.1 M TBAP.

The reaction of the *mer*-$[RuCl_3(dppb)(H_2O)]$ complex with mangiferin involves the dehydrogenation of this ligand as in Scheme 2, which is similar to the scheme suggested for the dehydrogenation of the *o*-phenylediamine ligand [14].

Moreover, intermediate 2 is oxidized very fast, since it was not detected in a $^{31}P\{^1H\}$ NMR experiment carried out immediately after the reagents were mixed.

H2Ac4mT can be oxidized to a sulfoxide or sulfone. Thus, in the reaction of the aqua complex with this ligand, in excess, part of the ligand may be oxidized, consequently reducing the Ru^{III} to Ru^{II} and forming [RuCl(2Ac4mT)(dppb)] (the ν_{SO} band of the oxidized ligand was detected in the IR spectrum of the solid obtained from mother liquor, as mentioned in the Section 2).

To confirm the above suggested mechanism an electrochemical experiment was done. A mixture of the mangiferin and 2,2′-bipyridine ligands (in the proportion 1:1) was dissolved in dichloromethane, and *mer*-$[RuCl_3(dppb)(H_2O)]$ was added, the reaction was followed by cyclic voltammetry. Thus, in the first cycle, performed immediately after the reagents were mixed, the voltammogram showed two oxidation processes: one at 420 mV and another, at 700 mV (Fig. 1). The first oxidation peak associated to the presence of the *trans*-$[RuCl_2(bipy)(dppb)]$ complex, and the second is associated with the *trans*-$[RuCl_2(dppb)(mang)]$ complex [16]. The solution used in the electrochemical experiment was concentrated; $^{31}P\{^1H\}$ NMR was recorded, and a peak at 33.0 ppm confirms the formation of *trans*-$[RuCl_2(bipy)(dppb)]$ [16]. Obviously, this was possible because the "$RuCl_2(dppb)$" (formed in the reaction of the aqua complex with the mangiferin, which reduces the original ruthenium(III) complex in solution) reacts with 2,2′-bipyridine. The formation of *trans*-$[RuCl_2(bipy)(dppb)]$ is in agreement with the previously published work, in which the reaction of *mer*-$[RuCl_3(dppb)(H_2O)]$ with *o*-phenylenediamine (opda) (1:1) yielded two different ruthenium(II) complexes, one with the ligand *o*-phenylenediamine, *trans*-$[RuCl_2(dppb)(opda)]$ and another with *o*-benzoquinonediimine (bdqi) – the two-electron oxidation product of opda, *trans*-$[RuCl_2(dppb)(bqdi)]$. With this in mind, it is not expected the formation of ruthenium(III) complexes in this type of reaction. This is confirmed by ^{31}P NMR and EPR analysis [14].

Also, immediately after the mixture of the reagents, the $^{31}P\{^1H\}$ NMR spectrum showed two signals, virtually with the same intensity: one at 33.0 ppm and another, at 56.9 ppm, the first attributed to the *trans*-$[RuCl_2(dppb)(bipy)]$ and the second, to the *trans*-$[RuCl_2(dppb)(mang)]$ complex.

It is well known [27] that the H2Ac4mT ligand can be found in two possible forms (Fig. 2):

As will be discussed below, in the [RuCl(2Ac4mT)(dppb)] complex this ligand is in the thiol form.

The $^{31}P\{^1H\}$ NMR spectra of *trans*-$[RuCl_2(dppb)(mang)]$, *tc*-$[RuCl_2(CO)_2(dppb)]$ and *ct*-$[RuCl_2(CO)_2(dppb)]$ show singlets at 56.9, 8.6, and 11.0 ppm, respectively.

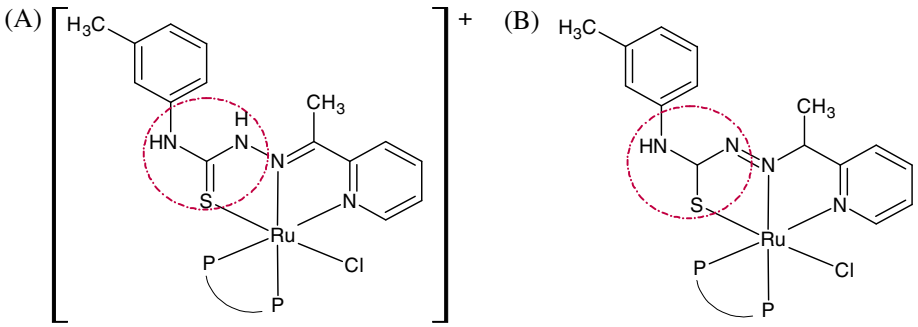


Fig. 2. Two possible forms of coordination of the ligand N(4)-*meta*-tolyl-2-acetylpyridine thiosemicarbazone to the metal center: (A) uncharged, thione form or (B) anionic (deprotonated, charged), thiol form.

FTIR was used to distinguish between the *ct*- and *tc*-[$RuCl_2(CO)_2$(dppb)] isomers. Thus, the IR spectrum of the *ct*-isomer shows just one ν_{CO} band at 2079 cm^{-1}, while the *tc*-isomer shows two ν_{CO} bands (2008 cm^{-1} and 2065 cm^{-1}), in agreement with the *trans* and *cis* positions of CO for *ct*- and *tc*-[$RuCl_2(CO)_2$(dppb)], respectively.

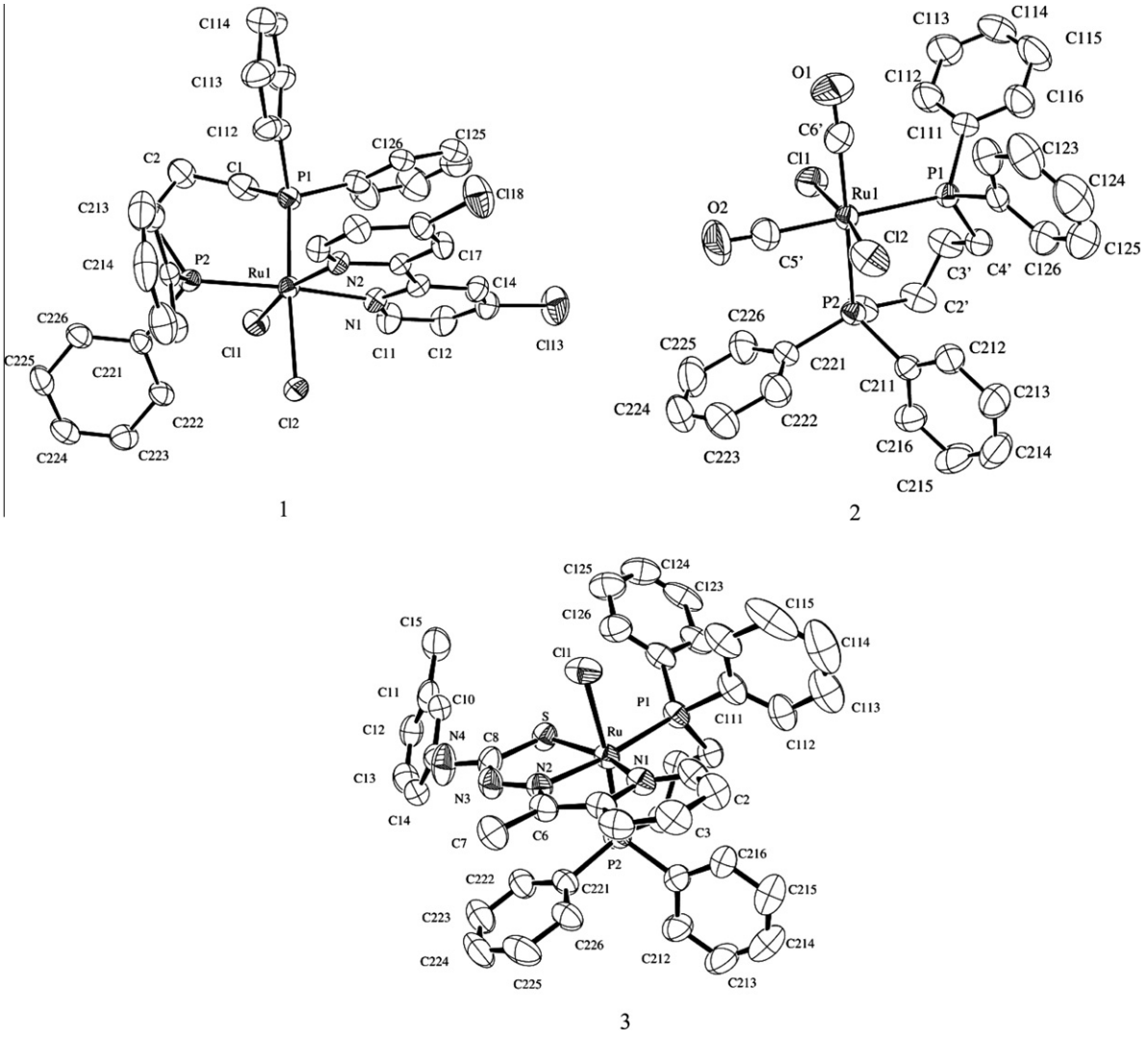


Fig. 3. ORTEP[6] view of the complexes: (1) *cis*-[$RuCl_2$(dppb)(Cl-bipy], (2) *tc*-[$RuCl_2(CO)_2$(dppb)] and (3) [RuCl(2Ac4mT)(dppb)] showing the atom labeling and the 50% probability ellipsoids.

Table 2
Selected bond lengths (Å) and angles (°) for *cis*-[$RuCl_2$(dppb)(Cl-bipy)] **(1)**, *tc*-[$RuCl_2(CO)_2$(dppb)] **(2)** and [RuCl(2Ac4mT)(dppb)] (**3**).

cis-[$RuCl_2$(dppb)(Cl-bipy)]		*tc*-[$RuCl_2(CO)_2$(dppb)]		[RuCl(2Ac4mT)(dppb)]	
Bond	Length (Å)	Bonds	Length (Å)	Bond	Length (Å)
Ru(1)–Cl(1)	2.4156(12)	Ru–Cl(1)	2.411(8)	Ru–Cl(1)	2.4597(13)
Ru(1)–Cl(2)	2.4777(12)	Ru–Cl(2)	2.412(8)	Ru–S(1)	2.3479(13)
Ru(1)–P(1)	2.3047(12)	Ru–P(1)	2.424(7)	Ru–P(1)	2.3315(11)
Ru(1)–P(2)	2.3382(12)	Ru–P(2)	2.449(7)	Ru–P(2)	2.3073(11)
Ru(1)–N(1)	2.121(3)	Ru–C(5′)	1.923(4)	Ru–N(1)	2.125(4)
Cl(18)–C(18)	1.727(4)	C(6′)–O(1)	1.118(4)	S(1)–C(8)	1.697(5)
P(2)–C(4)	1.834(5)	C(5′)–O(2)	1.128(4)	N(2)–N(3)	1.355(6)
	Angle (°)		Angle (°)		Angle (°)
N(2)–Ru(1)–P(1)	96.31(10)	O(2)–C(5′)–Ru(1)	177.2(3)	N(2)–Ru–P(2)	91.48(11)
N(1)–Ru(1)–P(1)	90.14(10)	P(1)–Ru(1)–P(2)	92.47(2)	N(1)–Ru–P(2)	96.41 (10)
N(2)–Ru(1)–P(2)	104.37(10)	C(5′)–Ru(1)–P(2)	88.80(10)	N(2)–Ru–P(1)	173.58(11)
N(1)–Ru(1)–P(2)	175.84(11)	C(5′)–Ru(1)–P(1)	177.61(12)	N(1)–Ru–P(1)	104.31(10)
P(1)–Ru(1)–P(2)	93.61(4)	C(6′)–Ru(1)–P(2)	177.21(10)	P(1)–Ru–P(2)	94.70(4)
N(2)–Ru(1)–Cl(1)	166.95(10)	C(6′)–Ru(1)–P(1)	88.37(10)	N(2)–Ru–S	83.20(12)
N(1)–Ru(1)–Cl(1)	90.49(11)	Cl(1)–Ru(1)–P(2)	88.60(3)	N(1)–Ru–S	159.49(10)
P(1)–Ru(1)–Cl(2)	175.84(4)	C(6′)–Ru(1)–Cl(2)	90.88(10)	P(2)–Ru–Cl(1)	174.17(4)

In the $^{31}P\{^{1}H\}$ NMR spectra of *cis*-[$RuCl_2$(dppb)(Cl-bipy)] and [RuCl(2Ac4mT)(dppb)] there are doublets, at 43.8 and 30.4 ppm ($^{2}J_{P-P}$ = 31.6 Hz), and 42.6 (P_1) and 32.9 (P_2) ppm ($^{2}J_{P-P}$ = 33.9 Hz), respectively. The presence of doublets, clearly exclude the coordination of $HAc4mT^{-}$ to the metal center through two nitrogen atoms [28].

The X-ray structures of the *cis*-[$RuCl_2$(dppb)(Cl-bipy)], *tc*-[$RuCl_2(CO)_2$(dppb)] and [RuCl(2Ac4mT)(dppb)] complexes are shown in Fig. 3, and the relevant bond lengths and angles are summarized in Table 2.

In *cis*-[$RuCl_2$(dppb)(Cl-bipy)], the Ru–Cl bond length is longer when the chlorine is *trans* to the phosphorus atom than *trans* to the nitrogen atom (2.4777(12) Å and 2.4156(12) Å, respectively), since the *trans* influence of the phosphorus atom is stronger than that of the nitrogen atom.

In [RuCl(2Ac4mT)(dppb)], the Ru–Cl bond length, 2.4597(13) Å is closer to the value observed for Ru–Cl *trans* to the phosphorus atoms in *cis*-[$RuCl_2$(dppb)(Cl-bipy)], since it is also *trans* to a phosphorus atom.

In the complex *tc*-[$RuCl_2(CO)_2$(dppb)], the bond lengths Ru–P are longer than in the other complexes [2.424(7) Å and 2.449(7) Å], owing to the competitive effect between two good π-acceptor ligands (phosphorus atom and CO) [29].

In the complex [RuCl(2Ac4mT)(dppb)], the bond lengths 1.697(5) Å and 1.355(6) Å are typical for C–S and N–N single bonds, respectively [30]. The distance Ru–S, 2.3479(13) Å is also in the normal range [30]. In this complex, the distance Ru–N(1) is longer than the distance Ru–N(2) [2.125(4) Å and 2.046(3) Å, respectively], in this case, the N(2) is *trans* to a phosphorus atom, which is a good π acceptor species, and N(1) is *trans* to the S^{-}, a good donor species. It is worth mentioning that the angle P(1)–Ru–N(2) is 173.58(11)°, while the angle N(1)–Ru–S is only 159.49(10)°, far from 180°.

4. Conclusions

mer-[$RuCl_3$(dppb)(H_2O)] has proved to be a extremely versatile precursor for the synthesis of different kinds of Ru^{II} complexes. In this study, it was used to obtain a ruthenium(II) complex containing the *m*-tolyl-2-acetylpyridine-thiosemicarbazone ion as a ligand. Also, the *mer*-[$RuCl_3$(dppb)(H_2O)] complex, in the presence of a reducing agent, was used to prepare new carbonylruthenium(II) complexes. The oxidizing property of this aqua complex allowed us to stabilize the compound *trans*-[$RuCl_2$(dppb)(mang)], containing the natural pharmaceutical product, mangiferin. The mechanism of the reaction between the mangiferin and *mer*-[$RuCl_3$(dppb)(H_2O)] was elucidated by cyclic voltammetry and pulse differential voltammetry, as well as by $^{31}P\{^{1}H\}$ experiments.

Acknowledgement

We thank FAPESP, CNPq, CAPES for the financial support and Johnson Matthey plc for the loan of $RuCl_3$ (to M.P.A).

Appendix A. Supplementary data

CCDC 746.020, 746.021 and 746.022 contains the supplementary crystallographic data for *cis*-[$RuCl_2$(dppb)(Cl-bipy)], *tc*-[$RuCl_2(CO)_2$(dppb)] and [RuCl(2Ac4mT)(dppb)]. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

[1] K. Abdur-Rashid, S.E. Clapham, A.J.N. Harvey, A.J. Lough, R.H. Morris, J. Am. Chem. Soc. 124 (2002) 15104.
[2] S.E. Clapham, A. Hadzovic, R.H. Morris, Coord. Chem. Rev. 248 (2004) 2201.
[3] H. Doucet, T. Ohkuma, K. Murata, T. Yokozawa, M. Kozawa, E. Katayama, A.F. England, T. Ikariya, R. Noyori, Angew. Chem., Int. Ed. 37 (1998) 1703.
[4] K. Murata, K. Okano, M. Miyagi, H. Iwane, R. Noyori, T. Ikariya, Org. Lett. 1 (1999) 1119.
[5] R. Noyori, T. Ohkuma, Pure Appl. Chem. 71 (1999) 1493.
[6] R. Noyori, T. Ohkuma, Angew. Chem., Int. Ed. 40 (2001) 40.
[7] R. Noyori, C.A. Sandoval, K. Muniz, T. Ohkuma, Philos. Trans. R. Soc. A 363 (2005) 901.
[8] R. Noyori, H. Takaya, Acc. Chem. Res. 23 (1990) 345.
[9] T. Ohkuma, H. Doucet, T. Pham, K. Mikami, T. Korenaga, M. Terada, R. Noyori, J. Am. Chem. Soc. 120 (1998) 1086.
[10] L.R. Dinelli, A.A. Batista, K. Wohnrath, M.P. de Araujo, S.L. Queiroz, M.R. Bonfadini, G. Oliva, O.R. Nascimento, P.W. Cyr, K.S. MacFarlane, B.R. James, Inorg. Chem. 38 (1999) 5341.
[11] K. Wohnrath, M.P. de Araujo, L.R. Dinelli, A.A. Batista, I.S. Moreira, E.E. Castellano, J. Ellena, Dalton Trans. (2000) 3383.
[12] M.P. de Araujo, E.M.A. Valle, J. Ellena, E.E. Castellano, E.N. dos Santos, A.A. Batista, Polyhedron 23 (2004) 3163.
[13] G. Von Poelhsitz, M.P. de Araujo, L.A.A. de Oliveira, S.L. Queiroz, J. Ellena, E.E. Castellano, A.G. Ferreira, A.A. Batista, Polyhedron 21 (2002) 2221.
[14] A.L.R. Silva, M.O. Santiago, I.C.N. Diogenes, S.O. Pinheiro, E.E. Castellano, J. Ellena, A.A. Batista, F.B. do Nascimento, I.S. Moreira, Inorg. Chem. Commun. 8 (2005) 1154.
[15] A.E. Graminha, A.A. Batista, J. Ellena, E.E. Castellano, L.R. Teixeira, I.C. Mendes, H. Beraldo, J. Mol. Struct. 875 (2008) 219.
[16] S.L. Queiroz, A.A. Batista, G. Oliva, M. Gambardella, R.H.A. Santos, K.S. MacFarlane, S.J. Rettig, B.R. James, Inorg. Chim. Acta 267 (1998) 209.
[17] M. Bressan, P. Rigo, Inorg. Chem. 14 (1975) 2286.
[18] J.C. Barreto, M.T.S. Trevisan, W.E. Hull, G. Erben, E.S. de Brito, B. Pfundstein, G. Wortele, B. Spiegelhalder, R.W. Owen, J. Agric. Food Chem. 56 (2008) 5599.
[19] L. Lai, L.C. Lin, J.H. Lin, T.H. Tsai, J. Chromatogr. A 987 (2003) 367.
[20] Collect, Enraf-Nonius, Nonius BV, Delft, The Netherlands, 1997–2000.
[21] Z. Otwinowski, W. Minor, Macromol. Crystallogr., Pt. A 276 (1997) 307.
[22] R.H. Blessing, Acta Crystallogr., Sect. A 51 (1995) 33.
[23] G.M. Sheldrick, SHELXS-97. Program for Crystal Structure Resolution, University of Göttingen, Göttingen, Germany, 1997.
[24] G.M. Sheldrick, SHELXL-97. Program for Crystal Structures Analysis, University of Göttingen, Göttingen, Germany, 1997.
[25] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.
[26] R.P. Tenório, A.J.S. Góes, J.G. Lima, A.R. Faria, A.J. Alves, T.M. Aquino, Quim. Nova 28 (2005) 1030.
[27] M.O. Santiago, C.L. Donicci, I.D. Moreira, R.M. Carlos, S.L. Queiroz, A.A. Batista, Polyhedron 22 (2003) 3205.
[28] E.M.A. Valle, F.B. do Nascimento, A.G. Ferreira, A.A. Batista, M.C.R. Monteiro, S.P. Machado, J. Ellena, E.E. Castellano, E.R. de Azevedo, Quim. Nova 31 (2008) 807.
[29] M.P. de Araujo, A.T. de Figueiredo, A.L. Bogado, G. Von Poelhsitz, J. Ellena, E.E. Castellano, C.L. Donnici, J.V. Comasseto, A.A. Batista, Organometallics 24 (2005) 6159.
[30] C. Rodrigues, A.A. Batista, R.Q. Aucélio, L.R. Teixeira, L.do.C. Visentin,, H. Beraldo, Polyhedron 27 (2008) 3061.