

Article

RuCl₂(CO)₂(N-methylimidazole)₂ Isomers: Synthesis, Characterization and Reactivity

Alzir A. Batista^{*a}, Lis R.V. Olmo^a, Marcos R.M. Fontes^b and Glaucius Oliva^b

^aDepartamento de Química, Universidade Federal de São Carlos, C.P. 676,
13560 São Carlos - SP, Brazil

^bInstituto de Física e Química de São Carlos, Universidade de São Paulo, C.P. 369,
13560 São Carlos - SP, Brazil

Received: September 29, 1995

O complexo RuCl₂(CO)₂(MeIm)₂ (MeIm = N-metilimidazol) foi sintetizado e os isômeros ttt, tcc e ctc foram caracterizados por espectroscopia de absorção na região do infravermelho e UV/Vis e suas propriedades redox foram estudadas por voltametria cíclica. Dentre estes isômeros, apenas o ttt catalisa reações de hidrogenação/isomerização do álcool alílico em presença de 1 atm de hidrogênio a 70 °C. Isto pode ser associado à facilidade de dissociação do ligante monóxido de carbono do metal no isômero ttt. A recristalização do *trans,trans,trans* (ttt) isômero em CH₂Cl₂/MeOH produz o complexo RuCl₂(CO)(MeIm)₂(MeOH). Sua estrutura foi determinada por cristalografia de raios-X. Os cristais são triclinicos $\overline{P}1$ $\mathbf{a} = 8.609(3)$, $\mathbf{b} = 8.060(3)$, $\mathbf{c} = 10.581(4)$ Å, $\alpha = 77.78(3)$, $\beta = 88.43(3)$, $\gamma = 66.88(3)^\circ$, $V = 740.4(5)$ Å³, $M_r = 396.24$, $Z = 2$, $D_x = 1.777$ mg·m⁻³, $\lambda(\text{MoK } \alpha) = 0.71073$ Å, $\mu = 12.80$ cm⁻¹, $F(000) = 396$, $T = 296$ K, $R_{\text{int}} = 0.004$, final $R = 0.025$ e $R_w = 0.027$ para 2489 reflexões observadas independentemente [$I > 3 \sigma(I)$].

The N-methylimidazole complex was synthesized and the ttt, tcc and ctc isomers were characterized by infrared and UV/Vis spectroscopy and their redox properties were studied by cyclic voltammetry. Of these isomers only the ttt species catalyzes the hydrogenation/isomerization reactions of allyl alcohol in the presence of 1 atm hydrogen at 70 °C. This may be associated with the easy dissociation of the carbon monoxide ligand from the metal in the ttt isomer. Recrystallization of the *trans,trans,trans* (ttt) isomer in CH₂Cl₂/MeOH produces the *trans* RuCl₂(CO)(MeIm)₂(MeOH) complex. Its structure was determined by X-ray crystallography. The crystals are triclinic, $\overline{P}1$ $\mathbf{a} = 8.609(3)$, $\mathbf{b} = 8.060(3)$, $\mathbf{c} = 10.581(4)$ Å, $\alpha = 77.78(3)$, $\beta = 88.43(3)$, $\gamma = 66.88(3)^\circ$, $V = 740.4(5)$ Å³, $M_r = 396.24$, $Z = 2$, $D_x = 1.777$ mg · m⁻³, $\lambda(\text{MoK } \alpha) = 0.71073$ Å, $\mu = 12.80$ cm⁻¹, $F(000) = 396$, $T = 296$ K, $R_{\text{int}} = 0.004$, final $R = 0.025$ and $R_w = 0.027$ for 2489 independently observed reflections [$I > \sigma(I)$].

Keywords: carbonyl ruthenium complexes, catalysis, X-ray structure

Introduction

The importance of the oxidative addition of hydrogen to ruthenium complexes in catalytic hydrogenation systems has been previously reported¹. This implies the expectation of the easy addition of hydrogen and the parallel oxidation of the complex, which depends on the electron density of the metal center^{2,3}. It is important to consider that the activity and specificity of the hydrogenation catalyst, for

instance, are further influenced by electron properties of the metal, including π and σ effects and also by the steric properties of the surrounding ligands^{4,5}.

For a metal complex to be able to activate hydrogen or the substrate, coordinative unsaturation at the metal center is usually essential. Coordinatively saturated complexes, which are generally unreactive toward hydrogen for lack of a vacant active site, may become active in solution through dissociation of a labile ligand. Not surprisingly,

complexes with a d^8 electron configuration which are often coordinatively unsaturated, or d^6 complexes which can easily become so by the loss of a ligand, constitute the largest group of hydrogenation catalysts. The nature of the interaction between molecular hydrogen and a metal complex is also dictated by the electronic and steric properties of the surrounding ligands. Thus, knowledge of the properties of the metal center can provide the basis for catalyst design.

In this paper we present the synthesis and characterization of some isomers with the general formula $\text{RuCl}_2(\text{CO})_2(\text{MeIm})_2$ and the catalytic hydrogenation reactivity of the *trans*, *trans*, *trans* species.

Experimental

Preparation

The isomers of the $\text{RuCl}_2(\text{CO})_2(\text{MeIm})_2$ complex were prepared similar to the literature methods⁶, using methylimidazole ligand (Aldrich) and commercial ruthenium trichloride (Degussa) in methanol.

ttt- $\text{RuCl}_2(\text{CO})_2(\text{MeIm})_2$

Ruthenium trichloride trihydrate (0.34 g, 1.30 mmol) was dissolved in 10 mL of methanol under 1 atm CO. This solution was stirred for 48 h at 25 °C, when 1-methylimidazole (0.22 g, 2.60 mmol) dissolved in 3 mL of deoxygenated methanol was added. The red solution obtained was then refluxed for 4 h and cooled, at which point yellow crystals separated which were washed with methanol. (Found: C, 30.83; H, 3.07; N, 14.15. Anal. calc. for $\text{C}_{10}\text{H}_{12}\text{N}_4\text{O}_2\text{Cl}_2\text{Ru}$: C, 30.62; H, 3.08; N, 14.28%). The recrystallization of this isomer from $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{ether}$ gave reddish-brown crystals of the complex $\text{RuCl}_2(\text{CO})(\text{MeIm})_2(\text{MeOH})$, suitable for X-ray analysis. Anal. Calc. for $\text{C}_{10}\text{H}_{16}\text{N}_4\text{O}_2\text{Cl}_2\text{Ru}$: C, 30.32; H, 4.04; N, 14.14. Found: C, 30.11; H, 3.90; N, 14.10%.

tcc- $\text{RuCl}_2(\text{CO})_2(\text{MeIm})_2$

Ruthenium trichloride trihydrate (1.00 g, 3.80 mmol) was dissolved in 15 mL of methanol at 35 °C under 1 atm CO with stirring for 3 days, after which 1-methylimidazole (0.63 g, 7.70 mmol) dissolved in 5 mL of deoxygenated methanol was added to the yellow solution obtained. This mixture was refluxed for 4 h and cooled, at which point yellowish crystals separated and these were washed with methanol. (Found: C, 30.80; H, 3.00; N, 14.10%).

ctc- $\text{RuCl}_2(\text{CO})_2(\text{MeIm})_2$

Ruthenium trichloride trihydrate (0.20 g, 0.76 mmol) was dissolved in 10 mL of methanol under 1 atm CO at 20 °C for 48 h. 1-methylimidazole (0.13 g, 1.58 mmol) dissolved in 5 mL of deoxygenated methanol was added to this red solution and this mixture was stirred for 12 h at

room temperature at which point yellow crystals separated and were washed with methanol. (Found: C, 30.72; H, 3.12; N, 14.30%).

Elemental Analysis

Standard microanalyses were performed on crystalline samples by the Laboratório de Microanálise do Instituto de Química of the Universidade de São Paulo.

Spectroscopy

IR spectra: pellets were prepared from crystalline powder samples diluted in CsI. The measurements were performed on a Bomem-Michelson 102 spectrophotometer in the range 4000–200 cm^{-1} .

UV/Vis spectra were measured in CH_2Cl_2 solution (4.0×10^{-4} M) on a Varian DMS100 spectrophotometer.

Electrochemistry

The cyclic voltammograms were recorded at $(25.0 \pm 0.1$ °C) in freshly distilled dichloromethane containing 0.1 M tetrabutylammonium perchlorate (TBAP) using an EG&G PAR electrochemical system consisting of a model RE0073 recorder, model 173 potentiostat, and a model 175 universal programmer. As recommended by IUPAC⁷, the ferrocinium (Fc^+) ferrocene (Fc) couple was employed as the internal reference. A three-electrode system consisting of a glassy carbon working electrode and a platinum foil electrode as the auxiliary was used. The reference electrode was Ag/AgI (TBAP 0.2 M in CH_2Cl_2), a medium in which ferrocene is oxidized at 0.55 V; all potentials are referred to the Ag/AgI electrode. The working solution was separated from the reference electrode with a Luggin-Haber containing salt bridge filled with the solvent and supporting electrolyte. The temperature was stabilized with the electrochemical cell immersed in a bath at a constant temperature. TBAP (Fluka purum) was recrystallized from ethanol/water and dried overnight under vacuum at 100 °C. All solvents used in these experiments were purified by standard procedures⁸, dried before use, and stored over Linde 4 Å molecular sieves. All working solutions were deoxygenated with pre-purified argon before measurement, and were kept under an argon blanket during the experiments.

Hydrogenation/isomerization reactions were carried out in a glass high-pressure vessel (2 mL allyl alcohol and 0.05 mmol of the complex were dissolved in 3 mL dimethyl formamide). A small stirring bar was placed in the solution, the reaction mixture was purged with H_2 , and the vessel was sealed, pressurized to 1 atm (H_2), and then lowered into an oil bath at a constant temperature (70.0 ± 0.5 °C), supported by a magnetic stirrer. The analysis of the reaction products was carried out using a Bruker AC 200 MHz spectrometer, and $^1\text{H-NMR}$ spectra were recorded in

CDCl₃. Under the same reaction conditions, but only in the presence of the free methylimidazole and 1 atm carbon monoxide ligands, no catalytic reaction was observed.

X-Ray Structure Determination

[RuCl₂(CO)(MeIm)₂(MeOH)], M_r = 396.24, triclinic, P1 **a** = 8.609(3), **b** = 8.060(3), **c** = 10.581(4) Å, α = 77.78(3), β = 88.43(3), γ = 66.88(3)°, V = 740.4(5) Å³, Z = 2, D_x = 1.777 mg · cm⁻³, μ = 12.80 cm⁻¹, F(000) = 396. A single crystal with the approximate dimensions 0.17 × 0.17 × 0.03 mm was used for data collection and cell determination on an Enraf-Nonius CAD4 diffractometer with graphite monochromatized MoKα (λ = 0.71073 Å) radiation at room temperature. Unit-cell parameters were obtained from a least-squares refinement of the setting angles of 18 reflections in the θ range of 12 to 25°. Intensity data were collected in the ω – 2θ scan mode up to θ_{max} = 25°, using minimum and maximum scan speeds of 1.7 – 5.5° min⁻¹; 2760 reflections were measured, of which 2600 were independent (R_{int} = 0.004), -10 ≤ h ≤ 10, -10 ≤ k ≤ 10, 0 ≤ l ≤ 12, and 2490 with I > 3σ(I) were employed in the refinement procedure (173 parameters refined). Data were corrected for Lp and absorption effects, with maximum and minimum correction factors of 1.26 and 0.85, respectively, using the method of Walker and Stuart⁹. The intensity of one standard reflection was essentially constant throughout the experiment.

The structure was solved using the heavy atom method and the Fourier difference technique. In the final cycles of the least-squares refinement, all non-H atoms were treated anisotropically, excluding H atoms which were refined isotropically. The H atoms were found according to the Fourier difference map, and their coordinates were refined relative their ideal positions. The function minimized was Σw(|F_o - |F_c||²), where w = k'(σ²(F_o) + cF_o²)⁻¹, with k' = 7.0302 and c = 0.00005, resulting in R = 0.025, wR = 0.027, and S = 3.08 [S = (Σw(|F_o - |F_c||²)/(MN))], where M = number of observations, and N = number of refined parameters]. The maximum shift-to-e.s.d. ratio was 0.02, and the maximum and minimum electron densities in the final difference map were 0.90 and -0.70 eÅ⁻³, respectively. Scattering factors for non-H atoms were taken from Cromer and Mann¹⁰, with corrections for anomalous dispersion from Cromer and Liberman¹¹, and for H atoms from Stewart *et al.*¹² The programs used were SHELX76¹³ and ORTEP¹⁴.

Lists of H-atom positions, anisotropic thermal parameters and structure factors are available on request from the authors.

Results and Discussion

A projection of the RuCl₂(CO)(MeIm)₂(MeOH) compound with all *trans* geometry is shown in Fig. 1 together

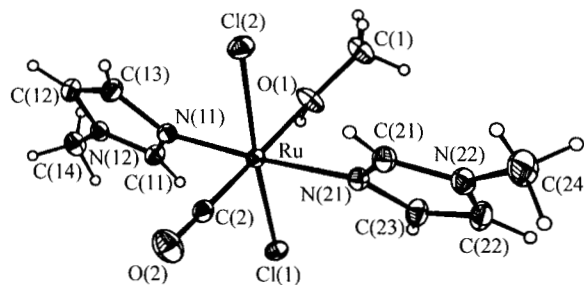


Figure 1. Perspective view of the molecule of *trans*-RuCl₂(CO)(MeIm)₂(MeOH) showing the atom labeling (except hydrogen atoms).

Table 1. Final atomic coordinates and isotropic temperature factors (Å²) for the RuCl₂(CO)(MeIm)₂(MeOH) complex.

Atom	X/A	Y/B	Z/C	B _{eq} *
Ru	0.2245(1)	0.2221(1)	1.2327(1)	2.30(1)
Cl(1)	0.2407(1)	0.3078(1)	1.0031(1)	3.12(4)
Cl(2)	0.1905(1)	0.1646(1)	1.4591(1)	3.56(4)
N(11)	0.0305(3)	0.1485(3)	1.1978(2)	2.7(1)
N(12)	0.1729(3)	0.1177(3)	1.1008(2)	3.0(1)
N(21)	0.4007(3)	0.3166(3)	1.2682(2)	2.9(1)
N(22)	0.5929(3)	0.3629(3)	1.3649(3)	3.6(1)
O(1)	0.0261(3)	0.4671(3)	1.2188(2)	4.0(1)
O(2)	0.4881(3)	0.1098(3)	1.2582(3)	5.2(1)
C(1)	0.0002(5)	0.5769(4)	1.3015(3)	4.9(2)
C(2)	0.3883(4)	0.0162(4)	1.2469(3)	2.8(1)
C(11)	0.0614(4)	0.1884(4)	1.0886(3)	3.2(2)
C(12)	0.1524(4)	0.0292(4)	1.2244(3)	3.6(2)
C(13)	0.0266(4)	0.0473(4)	1.2834(3)	3.6(2)
C(14)	0.2938(4)	0.1317(4)	1.0005(3)	4.1(2)
C(21)	0.4997(4)	0.2717(4)	1.3744(3)	3.3(2)
C(22)	0.5527(5)	0.4685(4)	1.2471(3)	4.3(2)
C(23)	0.4344(4)	0.4396(4)	1.1879(3)	3.9(2)
C(24)	0.7165(5)	0.3461(5)	1.4649(4)	5.4(2)

$$* B_{eq} = \frac{4}{3} \sum_{ij} \beta_{ij} a_i a_j$$

with the atom numbering scheme. Final atomic parameters for non-H atoms are given in Table 1, and interatomic distances and angles are in Table 2.

The MeIm rings are planar, within experimental accuracy [σ_{av} , defined as (Σd_i^2)/(N3), are 0.008 and 0.006 Å for the rings]. The MeOH and CO groups essentially lie in a plane (σ_{av} is 0.01 Å).

The Ru-CO distance (*ca.* 1.822 Å) for this compound is shorter than those found in the isomers of the [RuCl₂

Table 2. Interatomic distances (Å) and angles (°) for the RuCl₂(CO)(MeIm)₂(MeOH) complex.

Ru - Cl(1)	2.4067(7)	Cl(2) - Ru - C(2)	90.3(1)
Ru - Cl(2)	2.3767(8)	N(11) - Ru - N(21)	174.73(9)
Ru - N(11)	2.094(3)	N(11) - Ru - O(1)	86.37(9)
Ru - N(21)	2.089(3)	N(11) - Ru - C(2)	93.1(1)
Ru - O(1)	2.183(2)	N(21) - Ru - O(1)	88.38(9)
Ru - C(2)	1.822(3)	N(21) - Ru - C(2)	92.1(1)
O(1) - C(1)	1.410(4)	C(2) - Ru - O(1)	178.9(1)
C(2) - O(2)	1.111(4)	Ru - C(2) - O(2)	178.6(3)
N(11) - C(11)	1.319(4)	Ru - O(1) - C(1)	129.1(2)
N(11) - C(13)	1.371(4)	Ru - N(11) - C(11)	127.3(2)
N(12) - C(11)	1.338(4)	Ru - N(11) - C(13)	127.2(2)
N(12) - C(12)	1.357(4)	Cl(1) - N(11) - C(13)	105.5(3)
N(12) - C(14)	1.458(4)	N(11) - C(11) - N(12)	111.1(3)
N(21) - C(21)	1.320(4)	C(11) - N(12) - C(12)	107.2(3)
N(21) - C(23)	1.374(4)	N(12) - C(12) - C(13)	106.8(3)
N(22) - C(21)	1.348(4)	N(11) - C(13) - C(12)	109.3(3)
N(22) - C(22)	1.359(5)	C(11) - N(12) - C(14)	126.7(3)
N(22) - C(24)	1.463(5)	C(12) - N(12) - C(14)	126.0(3)
C(12) - C(13)	1.345(5)	Ru - N(21) - C(21)	126.5(2)
C(22) - C(23)	1.346(6)	Ru - N(21) - C(23)	127.3(2)
Cl(1) - Ru - Cl(2)	174.39(3)	C(21) - N(21) - C(23)	106.2(3)
Cl(1) - Ru - N(11)	90.09(7)	N(21) - C(21) - N(22)	110.1(3)
Cl(1) - Ru - N(21)	90.05(7)	C(21) - N(22) - C(22)	107.9(3)
Cl(1) - Ru - O(1)	85.73(6)	N(22) - C(22) - C(23)	106.5(3)
Cl(1) - Ru - C(2)	95.2(1)	N(21) - C(23) - C(22)	109.3(3)
Cl(2) - Ru - N(11)	90.39(7)	C(21) - N(22) - C(24)	124.9(3)
Cl(2) - Ru - N(21)	88.96(7)	C(22) - N(22) - C(24)	127.3(3)
Cl(2) - Ru - O(1)	88.72(6)	Ru - O(1) - H(1)	108.1(1)

(CO)₂(PPh₃)₂]¹⁵ (average Ru-CO *ca.* 1.860 Å) and [RuCl₂(CO)₂(BzI₃P)₂]¹⁶ (1.863 Å), where the CO are in *cis* positions to relation to each other (*cct* isomers).

For this last complex, when the CO molecules are *trans* to each other (*ttt* isomer) the Ru-CO distance was found to be 1.948 Å¹⁶. This fact can be explained by the stronger *trans* influence of carbon monoxide when compared to chlorine or methanol¹⁷⁻²⁰. In [RuCl₂(CO)(C₂H₄)(Me₂PPh)₂], where the CO is *trans* to chlorine, the distance Ru-CO is 1.831 Å²¹, and for the [Ru(OAc)(*p*-MeC₆H₄NCH)(CO)(PPh₃)₂], where the CO molecule is *trans* to the acetate ion, this distance is 1.81(1) Å²². The Ru-Cl bond lengths *trans* to Cl found in this work [2.4067(7) and 2.3767(8) Å] are fairly close to those reported in the literature^{16,21,23,24}. The Ru-N distances for the RuCl₂(CO)(MeIm)₂(MeOH) are 2.094(3) and 2.089(3) Å (Table 2).

These values, larger than the Ru-CO values, show that the methylimidazole ligand is indeed a weaker π acid ligand than carbon monoxide²⁵. The longer distance found for the Ru-O (MeOH) bond, 2.183(2) Å compared to that found for the Ru-N (methylimidazole) bond [2.094(3) and 2.089(3) Å], agrees with the expectation for a harder ligand such as oxygen, compared to nitrogen, bonding to a soft Ru(II) center²⁶.

The carbonylmethylimidazole complexes present characteristic ν_{CO} and ν_{RuCl} bands in the IR spectra (Table 3), which are useful for the tentative assignments of the structures of the synthesized isomers. In this case, the *trans* CO isomers (*ttt* and *ctc*) show only one band in the carbonyl range of the infrared spectra while the *tcc* species (CO in *cis* position to each other) shows two ν_{CO} bands. Likewise,

the ttt and tcc isomers show only one $\nu_{\text{Ru-Cl}}$ band, while the ctc shows two ν_{Cl} bands in the IR spectrum. The electronic spectra of the isomers consist of bands ascribed to possible charge transfer transitions ($d\pi_{\text{Ru}} \rightarrow \pi^*\text{MeIm}$) (Table 3). A typical cyclic voltammogram of a RuCl₂(CO)₂(MeIm)₂ complex is shown in Fig. 2 for the ttt isomer. The redox potentials obtained for the isolated isomers are also given in Table 3.

These data show that the redox potential of the isomers is dependent on the geometry of the complex: the ttt isomer is more easily oxidized than the other two, an observation also made for carbonylphosphine complexes of the type RuCl₂(CO)₂(PPR₃)₂²⁷. This is consistent with the fact that when the same two equal ligands are mutually *trans*, they compete for the same electron density of the metal, allowing for easier oxidation of the metal, because mutual repulsion of these ligands leaves the metal center richer in electron density. Such rationalization is related to the relatively weak MC bond in the ttt isomer of (RuCl₂(CO)₂(PR₃)₂)¹⁷, and accounts for the easier dissociation of CO from the ttt than from the cct isomer. In the case where two

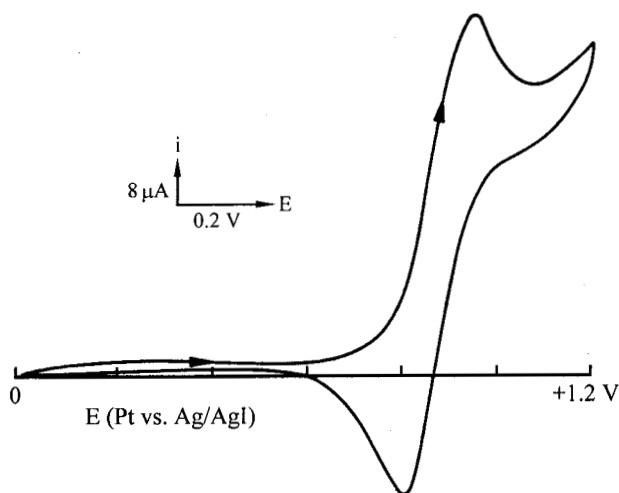


Figure 2. Cyclic voltammogram of ttt RuCl₂(CO)₂(MeIm)₂ isomer measured at a platinum foil electrode. Scan rate 100 mV s⁻¹ (1.0 × 10⁻³ M in CH₂Cl₂, 0.1 M PTBA, reference electrode Ag/AgCl).

CO ligands are in *trans* positions, the degree of MCO backbonding is reduced and the ligands tend to labilize each other⁶. Since CO is a strong π acceptor, *i.e.* better than phosphines, N-heterocyclic or chloride ligands, in ttt isomers with the general formula RuCl₂(CO)₂(L)₂ (where L = phosphine or N-heterocyclic ligands), dissociation of CO is more likely. Thus, recrystallization of the ttt RuCl₂(CO)₂(MeIm)₂ isomer from dichloromethane/methanol/ether produces the RuCl₂(CO)(MeIm)₂(MeOH) complex with corresponding geometry.

The mechanism for the isomerization of RuCl₂(CO)₂(PR₃)₂ complexes from the ttt to the cct isomer, in the presence of excess CO ligand, involves a dissociation and reattachment of the CO ligand²⁸. When the methanol solvent is in excess, in the case of the ttt-RuCl₂(CO)₂(MeIm)₂ isomer, this isomerization process does not happen; the reaction probably proceeds through a pentacoordinated intermediate following the dissociation of one CO ligand, and the subsequent rapid attachment of the MeOH molecule. This mechanism finds support in the fact that carbon monoxide is a good *trans*-directing ligand and that the rate of isomerization of the ttt isomers within RuCl₂(CO)₂(PR₃)₂ complexes is much slower than the substitution of CO by an excess of phosphine, where the reattachment of CO is negligible²⁹.

The catalytic properties of the ttt-, tcc- and ctc-RuCl₂(CO)₂(MeIm)₂ isomers were qualitatively tested in the reaction with allyl alcohol, which presumably also replaces a CO group, forming the precursor RuCl₂(CO)(MeIm)₂(allyl alcohol), in the presence of H₂ at 70 °C and 1 atm for 7 days. Under these conditions, only the ttt isomer has shown to be an effective catalyst, producing propanol and propionaldehyde, which were detected by ¹H-NMR from the singlet at 9.50 ppm (aldehyde), and the multiplets at 1.40 and 2.25 ppm ascribed to CH₂ of propanol and propionaldehyde, respectively. The two triplets are present at 0.65 and 0.90 ppm in the ¹H-NMR spectrum of the methyl proton of the reaction products.

Table 3. Spectroscopic and Electrochemical properties of the RuCl₂(CO)₂(MeIm)₂ isomers.

Isomer	$\nu_{\text{CO}}(\text{cm}^{-1})^{\text{a}}$	$\nu_{\text{Ru-Cl}}(\text{cm}^{-1})^{\text{a}}$	$\lambda_{\text{m\acute{a}x}}(\text{nm})^{\text{b}}$	$\epsilon(\text{M}^{-1}\text{cm}^{-1})$	E1/2(mV) ^c
ttt	1930	315	356	870	85
tcc	2046	330	352	1030	151
	1975				
ctc	1933	310	370	664	175
		279			

^a CsI pellets.

^b CH₂Cl₂ solution (4.0 × 10⁻⁴ M).

^c Measured at 100 mV/s. (Glassy carbon working electrode and Ag/AgCl as reference electrode in CH₂Cl₂, TBAP 0.2M. Internal reference (Fe⁺)/(Fe) whose oxidation potential is at 0.55 V).

Acknowledgments

This work received partial support from CNPq, FAPESP, CAPES and FINEP, which are gratefully acknowledged. We are especially thank Professor Brian R. James, from The University of British Columbia, Vancouver, Canada, for valuable comments.

References

1. Krassowski, D.W.; Nelson J.H.; Brower K.R.; Hauenstein; D. *Inorg. Chem.* **1989**, *28*, 3831.
2. Joseph, M.F.; Page, J.A.; Baird, M.C. *Organometallics* **1984**, *3*, 1749.
3. James, B.R. In: *Homogeneous Hydrogenation*; Wiley & Sons, New York, 1973, p. 99.
4. Harmon, R.E.; Gupta, S.K.; Brown, D.J. *Chem. Rev.* **1983**, *73* (1), 21.
5. Henrici Olivé, G.; Olivé S. *Angew. Chem. Int. Ed.*, **1971**, *10*, 105.
6. Chatt, J.; Shaw, B.L.; Field, A.E. *J. Chem. Soc.* **1964**, 3466.
7. Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1982**, *54*, 1528.
8. Perrin, D.D.; Armarengo, W.L.F.; Perrin, D.P. In: *Purification of Laboratory Chemicals*; Pergamon Press, 3rd ed. New York, NY, 1976.
9. Walker, N.; Stuart, D. *Acta Cryst.* **1983**, A39, 158.
10. Cromer, D.T.; Mann, J.B. *Acta Cryst.* **1968**, A24, 321.
11. Cromer, D.T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.
12. Stewart, R.F.; Davidson, E.R.; Simpson, W.T. *J. Chem. Phys.* **1965**, *42*, 3175.
13. Sheldrick, G.M.; - SHELX76: Program for Crystal Structure Determination; Univ. Cambridge, England, 1976.
14. Johnson, C.K. ORTEP: Report ORNL-3794. Oak Ridge National Laboratory. Tennessee, USA, 1965.
15. Batista, A.A.; Zukerman-Schpector, J.; Porcu, O.M.; Queiroz, S.L.; Araujo, M.P.; Oliva, G.; Souza, D.H.F. *Polyhedron* **1994**, *13*, 4, 689.
16. Wilkes, L.M.; Nelson, J.H.; Mitchener, J.P.; Babich, M.W.; Riley, W.C.; Helland B.J.; Jacobson, R.A.; Cheng; M.Y.; Seff, K.; McCusker, L.B. *Inorg. Chem.* **1982**, *21*, 1376.
17. Krassowski, D.W.; Nelson, J.H.; Brower, K.R.; Hauenstein, D.; Jacobson, R.A. *Inorg. Chem.* **1988**, *27*, 4294.
18. Appleton, T.G.; Clark, H.C.; Manzer, L.E. *Coord. Chem. Rev.* **1973**, *10*, 335.
19. Gofman, M.M.; Nefedov; V.I. *Inorg. Chim. Acta* **1978**, *28*, 1.
20. Lupin, M.S.; Shaw, B.L. *J. Chem. Soc. A* **1968**, 741.
21. Brown L.D.; Barnard, C.F.J.; Daniels, J.A.; Mawby, R.J.; Ibers, J.A. *Inorg. Chem.* **1978**, *17*, 2932.
22. Clark, G.R.; Waters, T.M.; Whittle, K.R. *J. Chem. Soc., Dalton Trans.* **1975**, 2556.
23. Mercer, A.; Trotter, J. *J. Chem. Soc. Dalton Trans.* **1975**, 2480.
24. Seddon, E.; Seddon, K. In: *The Chemistry of Ruthenium*, Ed.; Elsevier Publishing, New York, 1st ed., 1984.
25. Elschenbroich Ch.; Salzer, A. *Organometallics - A Concise Introduction*, Ed., VCH Verlagsgesellschaft, 1989; p. 230.
26. Einaga, H.; Yamakawa, T.; Shinoda, S. *J. Coord. Chem.* **1994**, *32*, 117.
27. Milosavljevic, E.B.; Solujic, Lj.; Krassowski D.W.; Nelson, J.H. *Organomet.* **1988**, *27*, 4294.
28. Golovin, M.N.; Rahman, M.M.; Belmonte, J.E.; Giering, W.P. *Organometallics* **1985**, *4*, 1981.
29. Barnard, C.F.J.; Daniels, J.A.; Jeffrey, J.; Marwby, R.J. *J. Chem. Soc. Dalton Trans.* **1976**, 953.

FAPESP helped in meeting the publication costs of this article