New Rh(III) complexes of 5-methyl-5-(pyridyl)2,4-imidazolidenedione; Synthesis, X-ray structure, electrochemical study and catalytic behavior for hydrogenation of ketones

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ABSTRACT

In this work we describe the reaction of anion $[RhCl_6]^{3-}$ with a series of hydantoin ligands (**HL1**, **HL2** and **HL3** = 5-methyl-5-(2, 3 and 4- pyridyl)-2,4-imidazolidenedione, respectively). Based on the spectroscopies, cyclic voltammetry, elemental and MS analyses, the complexes have the general formula K[$RhCl_2$(**L1**)$_2$] (**1**), *cis* and *trans* K[$RhCl_4$(**HL2**)$_2$] (**2a** and **2b**) and *cis* and *trans* K[$RhCl_4$(**HL3**)$_2$] (**3a** and **3b**). Complexes **2a, 2b**, **3a** and **3b** were characterized successfully by IR, ^{1}H and ^{13}C NMR spectral analyses. Dissolution of complex **1** in DMSO leads to elimination of one **KL1** ligand and coordination of two DMSO molecules as ligand and transformation of this complex to *cis*- and *trans*-[$RhCl_2$**L1**$(DMSO)_2$] **(1a, 1b)** complexes. Recrystallization of this solution led to separation and isolation of crystals of **1a** from the initial mixture. The X-ray analysis results showed that this complex was crystallized as solvated complex *cis*-[$RhCl_2$**L1**$(DMSO)_2$]DMSO. The catalytic activity of these complexes was then evaluated for the hydrogenation of various ketones.

Keywords: Rh(III) complexes; Synthesis; Spectroscopy; X-ray structure; Electrochemical study; Hydrogenation

Introduction

In recent years, the importance of metal complexes of hydantoins has been studied due to applications such as catalytic and biological activity of this class of compounds and new structural features presented by the metal complexes of such ligands.[1-5] Moreover, the ligating properties of several heterocyclic nitrogen-containing hydantoins and their metal complexes have been extensively studied.[6-9] The profound interest of different hydantoin derivatives stems from the well-established medical applications of some of them as antiepileptic drugs.[10, 11] The coordination behavior of these ligands towards several metal ions showed that they can coordinate to metal ions in three modes as depicted in Chart 1: monodentate, *N*-*N* bidentate and *O*-*O* bidentate modes.[12-15]

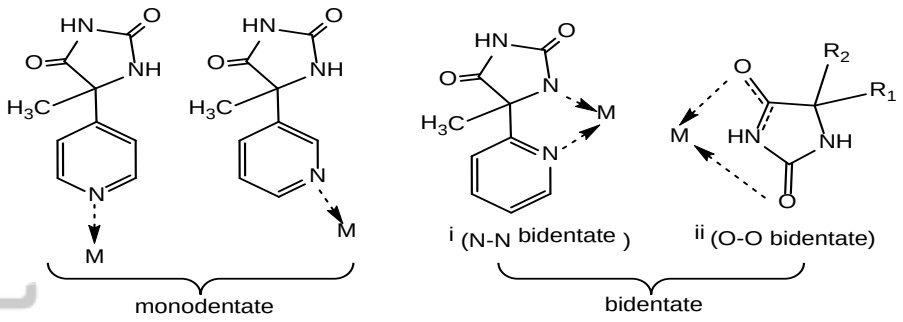


Chart 1. The possible bonding modes of hydantoin ligand to metal M.

Recently, our group [14, 16] reported the synthesis and biological application of Pd(II), Pt(II) and Au(III) complexes containing hydantoin ligands. It was shown that the reaction of hydantoin **HL1** ligand with Pd(II), Pt(II) and Au(III) give five-membered metallacycles complexes. Whereas the reaction of pyridylhydantoin **HL2** and **HL3** ligands with Au(III) give monodante complexes. Also, other research group have synthesized a series of Ni(II) and Cu(II) complexes with pyridylhydantoin ligands that led to formation of six-membered ring.[17] However, this feature was observed in relatively small number of N-heterocycles that undergo cyclometallation to give multi-membered rings metallacycles.[18–21]

In late nineteenth century, chemistry of a variety of Rh(III) complexes with several N-heterocycles and their derivatives have been widely investigated and it was attracted more attention in recent years.[22-29] For example, Mangiatordi *et al*. in 2015 reported the synthesis and catalytic application of Rh(III) complexes containing chelating pyridine-based ligands.[30] These complexes were shown to catalyze the aqueous transfer hydrogenation of an activated aryl ketone under mild conditions of temperature and pH with the phenanthroline complex being much more active than the bispyridine one. As seen from literature[29, 31], Rh(III)

complexes with N-heterocycles ligands can applied as efficient catalysts in the same catalytic organic reactions (transfer hydrogenation reaction of ketones).[32-34]

Synthesis of Rh(III) complexes with **HL1**, **HL2** and **HL3** is one of the most important purposes of this research. It was therefore of our interest to explore the structural aspects of complexes **1**, (**2a**, **2b**) and (**3a**, **3b**) and their application in catalytic transfer hydrogenation reactions of ketones.

Experimental

Materials and methods

All necessary chemicals obtained from commercial suppliers were reagent grade and used without further purifications and all of reactions were carried out under nitrogen using standard Schlenk tube techniques. IR spectra were recorded on Perkin-Elmer FT-IR spectrophotometer in the range of 4000-400 cm^{-1} as KBr cells. ^{1}H NMR and ^{13}C NMR spectra were obtained on 250 MHz Bruker and 90 MHz Jeol spectrometers in DMSO-d_6 or $CDCl_3$ as solvent at 25 ºC. Melting points were determined using a SMP3 apparatus. The rhodium content was recorded by a ESI-MS spectrometer performed on a wear metal analyser 400. Cyclic voltammetry was performed using an Autolab model PGSTAT 20 potentiostat/galvanostat. The working electrode used in the voltammetry experiments was a Glassy disc (3 mm diameter) and a platinum wire was used as the counter electrode. The working electrode potentials were measured versus the Ag wire electrode (all electrodes were purchased from AZAR Electrodes co.).

Crystallography

A suitable crystal was selected and mounted on a SuperNova, Dual, Cu at zero, Atlas diffractometer. The crystal was kept at 130.00(10) K during data collection. Using Olex2[35], the structure was solved with the ShelXT[36] structure solution program using Direct Methods and refined with the ShelXL[37] refinement package using Least Squares minimization. All non-hydrogen atoms were refined with anisotropic displacement parameters; H-atoms were constrained to geometrical estimates, with an isotropic displacement parameter of 1.5 times (Me) or 1.2 times (other) the parent carbon atom.

Synthesis

Synthesis of Ligand: Ligands **HL1**, **HL2** and **HL3** was prepared according to the published procedure methods.[16]

Synthesis of complex ***K[RhCl$_2$(L1)$_2$]*** *(1)*

The solution $K_3[RhCl_6]$ (0.216 g, 0.5 mmol) in 3 ml water was added to the solution of **HL1** (0.191 g, 0.1 mmol) in 3 ml water-ethanol 50%. The orange mixture was heated at reflux for 2 h and orange precipitate of $K[RhCl_2(L1)_2]$ accumulated after standing for 3 days. The stable complex after cooling was filtered off and washed with cold water and next with EtOH and dried under vacuum. The purity was checked by thin layer chromatography with the eluent $CH_3COOC_2H_5/C_2H_3OH$ = 2:1. The complex is soluble in DMSO. Yield: 0.2410 g (81.3%); M.P. > 300 ºC; [Found: C, 36.60; H, 2.66; N, 14.27. $K[C_{18}H_{16}Cl_2N_6O_4Rh]$ requires C, 36.44; H, 2.72; N, 14.17%]; HRMS (*m/z*): $[M^{-}-K]$ calcd for, $C_{18}H_{16}Cl_2N_6O_4Rh$ Found: 554.2.

Synthesis of complexes cis- and trans-[RhCl$_2$(L1)(DMSO)$_2$] (1a, 1b)

Complex **1** (0.148 g, 0.25 mmol) was dissolved in 2 ml DMSO. Mixture of *cis*- and *trans* (**1a, 1b**) were obtained. Recrystallization of this solution gave the small orange well shaped crystals of complex **1a** suitable for x-ray analysis. Yield: 0.0951 g (73.3%); M.P. > 300 ^{o}C; ^{1}H NMR (250 MHz, DMSO-d_6), δ: 10.87 (br, 1H, N2-H2 $_{trans}$), 10.56 (br, 1H, N2-H2 $_{cis}$), 9.54 (br d, 1H, Ph $_{trans}$), 9.49 (br d, 1H, Ph $_{cis}$), 8.07-8.14 (m, 2H, Ph $_{cis\ and\ trans}$), 7.69-7.87 (m, 2H, Ph $_{cis}$ and $_{trans}$), 7.45-7.60 (m, 2H, Ph $_{cis}$ and $_{trans}$), 4.53 (br, 24H, CH_3 (DMSO), 1.77 (s, 3H, $CH_{3\ trans}$), 1.74 (s, 3H, $CH_{3\ cis}$), ^{13}C NMR (62.90 MHz, DMSO-d_6), δ: 178.77 (C-S $_{cis}$), 178.33 (C-S $_{trans}$), 175.24 (C1=O $_{cis}$), 175.12 (C1=O $_{trans}$), 163.93 (C $_{qurt}$), 163.27 (C $_{qurt}$), 161.87 (m, C2=O $_{cis}$), 161.60 (m, C2=O $_{trans}$), 157.67-157.17 (d, $^{2}J_{Rh\text{-}C}$ =31.45 Hz, CH $_{cis}$), 150.95-151.37 (d, $^{2}J_{Rh\text{-}C}$ =26.41 Hz, CH $_{trans}$), 140.45 (CH $_{cis}$), 139.47 (CH $_{trans}$), 125.29 (CH $_{cis}$), 124.76 (CH $_{trans}$); 122.78 (CH $_{trans}$), 122.07 (CH $_{cis}$), 74.99-76.88 (C $_{quat}$), 73.53-74.84 (C_{quat}), 30.55 ($CH_{3\ cis}$), 30.31 ($CH_{3\ trans}$), 27.16-27.30 (br, $CH_{3\ DMSO}$).

Synthesis of complexes cis- and trans-K[$RhCl_4$(HL2)$_2$] (2a, 2b)

$K_3[RhCl_6]$ (0.216 g, 0.5 mmol) in 3 ml water was added to a stirred solution of **HL2** (0.191 g, 0.1 mmol at 600 rpm in 6 cm^3 of a 50% water/ethanol mixture for 3 h at room temperature. The obtained solid was filtered off and washed with water and next with EtOH and dried under vacuum. The purity was checked by thin layer chromatography with the eluent $CH_3COOC_2H_5/C_2H_3OH$ = 2:1. The complex is soluble in DMSO. Yield: 0.1119 g (86.5%); M.P. > 300 ^{o}C. [Found: C, 32.41; H, 2.83; N, 12.71. $K[C_{18}H_{18}Cl_4N_6O_4Rh]$ requires: C, 32.45; H, 2.72; N, 12.62%]; ^{1}H NMR (250 MHz, DMSO-d_6), δ: 10.91 (br, 2H, N2-H2 $_{cis\ and\ trans}$), 8.76 (br, 2H, N1-H1 $_{cis\ and\ trans}$), 8.55 (m, 4H, Ph $_{cis\ and\ trans}$), 7.99-8.14 (m, 2H, Ph $_{cis\ and\ trans}$), 7.43-7.54 (m, 2H, Ph $_{cis\ and\ trans}$), 1.69 (s, 3H, $CH_{3\ trans}$), 1.54 (s, 3H, $CH_{3\ cis}$), ^{13}C NMR (62.90

MHz, DMSO-d_6), δ: 176.37 (C1=O *cis*), 176.01 (C1=O *trans*), 156.73 (C2=O *cis*), 156.46 (C2=O *trans*); 155.20 (CH *cis*); 154.26 (CH *trans*) 153.13 (CH *cis*); 151.94 (CH *trans*); 136.51 (CH *cis and trans*); 125.59 (CH *cis*); 124.62 (CH *trans*); 63.12 (C *quat*); 62.77 (C *quat*); 25.11 (m, CH_3 *cis and trans*); HRMS (*m/z*): $[M^{-}-K]$ calcd for, $[C_{18}H_{18}Cl_4N_6O_4Rh]$ Found: 629.0.

Synthesis of complexes cis- and trans-K[$RhCl_4$(HL3)$_2$] (3a, 3b)

$K_3[RhCl_6]$ (0.216 g, 0.5 mmol) in 3 ml water was added to a stirred solution of **HL3** (0.191 g, 0.1mmol at 600 rpm in 6 cm^3 of a 50% water/ethanol mixture for 3 h at room temperature. The obtained solid was filtered off and washed with water and next with EtOH and dried under vacuum. The purity was checked by thin layer chromatography with the eluent $CH_3COOC_2H_5/C_2H_3OH$ = 2:1. The complex is weakly soluble in DMSO. Yield: 0.1244 g (96.3%); M.P. > 300 ^oC; [Found: C, 32.39; H, 2.64; N, 12.74. $K[C_{18}H_{18}Cl_4N_6O_4Rh]$ requires: C, 32.45; H, 2.72; N, 12.62%]; ^1H NMR (250 MHz, DMSO-d_6), δ: 11.03 (br s, 2H, N2-H2 *cis and trans*), 9.15 (br s, 2H, N1-H1 *cis and trans*), 8.76-8.96 (m, 4H, Ph *cis and trans*), 7.61-7.63 (m, 4H, Ph *cis* and *trans*), 1.67 (s, 3H, CH_3 *trans*), 1.21 (s, 3H, CH_3 *cis*); HRMS (*m/z*): $[M^{-}-K]$ calcd for, $[C_{18}H_{18}Cl_4N_6O_4Rh]$ Found: 629.7.

General experimental procedure for hydrogenation of ketones

Ketones (2 mmol, 0.2 M) and KOH (0.12 mmol) were added to a solution of the Rh complex (0.005 mmol), in 10 ml of anhydrous 2-propanol Under N_2 atmosphere. Reaction mixture was stirred for 4 h at 80 ^oC until the substrates were vanished. Reactions progress was monitored by thin layer chromatography (TLC). After completion of the reaction, the solvent was removed under reduced pressure and the residue was purified by a chromatography (ethyl

acetate/petroleum ether= 1:15 to 1:10). Progress of reaction was monitored by IR, ^{1}H and ^{13}C NMR.

Characterization of hydrogenation Products

Data for 1-(4-nitrophenyl) ethanol (4): IR (KBr disk): ν(cm^{-1}) 3374 (OH); M.p. 112-114 °C (decomposition); ^{1}H NMR (250 MHz, $CDCl_3$), δ: 7.50-7.54 (d, 2H, phenyl), 8.16-8.19 (d, 2H, phenyl), 4.98-5.02 (m, 1H, OH), 3.44-3.46 (br, 1H, CH), 1.48-1.51 (s, 3H, Me). ^{13}C NMR (62.90 MHz, $CDCl_3$), δ: 153.14, 147.12, 125.71, 123.71, 69.45, 50.78, 24.46.

Data for 1-(4-methoxyphenyl) ethanol (5): IR (Nujol): ν(cm^{-1}) 3343 (OH); ^{1}H NMR (250 MHz, $CDCl_3$), δ: 6.58- 6.2 (d, 2H, phenyl), 7.26-7.30 (d, 2H, phenyl), 4.80- 4.87 (m, 1H, OH), 3.73- 3.79 (s, 3H, OMe), 3.45-3.52 (br, 1H, CH), 1.45- 1.48 (d, 3H, Me). ^{13}C NMR (62.90 MHz, $CDCl_3$), δ: 158.94, 137.99, 126.65, 113.81, 69.82, 55.27, 24.54.

Data for diphenylmethanol (6): IR (KBr disk): ν(cm^{-1}) 3387 (OH); M.p. 66-68 °C. ^{1}H NMR (89.60 MHz, $CDCl_3$), δ: 7.20-7.35 (m, 10H, phenyl), 5.97 (br, 1H, OH), 5.73 (br, 1H, CH).

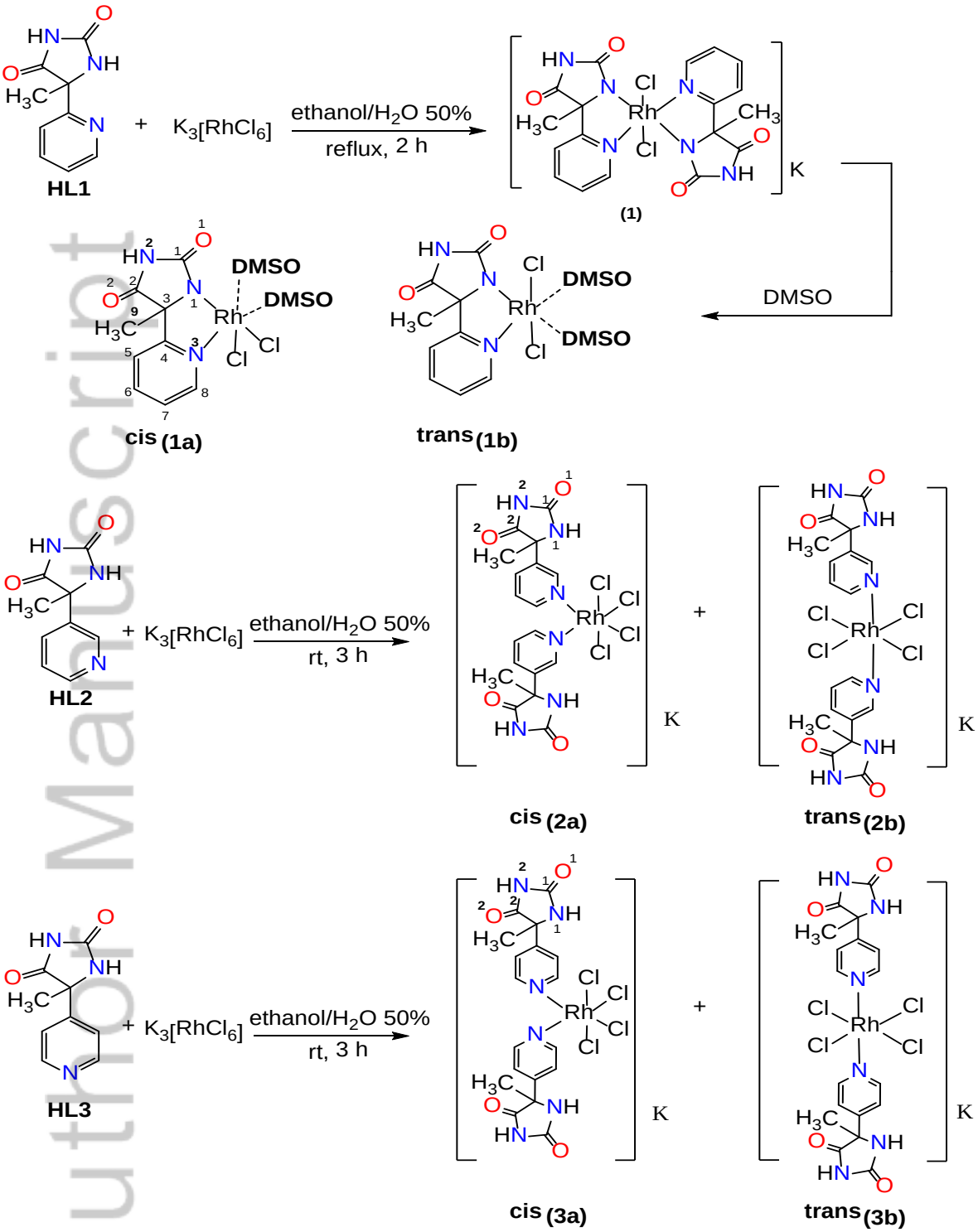
Data for 1-(4-chlorophenyl) ethanol (7): IR (Nujol): ν(cm^{-1}) 3350 (OH), ^{1}H NMR (250 MHz, $CDCl_3$), δ: 7.44-7.54 (m, 2H, phenyl), 8.16-8.25 (m, 2H, phenyl), 4.98-5.04 (m, H, OH) 2.29-2.33 (br, 1H, CH), 1.43-1.51 (d, 3H, Me).

Data for 1-(naphthalenyl) ethanol (8): IR (KBr disk): ν(cm^{-1}) 3262 (OH); M.p. 63-65 °C; ^{1}H NMR (89.60 MHz, $CDCl_3$), δ: 7.51-8.10 (m, 7H, phenyl), 5.46 (br, H, OH), 5.32 (br, 1H, CH), 1.47 (br, 3H, Me).

Results and discussion

Synthesis

Reaction of $K_3[RhCl_6]$ with **HL1, HL2** and **HL3** (1:2 M ratio) in aqueous H_2O/C_2H_5OH gave the complexes $K[RhCl_2(L1)_2]$ **(1)**, *cis* and *trans* $K[RhCl_4(HL2)_2]$ **(2a and 2b)** and *cis* and *trans* $K[RhCl_4(HL3)_2]$ **(3a** and **3b)** (Scheme 1). Complex **1** is insoluble in most of organic solvents such as chloroform, acetone and toluene. Dissolution of this complex in DMSO led to formation of complexes *cis*- and *trans*-$[RhCl_2(L1)(DMSO)_2]$ **(1a** and **1b)**. The formation of heavy metal complexes with solvent molecules is natural for solvents such as DMSO, which behave as strong ligands (L) and forms M-L bonds. Recently, synthesis and characterization of mononuclear Pt(II) complex containing one DMSO as ligand was reported by our group.[14] As seen from literature, the *trans* isomers **2b** and **3b** are more stable than the *cis* ones. This is due to the fact that the metal complexes with prolonged hydantoin ligands in cis positions have more steric hindrance than those of complexes with ligands in *trans* position.[14]



Scheme 1: Synthesis of complexes of **1**, **(1a**, **1b)**, **(2a, 2b)** and **(3a, 3b)**.

Spectroscopy

The structure of complex **1** was characterized successfully by IR and MS spectroscopies and other conventional techniques such as elemental analysis and cyclic voltammetry. The elemental analysis of Rh(III) complexes **1**, **(2a, 2b)** and **(3a**, **3b)** indicates 1:2 stoichiometry between the Rh(III) salt and ligand. Structures of **(1a, 1b), (2a, 2b)** and **(3a, 3b)** were determined by IR, ^{1}H, and ^{13}C NMR spectroscopies and unequivocal structure of complex **1a** was obtained by single crystal X-ray diffraction technique.

Table 1 shows the most important vibrational modes of the ligands and complexes in IR spectra. Comparative analysis of IR spectra of the complexes and free ligands revealed that stretching vibrations of ν(C=N) in pyridine ring shifted to higher frequencies (Table 1). This is due to the coordination of ligand through nitrogen atom of pyridine ring (chelating mode) to the metal ion that causes a significant increase in the ν(C=N) frequency. Identifying of the wave numbers of Rh–N vibrations are rather difficult since the M–N stretching modes (where M is a heavy atom) are usually of low intensity.[16]

Bands related to stretching vibrations of carbonyl groups and more acidic NH groups ν(N2–H2) in **HL1** □ **HL3** remained almost unchanged in all complexes. This fact is evidence that these groups are not involved in the complex formation. Band related to stretching vibration of ν(N1–H1) has disappeared in **1, 1a** and **1b** IR spectra. This shows the bidentate N-coordination of **L1** to the metal center, occurred through the nitrogen atom of the pyridine ring and deprotonated nitrogen of hydantoin ring. But, in **2a, 2b** and **3a, 3b** complexes only the nitrogen atom of the pyridine ring participates in the coordination and ν(N1–H1) in **2a, 2b** and **3a, 3b** IR spectra are shifted to higher frequencies.

Table 1 here

In the ^{1}H NMR spectra of the complexes **1a** and **1b**, proton signal of the pyridine ring is shifted to lower frequencies compared to that of ligand. Also, the ^{1}H NMR data for these complexes indicates that deprotonation at the NH group as the signal of N1–H1 is not observed in their spectra. By comparing the other chemical shifts of **HL1** and its complex, one can conclude that the NMR data support the participation of the hydantoin and pyridine ring in the coordination sphere. These show that the most probable bonding of the ligand with Rh(III) ion is through the nitrogen group of the pyridine ring. This fact indicates this NH group as the signal of N2-H2 group of the hydantoin ring is not involved in the coordination, therefor, signals for this group is slightly shifted. The coexistence of the *cis* and *trans* isomers is confirmed by the ^{1}H NMR spectra. Also, in the ^{1}H NMR spectra of complexes **2a**, **2b** and **3a**, **3b**, signals of the protons from the pyridine ring are shifted to lower frequencies compared to the spectra of the free ligands. Signals for the (N1-H1) and (N2-H2) of hydantoin ring are slightly shifted. This fact indicates these atoms are not involved in the coordination sphere and most probable bonding of the ligand with the Rh(III) ion is take place only through the nitrogen atom of the pyridine ring. It is worthwhile to indicate that the higher field pair of specially amine groups and methyl protons signals in these complexes may be assigned to the *trans* isomers.

In the ^{13}C NMR spectra of the *cis* and *trans* isomers of complex **1a** and **1b**, most changes are related to the carbon atoms of the pyridine ring as fallowing; upfield chemical shifts for C4 and C8 and downfield chemical shifts for C5, C6, and C7. These changes showed that the nitrogen atom of the pyridine ring participates in the binding with the metal ion. The signal of

carbon of methyl groups in the *cis* and *trans* isomers of complexes **1a**, **1b** and **2a, 2b**, are shifted to lower frequencies compared to carbon signal of methyl of the free ligand. The signals of two C=O groups from the hydration ring in both complexes **2a** and **2b** are slightly changed. C2–O2 show greater shift toward higher frequencies than C1–O1, which can be because these groups are nearer to the coordination site. These findings are an indication that the hydantoin ring does not participate in the coordination. As **3a** and **3b** complexes have low solubility in DMSO, it was not possible to obtain ^{13}C NMR spectrum.

X-ray crystallography

Orange single crystal of complex **1a**, $[C_{13}H_{20}Cl_2N_3O_4RhS_2].C_2H_6OS$ were grown by slow evaporation from DMSO. The molecular structure and packing structure of this complex were shown in Fig. 1 and Fig. 2, respectively. The experimental and crystallographic data for complex **1a** are given in Table 2. Selected bond distances and angles for the unit cell for the complex are displayed in Table 3.

The crystal structure shows that in this molecule the geometry around the Rh is in an octahedral, coordinated by one bidentate amine ligand, two chlorides and two DMSO molecules. The chlorides are coordinating in a *cis*-arrangement, as are the DMSO molecules. The pyridine ring of the ligand is *trans* to a DMSO molecule, while the 5-membered ring is trans to one of the chlorides. The dihedral angle between the heterocyclic rings of the ligand is 48.23(8)°. Based on crystal packing findings, Classical bonding interactions (N…O–S)

between adjacent ligand and DMSO solvent molecule result in a zigzag type arrangement of one chain, are driving forces for the formation of a very distorted structure. Also, the amine hydrogen is involved in hydrogen bonding interactions with both the S and O atoms of an adjacent DMSO solvent molecule. There are further weak inter-and intermolecular C-H…X interactions that link the molecules into a 3D network.

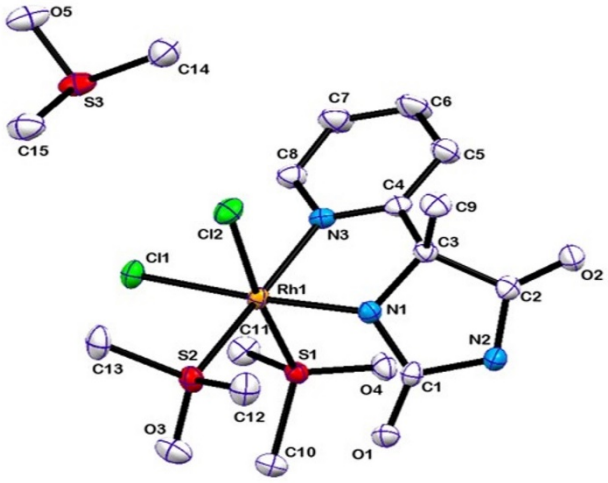


Fig. 1. ORTEP view of X-ray crystal structure **1a**.

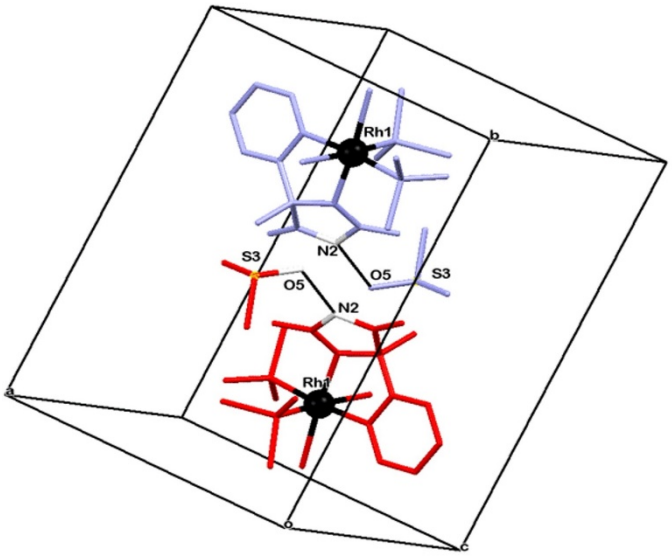


Fig. 2. A packing view of the complex **1a** along the axis.

Table 2 here

Table 3 here

Cyclic voltammetry

The cyclic voltammetry was performed in acetonitrile and dimetylsulfoxide solutions in order to obtain information on electrochemical oxidation of Rh (III) complexes. For example, the cyclic voltammograms of the complex **1** (1 mM) and hydantoin (**HL1**) in both acetonitrile and DMSO solvents containing Bu_4NClO_4 (0.1 M) in both the anodic and cathodic directions are shown in Fig. 3. In this figure curves **a** belong to the complex and curves **b** belong to the hydantoin. All voltammograms exhibit an irreversible feature with an anodic peak (A_1) in the positive-going scan and a cathodic peak in the negative-going scan. It can conclude from the

comparison of curves **a** and **b** that peaks A_1 and C_1 in Rh (III) complex is related to the oxidation and reduction of hydantoin moiety of the ligand. In addition, insets **1** and **2**, show the effect of potential scan rate on the cyclic voltammograms of Rh (III) complex in both the anodic and cathodic directions. As can be seen, with increasing potential scan rate from 100 to 250 mV/s, no significant change in the voltammograms is observed.

Another interesting aspect of the comparison between curves **a** and **b**, is the slight difference in peak potentials of hydantoin moiety in complex and hydantoin, so that in the negative-going scan, the cathodic peak potential of hydantoin moiety in complex (E_{pC1}^{Comp} = -1.70 V vs. Fc/Fc^{+}) is less negative than the cathodic peak potential of hydantoin (E_{pC1}^{Hyd} = -1.73 V vs. Fc/Fc^{+}). The easier reduction of hydantoin moiety in the complex than hydantoin has been ascribed to the relative contribution of hydantoin electrons in the reaction with Rh (III), which makes easier the reduction of hydantoin moiety in the complex in compared with hydantoin alone. In addition, in the positive-going scan, the anodic peak potential belongs to hydantoin moiety in complex (E^{Comp}_{pA1} = 0.99 V vs. Fc/Fc+) is more positive than the anodic peak potential of hydantoin (E^{Hyd}_{pA1} = 0.97 V vs. Fc/Fc+). These data confirm the above statements: the relative contribution of hydantoin electrons in the reaction with Rh(III), more difficult oxidation of the hydantoin moiety in the complex as compared to the hydantoin alone.[38]

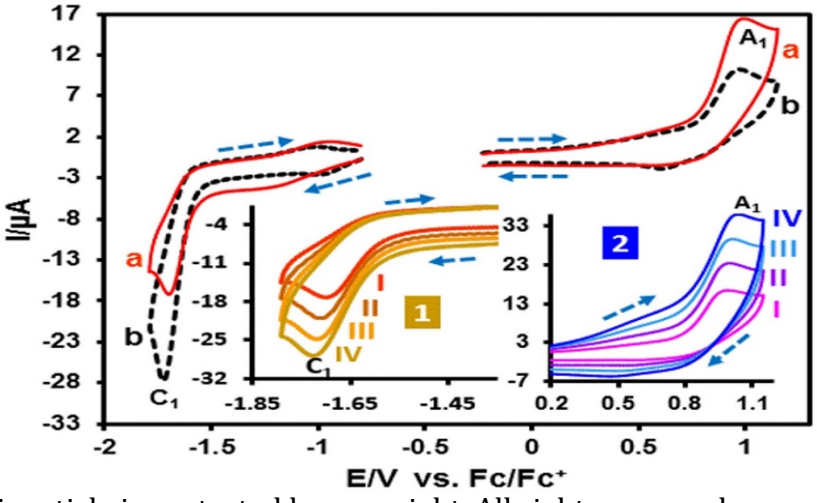


Fig. 3. (a) Cyclic voltammograms of Rh (III) complex **1** (1 mM) in CH_3CN (positive direction) and in DMSO (negative direction) at a scan rate of 100 mV/s. (b) Cyclic voltammograms of hydantoin **HL1** (1 mM) in the same conditions. Inset 1. Cyclic voltammograms of Rh (III) complex (1 mM) in DMSO at different scan rates. Inset 2. Cyclic voltammograms of Rh (III) complex (1 mM) in CH_3CN at different scan rates. In both insets 1 and 2, scan rate from I to IV is, 100, 150, 200 and 250 mV/s. Supporting electrolyte: Bu_4NClO_4 (0.1 M). Working electrode: 3 mm diameter GC-disk electrode. Temperature = 25 ± 1 ºC.

Hydrogenation of ketones

Hydrogenation of ketones is a useful method for producing alcohols. In recent years, significant progress has been achieved for hydrogenation of aryl ketones catalyzed by Rh complexes with chiral bidentate ligands. The catalytic performance of Rh(III) complexes **1, (2a, 2b**) and **(3a, 3b)** towards hydrogenation of ketones was then examined. Initially, we performed a model reaction to optimize the reaction conditions including catalyst loading, base and solvent (Table 4). We chose the hydrogenation reaction of 4-nitro acetophenone (0.2

M) in presence of complex **1** as catalyst precursor, 2-PrOH as solvent and KOH as base. This reaction led to formation of 1-(4-nitrophenyl) ethanol in moderate yield (Table 4, entry 1).

At the first stage of optimization, the influence of solvents on our catalytic system was studied. Various alcoholic solvents such as methanol, ethanol and 2-propanol were taken for screening influence of them on the catalytic system. Isopropanol is found to be a suitable solvent to achieve maximum conversion of 4-nitro acetophenone to corresponding alcohol (Table 4, entry 1). On the other hand ethanol solvent gave less conversion than isopropanol (Table 4, entry 2). The lowest conversion was obtained with methanol solvent (Table 4, entry 3).

Next, we study the efficiency of catalysts loading on the reaction. As expected, varying the catalyst loading has considerable effect on the activity of catalyst. When the loading of complex **1** decreased to 0.0005 mmol from 0.001 mmol, the reaction will proceed very slowly and even stop as if the catalyst was not there (Table 4, entries 4 and 5). At the high loading of complex **1** (0.005 mmol), the yield of coupled products for reactions shows a beat rise (Table 4, entry 6). If the catalyst loading is too high (> 0.005 mmol), the reaction gives maximum yield (Table 4, entry 7). Therefore, with respect to the economic aspect, low catalyst loading of 0.005 mmol was chosen as the best loading of catalyst.

Finally, hydrogenation reaction of 4-nitro acetophenone was investigated in presence of various organic and inorganic bases. Among the tested bases, KOH provided good amount of corresponding product (Table 4, entry 6). The high efficiency was exhibited in the hydrogenation of 4-nitro acetophenone to the corresponding alcohol in presence of Et_3N

(Table 4, entry 8). Other bases, such as K_2CO_3 and KOt-Bu proved to be less active (Table 4, entries 9 and 10). Therefore, the use of KOH as base, increased the catalytic activity.

Using the optimized reaction conditions (2-PrOH as solvent, 0.005 mmol of catalyst and KOH as base), complexes **1, (2a, 2b**) and **(3a, 3b)** were applied to a range of ketones in hydrogenation reaction. Various type of functionalized ketones were subjected to the reduction conditions**.** All the complexes efficiently catalyze the transfer hydrogenation of various ketones with maximum conversion within 4 h. Among the tested complexes, complexes **2a, 2b** and **3a, 3b** were highly efficient in the transfer hydrogenation of ketones to corresponding alcohols with a high conversion. The results of transformations are given in Table 5. It was observed that the presence of electron withdrawing groups possibly decreased the electron density on the metal center and hence the rate of transfer hydrogenation increases. Thus, complexes **2a, 2b** and **3a, 3b** containing more electron withdrawing groups -Cl in comparison with complex **1** show more effective conversions.

The introduction of electron withdrawing substituents to the *para* position of the aryl ring of acetophenone decreased the electron density on the C=O bond. Therefore, the improved activity of these ketones led to easier transfer hydrogenation. Order of the reactivity of substituted acetophenone is NO_2 > Cl > Ph > OMe, see Table 5. For example, excellent yields are achieved when 4-nitro acetophenone subjected to the transfer hydrogenation reaction (Table 5, entry 1). Deactivated ketones such as 1-(4-methoxyphenyl) ethanol give lower yields indicating that the reaction was sensitive to the electron density on the C=O bond (Table 5, entry 2). Moreover, sterically hindered ketone benzophenone (Table 5, entry 3) underwent hydrogenation to give the corresponding secondary alcohol in moderate

conversion of 90%. The alcohols produced in these reactions were obtained in good to excellent yields and purity, short reaction times and low catalyst loading.

Table 4 here

Table 5 here

Conclusion

In this report, we describe the synthesis and characterization of new Rh(III) complexes **1, (1a, 1b), (2a, 2b)** and **(3a, 3b)** with pyridylhydantoin ligands, **HL1-HL3**. In these complexes, containing octahedral Rh(III) center, bidentate ligand **HL1** is coordinated via the $N_{pyridine}$ ring and $N_{imidazolidenedione}$ while monodentate ligands **HL2** and **HL3** are coordinated via $N_{pyridine}$ to the metal center. Complexes **(1a, 1b), (2a, 2b)** and **(3a, 3b)** were characterized successfully by spectroscopic methods and other conventional techniques as well as IR and particulary for **1a**, by X-ray crystallography. Also, the catalytic activity of complexes **1, (2a, 2b)** and **(3a, 3b)** toward hydrogenation of ketones were investigated. Based on the obtained results, these complexes efficiently catalyze the transfer hydrogenation. The ease of preparation of the complexes, low catalyst loading and stability toward air and moisture make these complexes as an ideal catalytic system for hydrogenation of ketones. Also a comparative catalytic study between the complexes **1, (2a, 2b)** and **(3a, 3b)** was done and results showed that complexes **2a, 2b** and **3a, 3b** was more efficient than the complex **1**.

Acknowledgments

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Supplementary Material

Physical measurements and selected ^{31}P, ^{13}C and ^{1}H NMR spectra of some compounds can be found in the online version at. CCDC 1438731 contains the supplementary crystallographic data for the complex **1a**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK. Tel.: +44 0 1223 762911; or deposit@ccdc.cam.ac.uk.

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Table captions

Table 1. IR selected bands (ν_{max}/cm^{-1}) of the ligands (**HL1– HL3**) and complexes **1, (1a, 1b), (2a, 2b) and (3a, 3b)**, for the numbering of the atoms, see scheme **1**.

Table 2. Crystal data and structure refinement for complex **1a**.

Table 3. Selected bond lengths [Å] and bond angles [°] for complex **1a.**

Table 4. Optimizations for the hydrogenation of ketones with Rh(III) catalyst**.**

Table 5. Transfer hydrogenation of ketones catalyzed by Rh(III) catalyst.

Table 1. IR selected bands (ν_{max}/cm^{-1}) of the ligands (**HL1– HL3**) and complexes **1, (1a, 1b), (2a, 2b) and (3a, 3b)**, for the numbering of the atoms, see scheme **1**.

compound	ν(NH) cm^{-1}	ν(CO) cm^{-1}	ν(CN) cm^{-1}	
HL1	3264(N1 –| 3166(N2 –|	1759 (C1 –C 1722 (C2 –C	1587	
1	- 3101	1783 1732	1613	
1a and **1b**	- 3104	1826 1745	1618	1119 **ν(SO) cm^{-1}**; 1025, 1017 **ρ_r (CH_3)**
HL2	3244(N1 –| 3170(N2 –|	1771 (C1 –C 1723 (C2 –C	1594	
2a and **2b**	3257 3125	1773 1724	1607	
HL3	3207(N1 –| 3113(N2 –|	1776 (C1 –C 1729 (C2 –C	1604	
3a and **3b**	3345 2992	1767 1716	1603	

Table 2. Crystal data and structure refinement for complex **1a**.

Empirical formula.	$C_{15}H_{26}Cl_2N_3O_5RhS_3$
Formula weight	598.38
Temperature/K	130.01(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.10929(15)
b/Å	14.9582(2)
c/Å	15.6451(2)
α/°	90
β/°	99.2142(13)
γ/°	90
Volume/Å^3	2335.27(6)
Z	4
ρ_{calc}g/cm^3	1.702
μ/mm^{-1}	10.807
F(000)	1216.0
Crystal size/mm^3	0.2471 × 0.2308 × 0.0444
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.23 to 154.194
Index ranges	-12 ≤ h ≤ 12, -18 ≤ k ≤ 18, -17 ≤ l ≤ 19
Reflections collected	24390

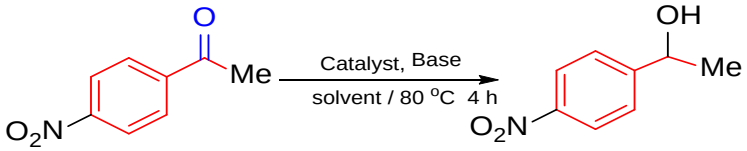
Independent reflections	4925 [R_{int} = 0.0282, R_{sigma} = 0.0189]
Data/restraints/parameters	4925/0/273
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0249, wR_2 = 0.0639
Final R indexes [all data]	R_1 = 0.0267, wR_2 = 0.0654
Largest diff. peak/hole / e $Å^{-3}$	1.01/-0.70

Table 3. Selected bond lengths [Å] and bond angles [°] for complex **1a.**

Bond distances			
Rh1- Cl1	2.3635(5)	S1 – O4	1.4727(16)
Rh1 - Cl2	2.3655(5)	S1 – C10	1.773(2)
Rh1 – S1	2.3130(5)	S1 – C11	1.773(2)
Rh1 - S1	2.2906(5)	S2 – O4	1.4680(18)
Rh1 - N1	2.0319(18)	S2 – C12	1.777(3)
Rh1 – N3	2.0877(18)	S2 – C13	1.783(2)
Bond angles			
Cl1- Rh1 - Cl2	90.235(19)	N3 - Rh1 – Cl1	95.35(5)
S1 - Rh1 - Cl1	90.688(19)	N3 - Rh1 – Cl2	87.35(5)
S1 - Rh1 - Cl2	172.97(2)	N3 - Rh1 – S1	85.62(5)
S2 - Rh1 - Cl1	88.077(19)	N3 - Rh1 – S2	173.19(5)
S2 - Rh1 - Cl2	86.75(2)	O4 – S1 - Rh1	111.30(7)
S2 - Rh1- S1	100.245(19)	O3 – S2 - Rh1	117.70(7)
N1 - Rh1 – Cl1	175.34(5)	Cl1 – S1 - Rh1	111.64(8)
N1 - Rh1 – Cl2	89.38(5)	Cl2 – S2 - Rh1	109.55(9)

N1 - Rh1 – N3	79.99(7)	Cl3 – S2 - Rh1	110.84(9)

Table 4. Optimizations for the hydrogenation of ketones with Rh(III) catalyst**.**

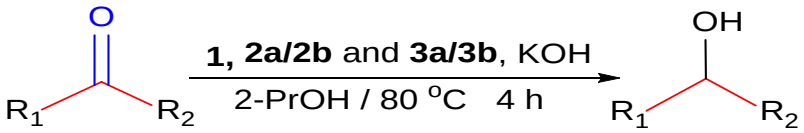


Entry	Base	Cat. (mmol)	solvent	Yield (%)[b]
1	KOH	0.001	2- PrOH	62
2	KOH	0.001	Ethanol	38
3	KOH	0.001	Methanol	18

4	KOH	0.0005	2- PrOH	32
5	KOH	-	2- PrOH	0
6	KOH	0.005	2- PrOH	84
7	KOH	0.01	2- PrOH	88
8	Et_3N	0.005	2- PrOH	71
9	K_2CO_3	0.005	2- PrOH	44
10	KOt-Bu	0.005	2- PrOH	40

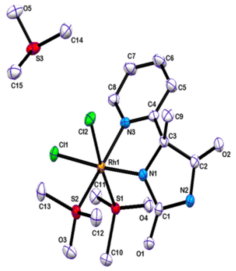
[a] Reaction conditions: 4-nitro acetophenone 0.2 M, solvent (10 ml), base (12 mol %), catalyst. Under N_2.
[b] Isolated yield

Table 5. Transfer hydrogenation of ketones catalyzed by Rh(III) catalyst.



Entry	Reduction Product[b]	Catalyst	Yield (%)	TON [c]
1	**1-(4-nitrophenyl) ethanol (4)**	**1**	84	336
		2a/2b	99	400
		3a/3b	97	388
2	**1-(4-methoxyphenyl) ethanol (5)**	**1**	57	228
		2a/2b	87	348
		3a/3b	88	352
3	**diphenylmethanol (6)**	**1**	61	244
		2a/2b	90	360
		3a/3b	90	360
4	**1-(4-chlorophenyl) ethanol (7)**	**1**	70	280
		2a/2b	92	368
		3a/3b	95	380
5	**1-(naphthalenyl) ethanol (8)**	**1**	65	260
		2a/2b	90	360
		3a/3b	92	368

[a] Reaction conditions: ketones (0.2 M), 2-propanol (10 ml). KOH (12 mol %), catalyst (0.005 mmol). Under N_2
[b] Isolated yield
[c] TON= mol product/mol catalyst



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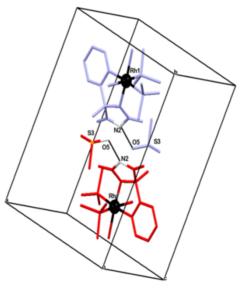

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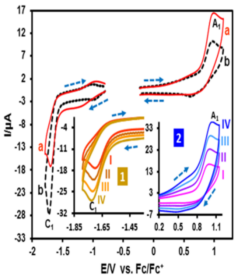

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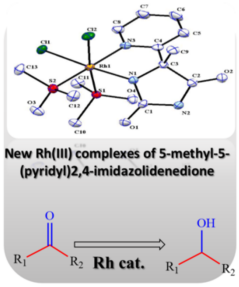

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