Received: 22 October 2016 | Revised: 22 November 2016 | Accepted: 25 November 2016

DOI 10.1002/aoc.3716

WILEY Applied Organometallic Chemistry

FULL PAPER

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

Seyyed Javad Sabounchei[1] | Mohsen Sayadi[1] | Mojdeh Sadat Hashemi[1] | Ali Hashemi[1] | Davood Nematollahi[1] | Eslam Salahifar[1] | Robert W. Gable[2]

[1] Faculty of Chemistry, Bu-Ali Sina University, Hamedan 65174, Iran

[2] School of Chemistry, University of Melbourne, Victoria 3010, Australia

Correspondence
Seyyed Javad Sabounchei, Faculty of Chemistry, Bu-Ali Sina University, Hamedan 65174, Iran.
Email: jsabounchei@yahoo.co.uk

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 spectroscopic, cyclic voltammetric, 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 using infrared, ^1H NMR and ^{13}C NMR spectral analyses. Dissolution of complex **1** in dimethylsulfoxide (DMSO) led to elimination of one KL1 ligand and coordination of two DMSO molecules as ligands and transformation of this complex to *cis*- and *trans*-$[RhCl_2L1(DMSO)_2]$ (**1a** and **1b**). Recrystallization led to separation and isolation of crystals of **1a** from the initial mixture. X-ray analysis results showed that this complex was crystallized as solvated complex *cis*-$[RhCl_2L1(DMSO)_2]DMSO$. The catalytic activity of these complexes was then evaluated for the hydrogenation of various ketones.

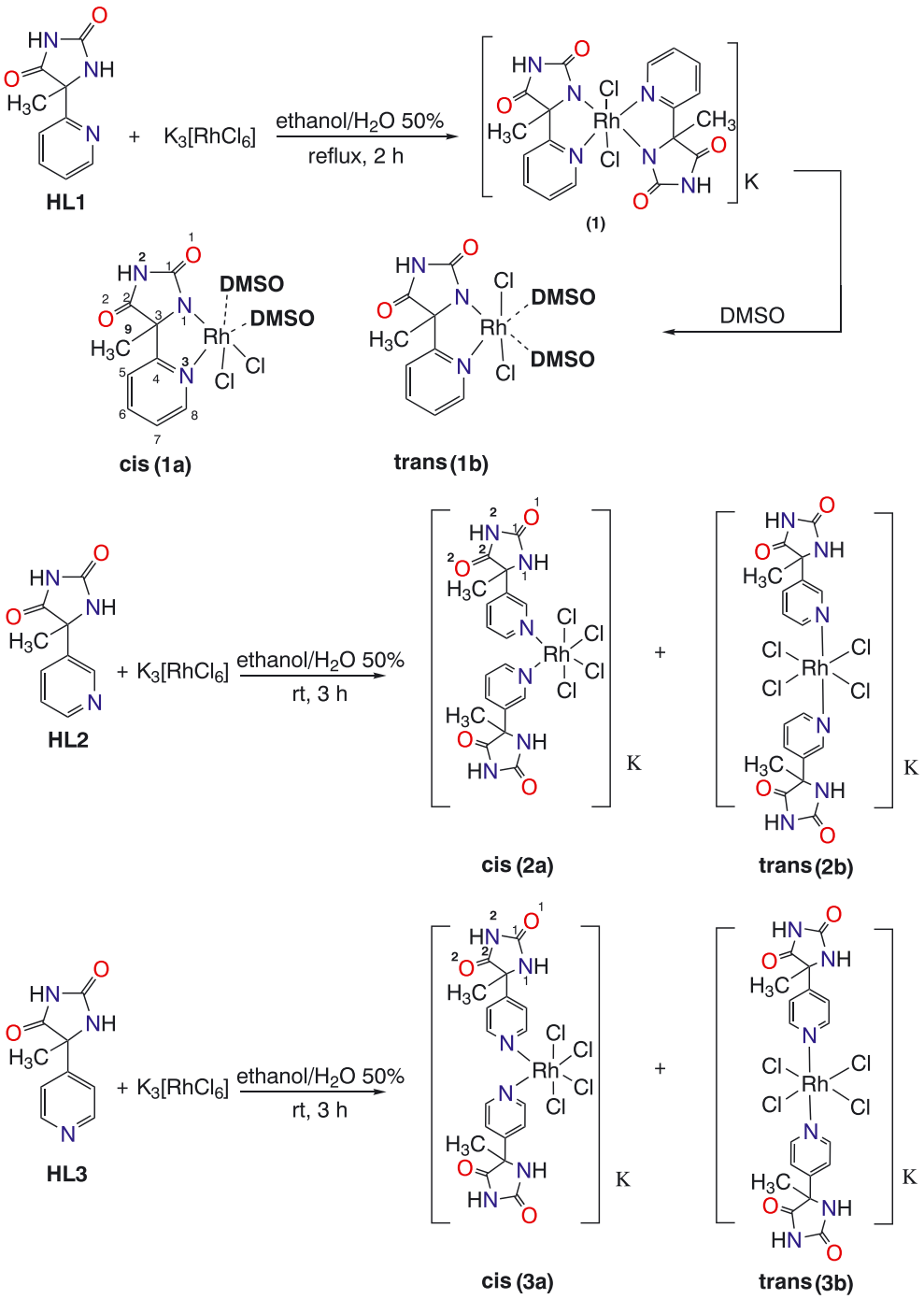
KEYWORDS

electrochemical study, hydrogenation, Rh(III) complexes, spectroscopy, synthesis, X-ray structure

1 | INTRODUCTION

In recent years, the importance of metal complexes of hydantoins has been recognized due to the 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 in various hydantoin derivatives stems from the well-established medical applications of some of them as antiepileptic drugs.[10,11] The coordination behaviour of these ligands towards several metal ions shows that they can coordinate to metal ions in three modes as depicted in Scheme 1: monodentate, *N–N* bidentate and *O–O* bidentate modes.[12–15]

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 ligand 5-methyl-5-(2-pyridyl)-2,4-imidazolidenedione (HL1) with Pd(II), Pt(II) and Au(III) gives five-membered metallacycle complexes. Whereas the reaction of hydantoin ligands 5-methyl-5-(3-pyridyl)-2,4-imidazolidenedione (HL2) and 5-methyl-5-(4-pyridyl)-2,4-imidazolidenedione (HL3) with Au(III) gives monodentate complexes. Also, other research groups have synthesized a series of Ni(II) and Cu(II) complexes with pyridylhydantoin ligands that led to formation of six-membered rings.[17] However, this feature was observed in a relatively small number of N-heterocycles that undergo cyclometallation to give multi-membered ring metallacycles.[18–21]



SCHEME 1 Possible bonding modes of hydantoin ligand to metal M

In the late twentieth century, the chemistry of a variety of Rh(III) complexes with several N-heterocycles and their derivatives was widely investigated and it has attracted more attention in recent years.[22–29] For example, Mangiatordi and co-workers in 2015 reported the synthesis and catalytic application of Rh(III) complexes containing chelating pyridine-based ligands.[30] These complexes were shown to catalyse 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 evident from the literature,[29,31] Rh(III) complexes with N-heterocycle ligands can be 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 interest for us to explore the structural aspects of 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**) and their application in catalytic transfer hydrogenation reactions of ketones.

2 | EXPERIMENTAL

2.1 | Materials and methods

All necessary chemicals obtained from commercial suppliers were of reagent grade and used without further purification. All reactions were carried out under nitrogen using standard Schlenk tube techniques. Infrared (IR) spectra were recorded with a PerkinElmer FT-IR spectrophotometer in the range 400–4000 cm^{-1} as KBr cells. ^1H NMR and ^{13}C NMR spectra were obtained with 250 MHz Bruker and 90 MHz Jeol spectrometers in deuterated dimethylsulfoxide (DMSO-d_6) or $CDCl_3$ as solvent at 25 °C. Melting points were determined using an SMP3 apparatus. The rhodium content was determined using an electrospray ionization mass spectrometer performed with 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 in diameter) and a platinum wire was used as the counter electrode. The working electrode potentials were measured versus an Ag wire electrode (all electrodes were purchased from AZAR Electrodes Co.).

2.2 | 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; hydrogen 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.

2.3 | Synthesis

2.3.1 | Synthesis of ligands

Ligands HL1, HL2 and HL3 were prepared according to published procedures.[16]

2.3.2 | Synthesis of complex 1

A solution of $K_3[RhCl_6]$ (0.216 g, 0.5 mmol) in 3 ml of water was added to a solution of HL1 (0.191 g, 0.1 mmol) in 3 ml of water–ethanol (50%). The orange mixture was heated at reflux for 2 h and an orange precipitate of **1** accumulated after standing for three days. The stable complex after cooling was filtered off and washed with cold water and then with EtOH and dried under vacuum. The purity was checked using TLC with eluent of $CH_3COOC_2H_5$–C_2H_3OH (2:1). The complex was soluble in DMSO. Yield 0.2410 g (81.3%); m.p. > 300 °C. Anal. 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.

2.3.3 | Synthesis of complexes *cis*- and *trans*-[$RhCl_2$(L1)(DMSO)$_2$] (**1a** and **1b**)

Complex **1** (0.148 g, 0.25 mmol) was dissolved in 2 ml of DMSO. A mixture of **1a** and **1b** was obtained. Recrystallization of this solution gave small orange well-shaped crystals of complex **1a** suitable for X-ray analysis. Yield 0.0951 g (73.3%); m.p. > 300 °C. ^1H NMR (250 MHz, DMSO-d_6, δ, ppm): 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_{3trans}), 1.74 (s, 3H, CH_{3cis}). ^{13}C NMR (62.90 MHz, DMSO-d_6, δ, ppm): 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, $^2J_{Rh-C}$ = 31.45 Hz, CH_{cis}), 150.95–151.37 (d, $^2J_{Rh-C}$ = 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_{3cis}), 30.31 (CH_{3trans}), 27.16–27.30 (br, CH_{3DMSO}).

2.3.4 | Synthesis of complexes **2a** and **2b**

$K_3[RhCl_6]$ (0.216 g, 0.5 mmol) in 3 ml of 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 then with EtOH and dried under vacuum. The purity was checked using TLC with eluent of $CH_3COOC_2H_5$–C_2H_3OH (2:1). The complex was soluble in DMSO. Yield 0.1119 g (86.5%); m.p. > 300 °C. Anal. 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). ^1H NMR (250 MHz, DMSO-d_6, δ, ppm): 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_{3trans}), 1.54 (s, 3H, CH_{3cis}). ^{13}C NMR (62.90 MHz, DMSO-d_6, δ, ppm): 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, $CH_{3cis\ and\ trans}$). HRMS (*m/z*): $[M^- - K]$ calcd for $[C_{18}H_{18}Cl_4N_6O_4Rh]$; found: 629.0.

2.3.5 | Synthesis of complexes **3a** and **3b**

$K_3[RhCl_6]$ (0.216 g, 0.5 mmol) in 3 ml of water was added to a stirred solution of HL3 (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 then with EtOH and dried under vacuum. The purity was checked using TLC with eluent of $CH_3COOC_2H_5$–C_2H_3OH (2:1). The complex was weakly soluble in DMSO. Yield 0.1244 g (96.3%); m.p. > 300 °C. Anal. 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). ^{1}H NMR (250 MHz, DMSO-d_6, δ, ppm): 11.03 (br s, 2H, N2─H2$_{cis\text{ and }trans}$), 9.15 (br s, 2H, N1─H1$_{cis\text{ and }trans}$), 8.76–8.96 (m, 4H, Ph$_{cis\text{ and }trans}$), 7.61–7.63 (m, 4H, Ph$_{cis\text{ and }trans}$), 1.67 (s, 3H, CH_{3trans}), 1.21 (s, 3H, CH_{3cis}). HRMS (m/z): [M^- − K] calcd for [$C_{18}H_{18}Cl_4N_6O_4Rh$]; found: 629.7.

2.4 | 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 °C until the substrates vanished. Reaction progress was monitored by TLC. After completion of the reaction, the solvent was removed under reduced pressure and the residue was purified using chromatography (ethyl acetate–petroleum ether, 1:15 to 1:10). Progress of reaction was monitored using IR, ^{1}H NMR and ^{13}C NMR spectroscopies.

2.5 | Characterization of hydrogenation products

*Data for 1-(4-nitrophenyl)ethanol (**4**).* IR (KBr disc, ν, cm^{-1}): 3374 (OH). M.p. 112–114 °C (decomposition). ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 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, ppm): 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, ppm): 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, ppm): 158.94, 137.99, 126.65, 113.81, 69.82, 55.27, 24.54.

*Data for diphenylmethanol (**6**).* IR (KBr disc, ν, cm^{-1}): 3387 (OH). M.p. 66–68 °C. ^{1}H NMR (89.60 MHz, $CDCl_3$, δ, ppm): 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, ppm): 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 disc, ν, cm^{-1}): 3262 (OH). M.p. 63–65 °C. ^{1}H NMR (89.60 MHz, $CDCl_3$, δ, ppm): 7.51–8.10 (m, 7H, phenyl), 5.46 (br, H, OH), 5.32 (br, 1H, CH), 1.47 (br, 3H, Me).

3 | RESULTS AND DISCUSSION

3.1 | Synthesis

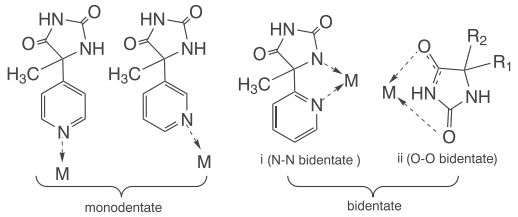
Reaction of $K_3[RhCl_6]$ with HL1, HL2 and HL3 (1:2 molar ratio) in aqueous H_2O–C_2H_5OH gave the complexes **1**, **2a** and **2b**, and **3a** and **3b** (Scheme 2). Complex **1** is insoluble in most organic solvents such as chloroform, acetone and toluene. Dissolution of this complex in DMSO leads to the formation of complexes **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 form M─L bonds. Recently, the synthesis and characterization of a mononuclear Pt(II) complex containing one DMSO as ligand were reported by our group.[14] As evident from the 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 hydantoin ligands in *cis* positions have more steric hindrance than that of complexes with ligands in *trans* positions.[14]

3.2 | Spectroscopy

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

Table 1 summarizes the most important vibrational modes of the ligands and complexes in IR spectra. Comparative analysis of IR spectra of the complexes and free ligands reveals that stretching vibrations of ν(C═N) in pyridine ring shift 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 wavenumbers of Rh─N vibrations is 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 the spectra of HL1–HL3 remain almost unchanged for all complexes. This



SCHEME 2 Synthesis of complexes **1**, **1a**, **1b**, **2a**, **2b**, **3a** and **3b**

TABLE 1 Selected IR bands (ν_{max}) of the ligands (HL1–HL3) and complexes (**1**, **1a**, **1b**, **2a**, **2b**, **3a** and **3b**); for the numbering of the atoms, see Scheme 2

Compound	ν(NH) (cm^{-1})	ν(CO) (cm^{-1})	ν(CN) (cm^{-1})	
HL1	3264 (N1—H1) 3166 (N2—H2)	1759 (C1—O1) 1722 (C2—O2)	1587	
1	—3101	1783 1732	1613	
1a and **1b**	—3104	1826 1745	1618	1119 ν(SO) 1025, 1017 $\rho_r(CH_3)$
HL2	3244(N1—H1) 3170(N2—H2)	1771 (C1—O1) 1723 (C2—O2)	1594	
2a and **2b**	3257 3125	1773 1724	1607	
HL3	3207(N1—H1) 3113(N2—H2)	1776 (C1—O1) 1729 (C2—O2)	1604	
3a and **3b**	3345 2992	1767 1716	1603	

fact is evidence that these groups are not involved in complex formation. Band related to stretching vibration of ν(N1—H1) is absent in the IR spectra of **1**, **1a** and **1b**. This shows the bidentate N-coordination of L1 to the metal centre occurs through the nitrogen atom of the pyridine ring and deprotonated nitrogen of hydantoin ring. But, in complexes **2a**, **2b**, **3a** and **3b** only the nitrogen atom of the pyridine ring participates in the coordination and ν(N1—H1) in IR spectra of **2a**, **2b**, **3a** and **3b** is shifted to higher frequencies.

In the ^{1}H NMR spectra of complexes **1a** and **1b**, proton signal of the pyridine ring is shifted to lower frequencies compared to that of the ligand. Also, the ^{1}H NMR data for these complexes indicate 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 results 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, and therefore signals for this group are 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**, **3a** and **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 takes place only through the nitrogen atom of the pyridine ring. It is worth mentioning that the higher field pair of especially amine group and methyl proton signals in these complexes may be assigned to the *trans* isomers.

In the ^{13}C NMR spectra of the *cis* and *trans* isomers **1a** and **1b**, most changes are related to the carbon atoms of the pyridine ring as follows: upfield chemical shifts for C4 and C8 and downfield chemical shifts for C5, C6 and C7. These changes show that the nitrogen atom of the pyridine ring participates in the binding with the metal ion. The signals of carbon of methyl groups in the *cis* and *trans* isomers **1a**, **1b**, **2a** and **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 shows greater shift towards 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 complexes **3a** and **3b** have low solubility in DMSO, it was not possible to obtain ^{13}C NMR spectra.

3.3 | X-ray crystallography

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

The crystal structure shows that in this molecule the geometry around the Rh is octahedral, coordinated by one bidentate amine ligand, two chlorides and two DMSO

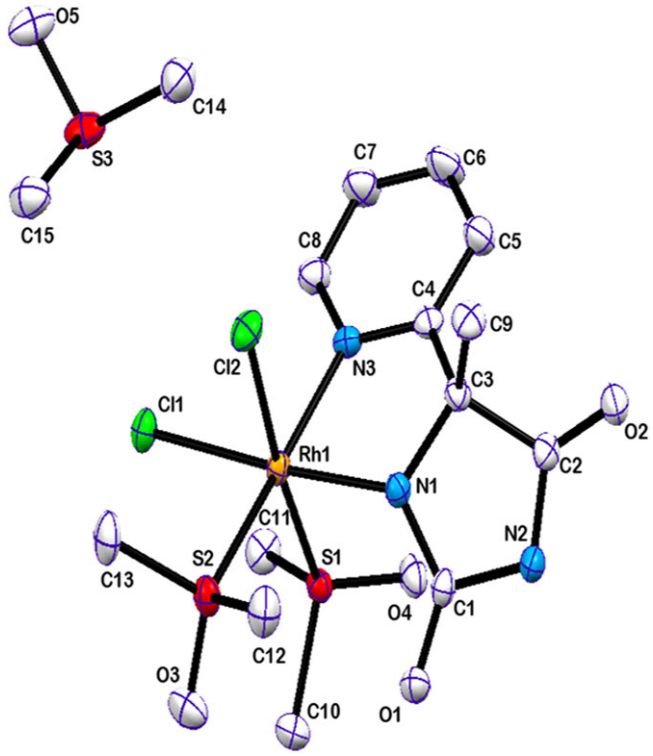


FIGURE 1 ORTEP view of X-ray crystal structure of **1a**

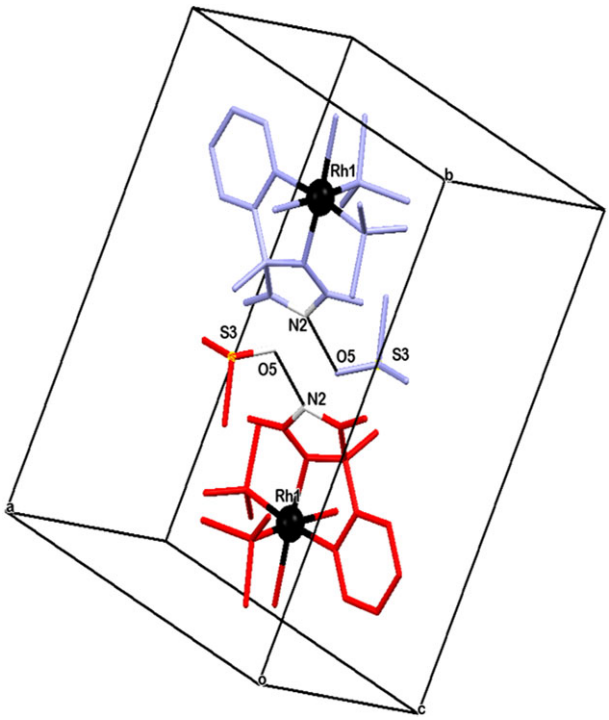


FIGURE 2 Packing view of complex **1a** along the axis

molecules. The chlorides coordinate in a *cis* arrangement, as do the DMSO molecules. The pyridine ring of the ligand is *trans* to a DMSO molecule, while the five-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, and 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 three-dimensional network.

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	Cu Kα (λ = 1.54184 Å)
2θ range for data collection (°)	8.23 to 154.194
Index ranges	$-12 \le h \le 12$, $-18 \le k \le 18$, $-17 \le l \le 19$
Reflections collected	24 390
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 [$I \ge 2\sigma(I)$]	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)

3.4 | Cyclic voltammetry

Cyclic voltammetry was performed in acetonitrile and DMSO solutions in order to obtain information on electrochemical oxidation of the Rh(III) complexes. For example, the cyclic voltammograms of 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 Figure 3. In this figure curves (a) correspond to the complex and curves (b) 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 be concluded from a comparison of curves (a) and (b) that peaks A_1 and C_1 for the Rh(III) complex are 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 the 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^{-1}, 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

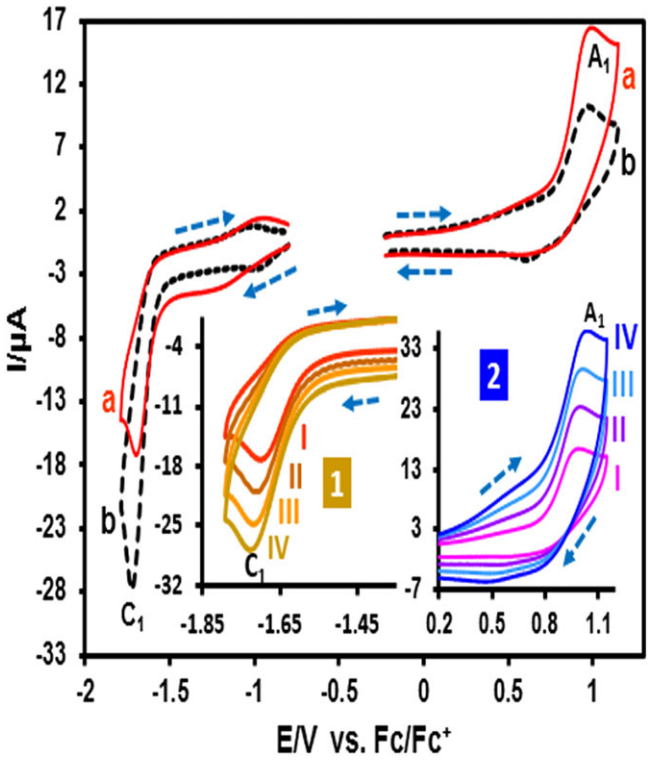


FIGURE 3 (a) Cyclic voltammograms of Rh(III) complex **1** (1 mM) in CH_3CN (positive direction) and in DMSO (negative direction) at a scan rate of 100 mV s^{-1}. (b) Cyclic voltammograms of hydantoin HL1 (1 mM) under the same conditions. Inset 1: cyclic voltammograms of Rh (III) complex (1 mM) in DMSO at various scan rates; inset 2: cyclic voltammograms of Rh(III) complex (1 mM) in CH_3CN at various scan rates (from I to IV is 100, 150, 200 and 250 mV s^{-1}). Supporting electrolyte: Bu_4NClO_4 (0.1 M). Working electrode: 3 mm diameter glassy carbon disc electrode. Temperature: 25 ± 1 °C

of hydantoin moiety in the complex and hydantoin, so that in the negative-going scan, the cathodic peak potential of hydantoin moiety in the complex ($E_{pC1}^{Comp} = -1.70$ V versus Fc/Fc^+) is less negative than the cathodic peak potential of hydantoin ($E_{pC1}^{Hyd} = -1.73$ V versus 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 compared with hydantoin alone. In addition, in the positive-going scan, the anodic peak potential corresponding to hydantoin moiety in the complex ($E_{pA1}^{Comp} = 0.99$ V versus Fc/Fc+) is more positive than the anodic peak potential of hydantoin ($E_{pA1}^{Hyd} = 0.97$ V versus Fc/Fc+). These data confirm the above statements: the relative contribution of hydantoin electrons in the reaction with Rh(III) makes more difficult the oxidation of the hydantoin moiety in the complex as compared to hydantoin alone.[38]

3.5 | Hydrogenation of Ketones

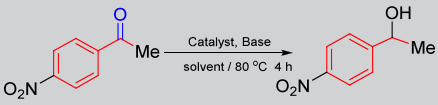
Hydrogenation of ketones is a useful method for producing alcohols. In recent years, significant progress has been achieved for hydrogenation of aryl ketones catalysed by Rh complexes with chiral bidentate ligands. The catalytic performance of Rh(III) complexes **1**, **2a**, **2b**, **3a** and **3b** towards hydrogenation of ketones was thus 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-nitroacetophenone (0.2 M) in the presence of complex **1** as catalyst precursor, isopropanol as solvent and KOH as base. This reaction leads to the formation of 1-(4-nitrophenyl)ethanol in moderate yield (Table 4, entry 1).

In the first stage of optimization, the influence of solvents on our catalytic system was studied. Various alcoholic solvents such as methanol, ethanol and isopropanol were screened for the influence of them on the catalytic system. Isopropanol is found to be a suitable solvent to achieve maximum conversion of 4-nitroacetophenone to corresponding alcohol (Table 4, entry 1). In contrast, ethanol as solvent gives lower conversion than isopropanol (Table 4, entry 2). The lowest conversion is obtained with methanol (Table 4, entry 3).

Next, we studied the effect of catalyst loading on the reaction. As expected, varying the catalyst loading has a considerable effect on the activity of catalyst. When the loading of complex **1** decreases to 0.0005 mmol from 0.001 mmol, the reaction proceeds very slowly and even stops if the catalyst is absent (Table 4, entries 4 and 5). At a high loading of complex **1** (0.005 mmol), the yield of coupled products of the reaction shows a significant increase (Table 4, entry 6). If the catalyst loading is too high (>0.005 mmol), the reaction gives a maximum yield (Table 4, entry 7). Therefore, with respect to the economic aspect, a low catalyst loading of 0.005 mmol is chosen as the best loading of catalyst.

Finally, the hydrogenation reaction of 4-nitroacetophenone was investigated in the presence of

TABLE 4 Optimization for hydrogenation of ketones with Rh(III) catalyst[a]



Entry	Base	Catalyst (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-nitroacetophenone (0.2 M), solvent (10 ml), base (12 mol%), catalyst, under N_2.

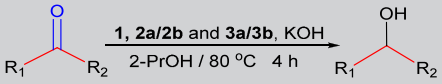
[b]Isolated yield.

various organic and inorganic bases. Among the tested bases, KOH provides a good amount of corresponding product (Table 4, entry 6). A high efficiency is exhibited in the hydrogenation of 4-nitroacetophenone to the corresponding alcohol in the presence of Et_3N (Table 4, entry 8). Other bases, K_2CO_3 and KO*t*-Bu, prove to be less active (Table 4, entries 9 and 10). Therefore, the use of KOH as base increases the catalytic activity.

Using the optimized reaction conditions (isopropanol as solvent, 0.005 mmol of catalyst and KOH as base), complexes **1**, **2a**, **2b**, **3a** and **3b** were applied as catalysts for a range of ketones in the hydrogenation reaction. Various types of functionalized ketones were subjected to the reduction conditions. All the complexes efficiently catalyse the transfer hydrogenation of various ketones with maximum conversion within 4 h. Among the tested complexes, **2a**, **2b**, **3a** and **3b** are 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 is observed that the presence of electron-withdrawing groups possibly decreases the electron density on the metal centre and hence the rate of transfer hydrogenation increases. Thus, complexes **2a**, **2b**, **3a** and **3b** containing more electron-withdrawing groups (—Cl) than complex **1** lead to more effective conversions.

The introduction of electron-withdrawing substituents to the *para* position of the aryl ring of acetophenone decreases the electron density on the C═O bond. Therefore, the improved activity of these ketones leads to easier transfer hydrogenation. The order of reactivity of substituted acetophenone is NO_2 > Cl > Ph > OMe (Table 5). For example, excellent yields are achieved when 4-nitroacetophenone is 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 is sensitive to the electron density on the C═O bond (Table 5, entry 2). Moreover, sterically hindered ketone benzophenone (Table 5, entry 3) undergoes hydrogenation to give the corresponding secondary alcohol in a moderate conversion of 90%. The alcohols produced in these reactions are obtained in good to excellent yields and purity, with short reaction times and with low catalyst loading.

TABLE 5 Transfer hydrogenation of ketones catalysed by Rh(III) catalysts[a]



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

[a]Reaction conditions: ketones (0.2 M), isopropanol (10 ml), KOH (12 mol%), catalyst (0.005 mmol), under N_2.

[b]Isolated yield.

[c]TON = moles product/moles catalyst.

4 | CONCLUSIONS

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

ACKNOWLEDGMENTS

Funding of our research from Bu-Ali Sina University is gratefully acknowledged.

REFERENCES

[1] M. F. Iskander, S. R. Zayan, M. A. Khalifa, L. El-Sayed, *J. Inorg. Nucl. Chem.* **1974**, *36*, 551.

[2] L. El-Sayed, M. F. Iskander, *J. Inorg. Nucl. Chem.* **1971**, *33*, 435.

[3] N. S. Biradar, B. R. Havinale, *Inorg. Chim. Acta* **1976**, *17*, 157.

[4] K. K. Narang, A. Aggarwal, *Inorg. Chim. Acta* **1974**, *9*, 137.

[5] M. Katyal, Y. Dutt, *Talanta* **1975**, *22*, 151.

[6] T. A. Manuel, *Adv. Organometal. Chem.* **1966**, *3*, 181.

[7] G. R. Dobson, I. W. Stolz, R. K. Sheline, *Adv. Inorg. Radiochem.* **1966**, *8*, 1.

[8] J. D. Curry, M. A. Robinson, D. H. Busch, *Inorg. Chem.* **1967**, *6*, 1570.

[9] C. N. Elgy, M. R. Harrison, D. Nicholls, *Inorg. Chim. Acta* **1982**, *57*, 21.

[10] E. A. Swinyard, J. A. Madsen, L. S. Goodman, *J. Pharm. Exp. Therap.* **1954**, *111*, 54.

[11] T. C. Butler, W. J. Waddell, *J. Pharm. Exp. Therap.* **1954**, *110*, 120.

[12] S. J. Sabounchei, P. Shahriary, S. Salehzadeh, Y. Gholiee, H. R. Khavasi, *J. Mol. Struct.* **2013**, *1051*, 15.

[13] S. J. Sabounchei, P. Shahriary, S. Salehzadeh, Y. Gholiee, A. Chehregani, *C. R. Chim.* **2015**, *18*, 564.

[14] S. J. Sabounchei, P. Shahriary, S. Salehzadeh, Y. Gholiee, D. Nematollahi, A. Chehreganib, A. Amania, *New J. Chem.* **2014**, *38*, 1199.

[15] L. N. Ambroladze, T. D. Turkadze, I. Z. Moseshvili, *Russian J. Inorg. Chem.* **2008**, *53*, 714.

[16] S. J. Sabounchei, P. Shahriary, Y. Gholiee, S. Salehzadeh, H. R. Khavasi, A. Chehregani, *Inorg. Chim. Acta* **2014**, *409*, 265.

[17] M. M. Chowdhry, A. D. Burrows, D. M. P. Mingos, A. J. P. White, D. J. Williams, *J. Chem. Soc., Chem. Commun.* **1995**, 1521.

[18] E. C. Constable, *Polyhedron* **1984**, *3*, 1037.

[19] D. W. Evans, G. R. Baker, G. R. Newkome, *Coord. Chem. Rev.* **1989**, *93*, 155.

[20] P. J. Steel, *J. Organometal. Chem.* **1991**, *408*, 395.

[21] A. Zilan, U. Maeder, A. V. Zelewski, H. V. Gudel, *J. Am. Chem. Soc.* **1989**, *111*, 3855.

[22] M. P. Garcia, J. L. Millan, M. A. Esteruelas, L. A. Oro, *Polyhedron* **1987**, *6*, 1427.

[23] M. A. Garcia, M. A. Garralda, L. Ibarlucea, *Polyhedron* **1988**, *7*, 1067.

[24] L. A. Oro, M. T. Pinillos, C. Tejel, *J. Organometal. Chem.* **1985**, *280*, 261.

[25] M. T. Youinou, R. Ziessel, *J. Organometal. Chem.* **1989**, *363*, 197.

[26] M. A. Ciriano, F. Viguri, J. J. Perez-Torrente, F. J. Lahoz, L. A. Oro, *J. Chem. Soc. Dalton Trans.* **1989**, 25.

[27] J. C. Bayon, G. Net, J. Real, P. J. Rasussen, *J. Organometal. Chem.* **1990**, *385*, 409.

[28] G. Garcia, G. Sanchez, I. Romero, I. Solano, M. D. Santana, G. Lopez, *J. Organometal. Chem.* **1991**, *408*, 241.

[29] A. Kumar, A. Kumar, R. K. Gupta, R. P. Paitandi, K. B. Singh, S. K. Trigun, M. S. Hundal, D. S. Pandey, *J. Organometal. Chem.* **2016**, *801*, 68.

[30] N. Madern, N. Queyriaux, A. Chevalley, M. Ghasemi, O. Nicolotti, I. Ciofini, G. F. Mangiatordi, M. Salmain, *J. Mol. Catal. B* **2015**, *122*, 314.

[31] P. Gu, Q. Xu, M. Shi, *Tetrahedron* **2014**, *70*, 7886.

[32] A.-Q. Wu, Y. Li, F.-K. Zheng, G.-C. Guo, J.-S. Huang, *Cryst. Growth Des.* **2006**, *6*, 444.

[33] D. J. Cross, I. Houson, A. M. Kawamoto, M. Wills, *Tetrahedron Lett.* **2004**, *45*, 843.

[34] P. Singh, D. Das, M. Singh, A. K. Singh, *Inorg. Chem. Commun.* **2010**, *13*, 988.

[35] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339.

[36] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *A71*, 3.

[37] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *C71*, 3.

[38] S.-T. Mak, V. W.-W. Yam, C.-M. Che, T. C. W. Mak, *J. Chem. Soc. Dalton Trans.* **1990**, 2555.

SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

How to cite this article: Sabounchei SJ, Sayadi M, Hashemi MS, Hashemi A, Nematollahi D, Salahifar E, Gable RW. New Rh(III) complexes of 5-methyl-5-(pyridyl)-2,4-imidazolidenedione: Synthesis, X-ray structure, electrochemical study and catalytic behaviour for hydrogenation of ketones. *Appl Organometal Chem*. 2017;e3716. doi: 10.1002/aoc.3716