Rhodium assisted C—H activation of N-(2′-hydroxyphenyl)benzaldimines. Synthesis, structure and electrochemical properties of a group of organorhodium complexes

Semanti Basu [a], Swati Dutta [a], Michael G.B. Drew [b], Samaresh Bhattacharya [a,*]

[a] Department of Chemistry, Inorganic Chemistry Section, Jadavpur University, Kolkata 700 032, India
[b] Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK

Abstract

Reaction of a group of N-(2′-hydroxyphenyl)benzaldimines, derived from 2-aminophenol and five para-substituted benzaldehydes (the para substituents are OCH_3, CH_3, H, Cl and NO_2), with $[Rh(PPh_3)_3Cl]$ in refluxing toluene in the presence of a base (NEt_3) afforded a family of organometallic complexes of rhodium(III). The crystal structure of one complex has been determined by X-ray crystallography. In these complexes the benzaldimine ligands are coordinated to the metal center, via dissociation of the phenolic proton and the phenyl proton at the ortho position of the phenyl ring in the imine fragment, as dianionic tridentate C,N,O-donors, and the two PPh_3 ligands are trans. The complexes are diamagnetic (low-spin d^6, $S = 0$) and show intense MLCT transitions in the visible region. Cyclic voltammetry shows a Rh(III)—Rh(IV) oxidation within 0.63–0.93 V vs SCE followed by an oxidation of the coordinated benzaldimine ligand. A reduction of the coordinated benzaldimine is also observed within -0.96 to -1.04 V vs SCE. Potential of the Rh(III)—Rh(IV) oxidation is found to be sensitive to the nature of the para-substituent.
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Keywords: C—H activation; Schiff bases; Organorhodium complexes; Structure; Electrochemical properties

1. Introduction

Utilization of transition metals in promoting useful chemical transformations of organic substrates has been of considerable current interest [1]. Such transformations usually proceed via a C—H activation of the organic substrate [2], leading to the formation of a reactive organometallic intermediate, which then undergoes further reactions to yield the final product. Transition metal mediated C—H activation of organic molecules is therefore of significant importance and the present work has originated from our interest in this area [3]. For the present study, a group of five Schiff base ligands, viz. N-(2′-hydroxyphenyl)benzaldimines (1), derived from para-substituted benzaldehydes

and 2-aminophenol, have been selected as the target molecules for C—H activation and rhodium has been selected as the transition metal for promoting the C—H activation. These ligands have two potential donor sites, the phenolate-oxygen and the imine-nitrogen, and hence are expected to bind to metal ions, via dissociation of the phenolic proton, as bidentate N,O-donors forming five-membered chelate ring (2). In view of the closeness of the pendent phenyl ring to the metal center in 2, C—H activation at the ortho position of the phenyl ring leading to the formation of a cyclometallated species (3) appears to be a possibility. With the intention of inducing the said C—H activation of the N-(2′-hydroxyphenyl)benzaldimines (1), their reaction has been carried out with the Wilkinson's catalyst, viz. $[Rh(PPh_3)_3Cl]$. This particular complex has been picked up as the rhodium starting material for this reaction because of its demonstrated ability to promote C—H

* Corresponding author. Tel.: +91 3324146223; fax: +91 3324146584.
E-mail address: samaresh_b@hotmail.com (S. Bhattacharya).

activation, as well as to accommodate tridentate ligands [3a,4]. Reaction of the *N*-(2'-hydroxyphenyl)benzaldimines (**1**) with [Rh(PPh$_3$)$_3$Cl] has indeed afforded a family of organorhodium complexes, where the benzaldimines are coordinated to the metal center as in **3**. The present report deals with the chemistry of these organorhodium complexes, with special reference to their formation, structure and, spectral and electrochemical properties.

R = OCH$_3$, CH$_3$, H, Cl, NO$_2$
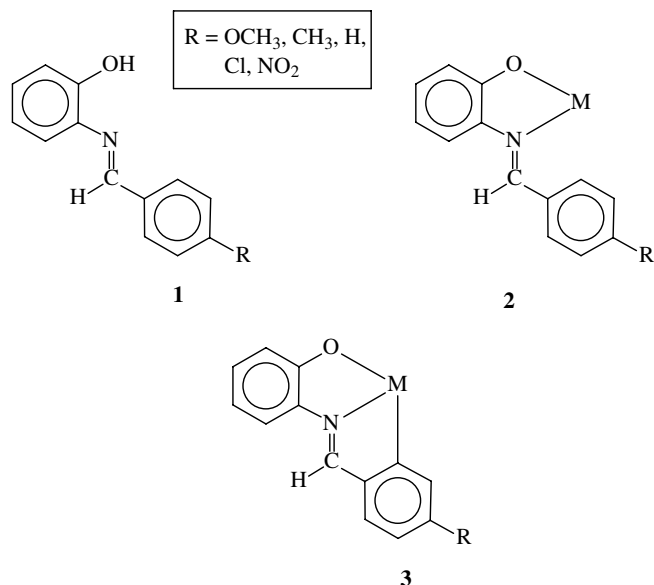
2. Results and discussion

2.1. Synthesis and characterization

Reactions of the *N*-(2'-hydroxyphenyl)benzaldimines (**1**) with [Rh(PPh$_3$)$_3$Cl] proceed smoothly in refluxing toluene in the presence of triethylamine to afford a group of pinkish-orange [5] complexes in decent yields. The preliminary characterization (microanalytical, magnetic susceptibility, IR, ^{1}H NMR) data of these complexes indicate that in each of them one benzaldimine, two triphenylphosphines and a chloride are coordinated to rhodium. To find out the stereochemistry of the complexes as well as to ascertain the coordination mode of the benzaldimines in them, structure of a selected member of this family, viz. that obtained from the reaction with *N*-(2'-hydroxyphenyl)-4-methoxybenzaldimine (**1**, R = OCH$_3$) has been determined by X-ray crystallography. The structure (Fig. 1) shows that the benzaldimine is coordinated to rhodium as a dianionic tridentate C,N,O-donor (**3**). The coordinated chloride shares the same equatorial plane with the tricoordinated benzaldimine ligand and the metal center, while the two PPh$_3$ ligands have taken up the remaining two axial positions and hence they are mutually trans. Rhodium is thus sitting in a CNOP$_2$Cl environment, which is significantly distorted from ideal octahedral geometry, as reflected in the bond parameters around the metal center. The Rh–C, Rh–N,
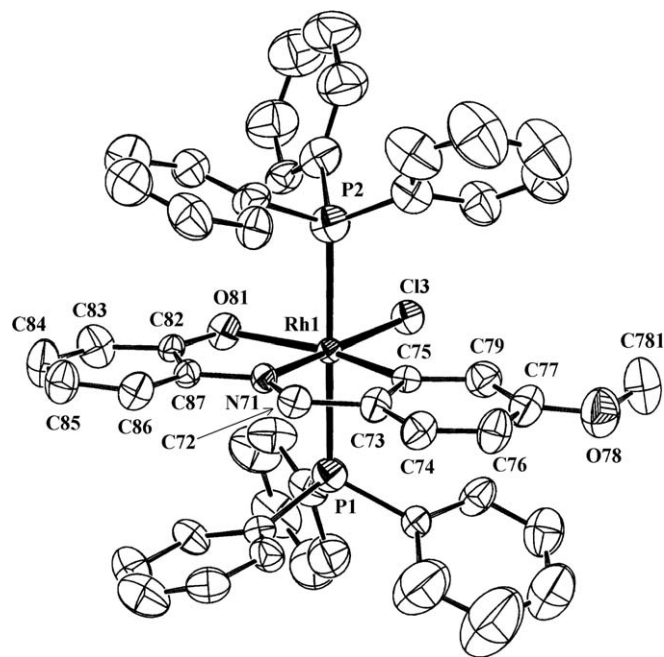

Fig. 1. View of the **4-OCH$_3$** molecule.

Rh–P and Rh–Cl distances (Table 1) are all quite normal [3a,4b] and so are those within the CNO-coordinated benzaldimine. However, the Rh–O bond is notably longer than normal and this elongation may be attributed to the strain developed due to the formation of two adjacent five-membered chelate rings by the benzaldimine. As all the five complexes in this family (**4**) have been prepared similarly and they display similar spectral and electrochemical properties (vide infra), the other four **4-R** (R ≠ OCH$_3$) complexes are assumed to have a similar structure as **4-OCH$_3$**.
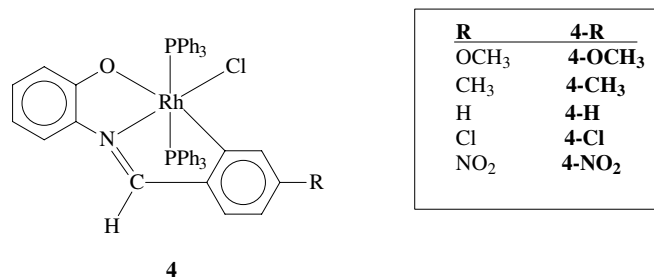

R	4-R
OCH$_3$	**4-OCH$_3$**
CH$_3$	**4-CH$_3$**
H	**4-H**
Cl	**4-Cl**
NO$_2$	**4-NO$_2$**

4

Table 1
Selected bond lengths (Å) and bond angles (°) for complex **4-OCH$_3$**

Bond lengths (Å)			
Rh(1)–C(75)	1.996(9)	C(72)–N(71)	1.345(11)
Rh(1)–N(71)	1.987(7)	C(87)–N(71)	1.413(11)
Rh(1)–O(81)	2.167(7)	C(82)–O(81)	1.329(10)
Rh(1)–P(1)	2.387(4)		
Rh(1)–P(2)	2.378(4)		
Rh(1)–Cl(3)	2.387(4)		
Bond angles (°)			
C(75)–Rh(1)–O(81)	162.5(2)	C(75)–Rh(1)–N(71)	82.0(3)
P(1)–Rh(1)–P(2)	176.24(10)	N(71)–Rh(1)–O(81)	80.6(2)
N(71)–Rh(1)–Cl(3)	179.83(16)		

The absence of any solvent of crystallization in the crystal lattice indicates the possible existence of some non-covalent interaction(s) between the individual complex molecules. A careful inspection of the packing pattern in the lattice reveals that non-covalent interactions of two different types, viz. C—H···Cl and C—H···π interactions, are active in the lattice (Fig. 2). The coordinated chloride in each complex molecule is found to be hydrogen-bonded to two hydrogens, viz. the azomethine hydrogen and one phenyl hydrogen in the phenol fragment of the benzaldimine ligand of an adjacent complex molecule (Fig. 2a). The Cl···H(azomethine) and Cl···H(phenyl) distances are 2.591 Å and 2.823 Å respectively, and the C—H···Cl angles are 164.76° and 168.90° respectively for these two hydrogens. One *meta*-phenyl proton of one coordinated PPh$_3$ ligand in each complex molecule is also found to be hydrogen bonded to the π cloud of the phenyl ring in the phenol fragment of the benzaldimine ligand of a neighboring molecule. However, this hydrogen-bonding interaction is directed to an edge of the phenyl ring in a η^2 fashion (Fig. 2b). The H···C distances from the meta-phenyl hydrogen to the

two carbon atoms constituting the edge are 2.773 Å and 2.792 Å. The observed C—H···Cl and C—H···π interactions have therefore been responsible for holding the crystal lattice together and it may be relevant to note here that both these interactions are of significant importance in molecular recognition processes as well as in crystal engineering [6,7].

The exact mechanism of the observed C—H activation is not completely clear to us. However, the sequences shown in Scheme 1 seem probable. In the initial step the benzaldimine binds, via loss of the phenolic proton, to the metal center in [Rh(PPh$_3$)$_3$Cl] as a bidentate N,O-donor with loss of an electron from the metal center and dissociation of one triphenylphosphine to afford reactive intermediates of type **5**, which then undergo cyclometallation via simultaneous loss of a proton and an electron affording complex **4**. Isolation of the speculated intermediates has not been possible, probably due to their rapid transformation into the corresponding cyclometallated species. It is relevant to note here that cyclometallation of such benzaldimines has precedence in the literature [8].
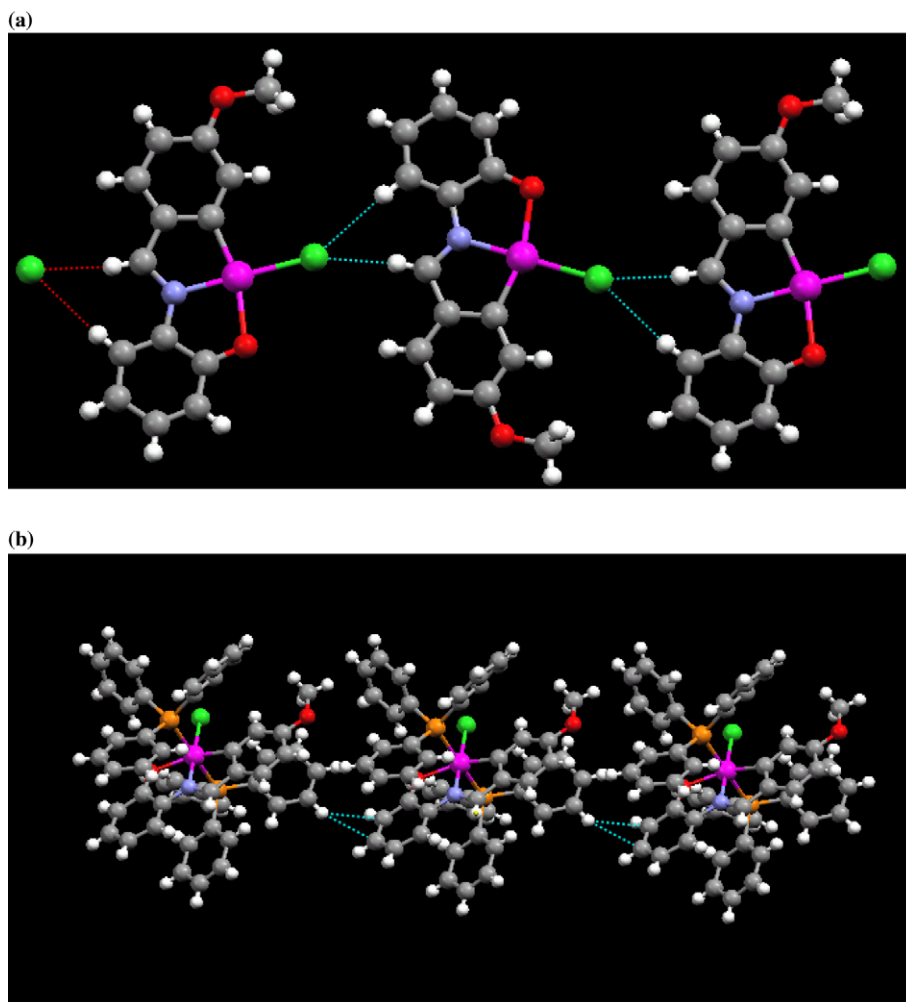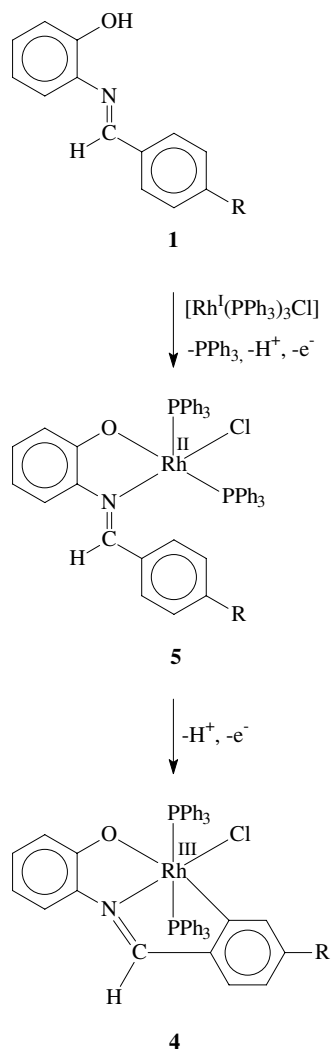

Fig. 2. The hydrogen bonding interactions in the crystal lattice of **4-OCH$_3$**. (a) C—H···Cl and (b) C—H···π interaction.

Scheme 1. Probable steps of the formation of the **4-R** complexes.

2.2. Spectral studies

Infrared spectra of all the complexes show several prominent bands within 4000–500 cm^{-1}. Each complex displays three strong bands near 520, 695 and 745 cm^{-1}, which are due to the coordinated PPh$_3$ ligands. Comparison with the spectrum of [Rh(PPh$_3$)$_3$Cl] shows the presence of many

new bands (viz. near 1590, 1505, 1394, 1334, 1317 and 1262 cm^{-1}) in the spectra of the **4-R** complexes, which are attributable to the coordinated benzaldimine ligand. ^{1}H NMR spectra of the complexes, recorded in CDCl$_3$ solutions, show broad signals within 7.1–7.8 ppm due to the coordinated PPh$_3$ ligands. The azomethine proton signal for the coordinated benzaldimine ligand is observed as a distinct singlet within 6.6–6.8 ppm. Most of the expected aromatic proton signals for the coordinated benzaldimines have been clearly observed, while few signals could not be detected due to their overlap with other signals. In the **4-OCH$_3$** and **4-CH$_3$** complexes signals for the methoxy and methyl hydrogens are observed at 3.46 and 1.92 ppm respectively. The infrared and ^{1}H NMR spectral data of the complexes are therefore consistent with their composition.

Electronic spectra of the complexes have been recorded in acetonitrile solution. Each complex shows several intense absorptions in the visible and ultraviolet region (Table 2). The absorptions in the ultraviolet region are assignable to transitions within the benzaldimine ligand orbitals and those in the visible region are probably due to metal to ligand charge-transfer transition. To have an insight into the nature of the absorptions in the visible region, qualitative EHMO calculations have been performed [9] on computer generated models of all the complexes, where phenyl rings of the triphenylphosphines have been replaced by hydrogens. The results are found to be similar for all the complexes [10]. Compositions of selected molecular orbitals are given in Table 3 and partial MO diagram of a selected complex is shown in Fig. 3. The highest occupied molecular orbital (HOMO) is localized primarily on the metal center and the next two filled orbitals (HOMO-1 and HOMO-2) also have major contribution from the metal. Hence these three filled orbitals may be considered as the rhodium t$_2$ orbitals. The lowest unoccupied molecular orbital (LUMO) is delocalized almost entirely on the benzaldimine ligand and is concentrated mostly on the imine fragment. The LUMO+1 and LUMO+2 are localized on other parts of the benzaldimine ligand. Hence the lowest energy absorption in the visible region may be attributed to the charge-transfer transition from the filled rhodium t$_2$-orbital to the vacant π^*(imine) orbital of the benzaldimine ligands. The other absorptions

Table 2
Electronic spectral and cyclic voltammetric data

Compound	Electronic spectral data λ_{max}, nm (ε, M^{-1} cm^{-1})[a]	Cyclic voltammetric data[b] E, V vs SCE
Complex **4-OCH$_3$**	528(2200), 500(2100)[c], 352(3400)[c], 280(10300),	0.63[d], 0.99[d], −0.98[e]
Complex **4-CH$_3$**	536(1600), 508(1600)[c], 352(2800)[c], 288(8500)	0.67[d], 1.00[d], −0.97[e]
Complex **4-H**	534(1600), 504(1800)[c], 342(2700)[c], 288(8400),	0.71[d], 0.95[d], −1.03[e]
Complex **4-Cl**	536(1700), 510(1800)[c], 352(4400)[c], 294(14900)	0.78[d], 1.10[d], −0.96[e]
Complex **4-NO$_2$**	608(1800), 576(1600), 390(1800)[c], 290(8900)	0.93[d], 1.27[d], −1.04[e]

[a] In acetonitrile.

[b] Solvent, acetonitrile; supporting electrolyte, TBAP; scan rate 50 mV s^{-1}.

[c] Shoulder.

[d] E_{pa} value.

[e] E_{pc} value.

Table 3
Composition of selected molecular orbitals

Compounds	Contributing fragments[a]	% contribution of fragments to					
		HOMO	HOMO-1	HOMO-2	LUMO	LUMO+1	LUMO+2
Complex	Rh	78	40	65	4	–	2
4-OCH₃	CNO—OCH₃	11	55	29	88 (C=N, 48)	98	93
Complex	Rh	76	42	65	4	–	2
4-CH₃	CNO—CH₃	11	54	28	92 (C=N, 47)	96	96
Complex	Rh	77	43	65	4	–	2
4-H	CNO—H	11	52	29	93 (C=N, 46)	96	95
Complex	Rh	78	40	65	4	–	2
4-Cl	CNO—Cl	11	53	29	87 (C=N, 47)	97	95
Complex	Rh	77	44	65	2	2	–
4-NO₂	CNO—NO₂	11	49	29	98 (C=N,15) (NO₂ = 53)	97	98

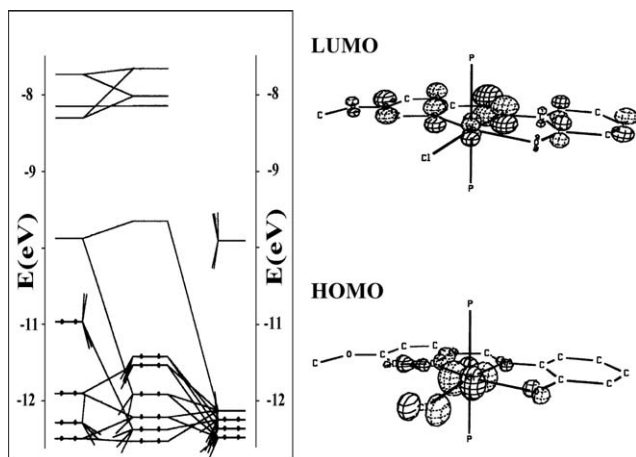[a] The coordinated ligands are referred as CNO—R (R = OCH₃, CH₃, H, Cl, NO₂).

Fig. 3. Partial molecular orbital diagram of **4-OCH₃**.

may be assigned to transitions from the filled metal t_2 orbitals to the higher energy vacant orbitals.

2.3. Electrochemical properties

Electrochemical properties of all the **4-R** complexes have been studied by cyclic voltammetry in acetonitrile solution (0.1 M TBAP). All the complexes show two irreversible oxidative responses on the positive side of SCE and an irreversible reductive response on the negative side (Table 2, Fig. S1). In view of the composition of the HOMO, the first oxidative response is assigned to Rh(III)—Rh(IV) oxidation. Potential of this oxidation is found to be sensitive to the nature of the substituent R in the coordinated benzaldimine ligand. The potential increases with increasing electron-withdrawing character of the substituent R. The plot of oxidation potential vs σ [σ = Hammett constant

of R [11], $OCH_3 = -0.27$, $CH_3 = -0.17$, $H = 0.00$, $Cl = 0.23$ and $NO_2 = 0.78$] is linear (Fig. S2) with slopes (ρ) of 0.28 V (ρ = reaction constant of this couple [12]), which shows that the substituent (R) on the coordinated benzaldimine ligand, which is four-bonds away from the metal center, can still influence the metal-centered oxidation potential in a predictable manner. The second oxidative response is tentatively assigned to oxidation of the coordinated benzaldimine ligand. In view of the nature of the LUMO, the reductive response on the negative side of SCE is also attributed to reduction of the benzaldimine ligand. The ligand-based redox responses do not show any systematic variation with the electronic nature of the substituent.

3. Conclusions

The present study shows that the *N*-(2′-hydroxyphenyl)benzaldimines (**1**) can undergo facile C—H activation at one ortho position of the aryl ring, mediated by [Rh(PPh₃)₃Cl]. This study also indicates that similar C—H activation of organic molecules having structural similarity with the *N*-(2′-hydroxyphenyl)benzaldimines may also be possible upon their reaction with [Rh(PPh₃)₃Cl], and such possibilities are currently under exploration.

4. Experimental

Rhodium trichloride was obtained from Arora Matthey, Kolkata, India. Triphenylphosphine, 2-aminophenol and the *para*-substituted benzaldehydes were obtained from Merck, India. [Rh(PPh₃)₃Cl] was synthesized by following a reported procedure [13]. The *N*-(2′-hydroxyphenyl)-

benzaldimines (**1**) were prepared by reacting equimolar amounts of respective *para*-substituted benzaldehyde and 2-aminophenol in ethanol. Purification of acetonitrile and preparation of tetrabutylammonium perchlorate (TBAP) for electrochemical work were performed as reported in the literature [14]. All other chemicals and solvents were reagent grade commercial materials and were used as received. Microanalyses (C, H, N) were performed using a Heraeus Carlo Erba 1108 elemental analyzer. Magnetic susceptibilities were measured using a PAR 155 vibrating sample magnetometer fitted with a Walker Scientific L75FBAL magnet. ^{1}H NMR spectra were recorded in $CDCl_3$ solution on a Bruker Avance DPX 300 NMR spectrometer using TMS as the internal standard. IR spectra were obtained on a Shimadzu FTIR-8300 spectrometer with samples prepared as KBr pellets. Electronic spectra were recorded on a JASCO V-570 spectrophotometer. Electrochemical measurements were made using a CH Instruments model 600A electrochemical analyzer. A platinum disc working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in the cyclic voltammetry experiments. All electrochemical experiments were performed under a dinitrogen atmosphere. All electrochemical data were collected at 298 K and are uncorrected for junction potentials.

4.1. Synthesis of complexes

The **4-R** complexes were prepared by following a general procedure. Specific details for a particular complex are given below.

4-OCH₃. N-(2′-hydroxyphenyl)-4-methoxybenzaldimine (25 mg, 0.11 mmol) was dissolved in toluene (50 mL) and triethylamine (22 mg, 0.22 mmol) was added to it. The solution was then purged with a stream of dinitrogen for 10 min and to it was added [$Rh(PPh_3)_3Cl$] (100 mg, 0.11 mmol). The mixture was refluxed under a dinitrogen atmosphere for 20 h, whereby a reddish-orange solution was obtained. Evaporation of this solution afforded a dark red solid, which was subjected to purification by thin layer chromatography on a silica plate. With 1:40 acetonitrile-benzene as the eluant, a distinct pinkish-orange band separated, which was extracted with 1:3 dichloromethane-acetonitrile. Evaporation of this extract gave **4-OCH₃** as a crystalline pinkish-orange solid. Yield: 70%. Anal. Calc.: C, 67.61; H, 4.62; N, 1.58. Found: C, 67.20; H, 4.67; N, 1.61. ^{1}H NMR [15]: 3.46 (OCH_3); 5.73–5.74 (2H)*; 6.26 (d, H, J = 8.23); 6.34 (d, H, J = 8.33); 6.52–6.65 (t, H); 6.66 (t, H, J = 2.06); 6.69 (s, 1H); 6.83 (d, H, J = 8.32); 7.09–7.63 (2PPh₃).

4-CH₃. Yield: 70%. Anal. Calc.: C, 68.85; H, 4.71; N, 1.61. Found: C, 68.33; H, 4.75; N, 1.64. ^{1}H NMR: 1.92 (CH_3); 5.73–5.74 (2H);*6.36 (d, H, J = 8.43); 6.50 (d, H, J = 7.41); 6.53–6.73 (t, 2H);*6.77 (d, H, J = 7.65); 7.01 (s, H); 7.05–7.61 (2PPh₃).

4-H. Yield: 67%. Anal. Calc.: C, 68.58; H, 4.55; N, 1.63. Found: C, 68.00; H, 4.59; N, 1.65. ^{1}H NMR: 7.23 (s, H);

Table 4
Selected crystallographic data for complex **4-OCH₃**

Empirical formula	$C_{50}H_{41}NO_2P_2ClRh$
F_w	888.14
Space group	Monoclinic, $P2_1/n$
Unit cell dimensions	
a (Å)	12.166(14)
b (Å)	17.078(18)
c (Å)	20.82(2)
β (°)	93.688(10)
V (Å³)	4317(8)
Z	4
λ (Å)	0.71073
Crystal size (mm)	$0.05 \times 0.05 \times 0.30$
T (K)	293
μ (mm^{-1})	0.572
$R_1{}^a$	0.0970
$WR_2{}^b$	0.1642
Goodness-of fit^c	1.12

^{a} $R1 = \sum \|F_o| - | F_c\|/\sum | F_o|$.
^{b} $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/ \sum[w(F_o^2)^2]]^{1/2}$.
^{c} $GOF = [\sum[w(F_o^2 - F_c^2)^2]/(M - N)]^{1/2}$, where M is the number of reflections and N is the number of parameters refined.

7.10–7.60 (2PPh₃); 5.74 (d, 2H, J = 3.76); 6.33 (d, H, J = 8.50); 6.66–6.69 (t, H); 6.81 (s, H); 6.90 (d, H, J = 8.24); 7.64–7.75 (t, H).

4-Cl. Yield: 68%. Anal. Calc.: C, 65.93; H, 4.26; N, 1.57. Found: C, 65.25; H, 4.30; N, 1.60. ^{1}H NMR: 5.53 (d, H); 6.76–6.91 (t, 3H)*; 7.05 (s, 1H); 7.14–7.57 (2PPh₃); 7.62–7.73 (t, 2H)*.

4-NO₂. Yield: 72%. Anal. Calc.: C, 65.16; H, 4.21; N, 3.10. Found: C, 65.09; H, 4.22; N, 3.11. ^{1}H NMR: 5.74 (d, 2H, J = 3.76); 6.33 (d, H, J = 8.50); 6.66–6.69 (t, H)*; 6.81 (s, H); 6.90 (d, H, J = 8.24); 7.10–7.64 (2PPh₃); 7.64–7.75 (t, H); 8.10 (s, 1H).

4.2. X-ray structure determination

Single crystals of the **4-OCH₃** complex were obtained by slow evaporation of a 1:3 dichloromethane-acetonitrile solution of the complex. Selected crystal data and data collection parameters are given in Table 4. Data were collected on a Marresearch Image Plate system using graphite monochromated Mo Kα radiation. X-ray data reduction and, structure solution and refinement were done using SHELXS-97 and SHELXL-97 programs [16]. The structure was solved by the direct methods.

Acknowledgements

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Appendix A. Supplementary data

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number 279097. Copy of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax. (int code): +44(1223)336 033] or email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk. One representative voltammogram (Fig. S1) and least-squares plots of E_{pa} values of Rh(III)-Rh(IV) couple vs σ for the **4-R** complexes (Fig. S2).

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