Rhodium and iridium complexes of N-(2′-hydroxyphenyl)pyrrole-2-aldimine: Synthesis, structure, and spectral and electrochemical properties

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Abstract. Reaction of N-(2′-hydroxyphenyl)pyrrole-2-aldimine (H_2L) with [M(PPh$_3$)$_3$Cl] (M = Rh, Ir) affords complexes of type [M(PPh$_3$)$_2$(L)Cl]. Structures of both complexes have been determined by X-ray crystallography. In both complexes, the N-(2′-hydroxyphenyl)pyrrole-2-aldimine ligand is coordinated to the metal centre, via dissociation of the acidic protons, as a dianionic tridentate N,N,O-donor. The M(L)Cl fragment constitutes an equatorial plane with the metal at the centre and the two PPh$_3$ ligands occupying axial positions. The complexes are diamagnetic (low-spin d^6, $S = 0$) and show intense MLCT transitions in the visible region. Cyclic voltammetry of the [M(PPh$_3$)$_2$(L)Cl] complexes shows reversible M(III)–M(IV) oxidation near 0·5 V vs SCE and quasi-reversible ligand-centred oxidative response near 1·0 V vs SCE.

Keywords. N-(2′-hydroxyphenyl)pyrrole-2-aldimine; rhodium and iridium complexes; crystal structure; spectral and electrochemical properties.

1. Introduction

The chemistry of rhodium and iridium has been receiving considerable current attention,[1] largely because of the interesting chemical properties exhibited by the complexes of these two metals. Though neither of these two metals is a bioessential element, their compounds have useful applications in the biological field.[2] For the present study, which has originated from our interest in the properties of rhodium and iridium in different coordination environments,[3] we have chosen N-(2′-hydroxyphenyl)pyrrole-2-aldimine (**1**) as the principal ligand. This Schiff base ligand is abbreviated as H_2L, where H_2 stands for the two potentially dissociable protons, viz. the O–H proton and the N–H proton. Ligand **1** is known to bind to metal ions, via dissociation of the acidic protons, as a dianionic tridentate N,N,O-donor forming two stable five-membered chelate rings (**2**).[4] It may be relevant to note here that some transition metal complexes of this Schiff-base ligand, as well as its two components (viz. pyrrole-2-aldehyde and 2-aminophenol), have applications in the biological field.[5–7] It may also be

mentioned here that though the chemistry of several metal complexes of ligand **1** has received some attention,[4,5,8] that with rhodium and iridium appears to have remained unexplored. The [Rh(PPh$_3$)$_3$Cl] and [Ir(PPh$_3$)$_3$Cl] complexes have been used respectively as sources of rhodium and iridium. These two complexes have been observed to serve as efficient starting materials for the syntheses of some interesting mixed-ligand complexes.[3a–g] In particular, they have demonstrated their ability to accommodate tridentate ligands via dissociation of one PPh$_3$,[3b,d–g] which is a necessary prerequisite for coordination of ligand **1** in tridentate fashion (**2**). The main objective of the present work has been to synthesize mixed-ligand complexes of rhodium and iridium, incorporating one N-(2′-hydroxyphenyl)pyrrole-2-aldimine ligand,
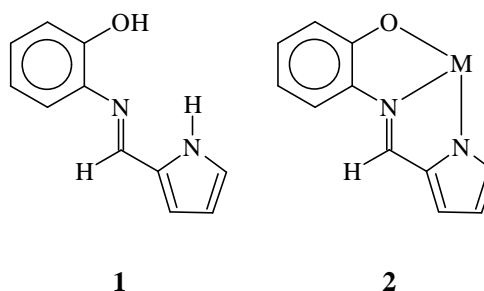
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and to study their physicochemical properties. Reaction of ligand **1** with the [M(PPh$_3$)$_3$Cl] (M = Rh, Ir) complexes has been found to afford complexes of the type [M(PPh$_3$)$_2$(L)Cl]. The chemistry of these two complexes is reported in this paper with special reference to their synthesis, structure, and spectroscopic and electrochemical properties.

2. Experimental section

2.1 *Materials*

Trichlorides of rhodium and iridium were obtained from Arora Matthey, Kolkata. Triphenylphosphine, pyrrole-2-aldehyde and 2-aminophenol were purchased from E Merck, India. The [M(PPh$_3$)$_3$Cl] (M = Rh and Ir) complexes were prepared by following reported procedures.[9] N-(2′-hydroxyphenyl)pyrrole-2-aldimine ligand was prepared by condensation of pyrrole-2-aldehyde and 2-aminophenol in hot ethanol. All other chemicals and solvents were reagent-grade commercial materials and were used as received. Purification of acetonitrile and preparation of tetrabutylammonium perchlorate (TBAP) for electrochemical work were carried out as reported in the literature.[10]

2.2 *Synthesis of [Rh(PPh$_3$)$_2$(L)Cl]*

N-(2′-hydroxyphenyl)pyrrole-2-aldimine (20 mg, 0·11 mmol) was taken in toluene (40 ml) and triethylamine (22 mg, 0·22 mmol) was added to it. The solution was purged with a stream of nitrogen for 5 min. Then [Rh(PPh$_3$)$_3$Cl] (100 mg, 0·11 mmol) was added and the mixture was heated at reflux under nitrogen atmosphere for 7 h to yield a maroon solution. Evaporation of this solution gave a dark coloured solid, which was subjected to purification by thin layer chromatography on a silica plate. With benzene as the eluant, an orange band separated, which was extracted with acetonitrile. Evaporation of the acetonitrile extract gave [Rh(PPh$_3$)$_2$(L)Cl] as a crystalline orange solid. Yield: 76%.

Analysis: Calc. for C$_{47}$H$_{38}$N$_2$OP$_2$ClRh: C, 66·59; H, 4·49; N, 3·31%. Found: C, 66·13; H, 4·41; N, 3·28%.

2.3 *Synthesis of [Ir(PPh$_3$)$_2$(L)Cl]*

This complex was prepared by following the same procedure as above, using [Ir(PPh$_3$)$_3$Cl] instead of

[Rh(PPh$_3$)$_3$Cl] and with a reflux time of 12 h instead of 7 h. Yield: 72%.

Analysis: Calc. for C$_{47}$H$_{38}$N$_2$OP$_2$ClIr: C, 60·23; H, 4·06; N, 2·99%. Found: C, 60·09; H, 4·00; N, 2·97%.

2.4 *Physical measurements*

Microanalyses (C, H, N) were done using a Heraeus Carlo Erba 1108 elemental analyser. Magnetic susceptibilities were measured using a PAR 155 vibrating sample magnetometer fitted with a Walker Scientific L75FBAL magnet. ^{1}H NMR spectra in CDCl$_3$ solutions were obtained on a Bruker Avance 300 NMR spectrometer using TMS as the internal standard. IR spectra were obtained on a Perkin–Elmer 783 spectrometer with samples prepared as KBr pellets. Electronic spectra were recorded on a Jasco V-570 spectrophotometer. Cyclic voltammetric measurements were made with a CH Instruments model 600A electrochemical analyser, using a platinum disc working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE). All cyclic voltammetric experiments were performed under a dinitrogen atmosphere in 1 : 9 dichloromethane–acetonitrile solution (0·1 M TBAP). Cyclic voltammetric data were collected at 298 K and are uncorrected for junction potentials.

2.5 *X-ray crystallographic analysis for complexes [Rh(PPh$_3$)$_2$(L)Cl] and [Ir(PPh$_3$)$_2$(L)Cl]*

Single crystals of both [Rh(PPh$_3$)$_2$(L)Cl] and [Ir(PPh$_3$)$_2$(L)Cl] were obtained by slow evaporation of solutions of the complexes in acetonitrile. Selected crystal data and data collection parameters are given in table 1. Data were collected on a Bruker CCD diffractometer using graphite monochromated Mo-K$_a$ radiation by f and w scans. X-ray data reduction, and structure solution and refinement were done using SHELXS-97 and SHELXL-97 programs.[11] Structures were solved by direct methods. Both the structures were found to have disorder problem.

3. Results and discussion

3.1 *Synthesis and structure*

Reaction of N-(2′-hydroxyphenyl)pyrrole-2-aldimine (**1**, H$_2$L) with [Rh(PPh$_3$)$_3$Cl] proceeds smoothly in

Table 1. Summary of structure determination of [Rh(PPh$_3$)$_2$(L)Cl] and [Ir(PPh$_3$)$_2$(L)Cl].

Formula	C$_{47}$H$_{38}$N$_2$OP$_2$ClRh	C$_{47}$H$_{38}$N$_2$OP$_2$ClIr
Formula weight	847·2	936·38
Crystal system	Monoclinic	Monoclinic
Space group	*C2/c*	*C2/c*
Z	4	4
a (Å)	23·598(5)	23·659(2)
b (Å)	8·756(5)	8·8202(7)
c (Å)	20·712(5)	20·7055(17)
b (°)	115·963(5)	115·920(1)
V (Å^3)	3848(3)	3886·1(6)
m (mm^{-1})	0·634	3·627
Crystal size (mm^3)	0·28 × 0·16 × 0·06	0·45 × 0·35 × 0·08
T (K)	100(2)	293(2)
D$_{calc}$ (g/cm^3)	1·46	1·60
l (Å)	0·71069	0·71073
2*q* range	1·92–30·42°	1·91–28·29°
hkl collected	–33 ≤ h ≤ 32;	–30 ≤ h ≤ 31;
	–12 ≤ k ≤ 11;	–11 ≤ k ≤ 11;
	–28 ≤ l ≤ 28	–25 ≤ l ≤ 27
No. of reflections measured	57244	14458
No. of unique reflections	5336 (*R*$_{int}$ = 0·0357)	4741 (*R*$_{int}$ = 0·0416)
R indices[a,b] (F > 4*s*(F))	R_1 = 0·0992	R_1 = 0·0402
	wR_2 = 0·2937	wR_2 = 0·0845
R indices[a,b] (all data)	R_1 = 0·1174	R_1 = 0·0528
	wR_2 = 0·3080	wR_2 = 0·0887
GOF[c]	1·065	1·101

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma\{w(F_o^2-F_c^2)^2\}/\Sigma\{w(F_o^2)\}]^{1/2}$. [c] $GOF = [\Sigma(w(F_o^2-F_c^2)^2)/(M-N)]^{1/2}$, where M is the number of reflections and N is the number of parameters refined
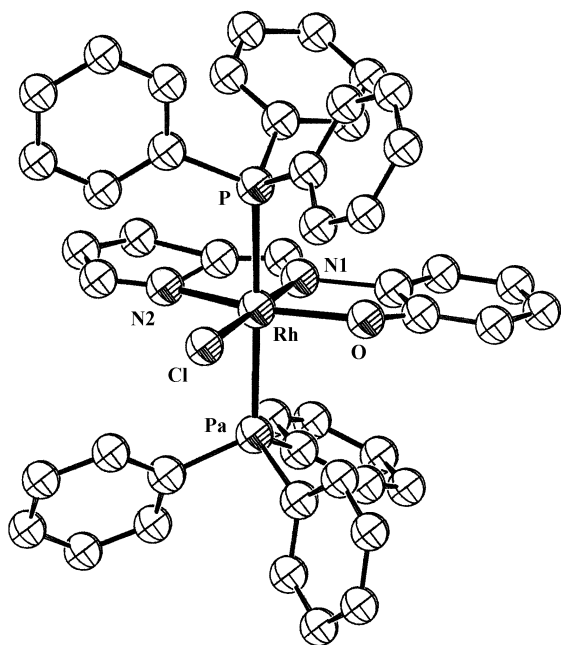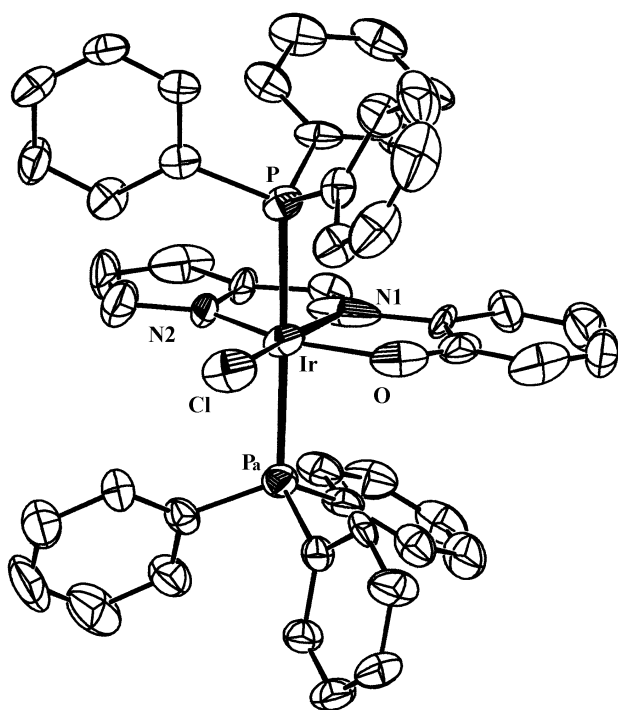

Figure 1. View of the [Rh(PPh$_3$)$_2$(L)Cl] complex.

refluxing toluene in the presence of triethylamine to afford a mixed-ligand complex of rhodium(III), viz. [Rh(PPh$_3$)$_2$(L)Cl], in decent yield. The analogous iridium complex, [Ir(PPh$_3$)$_2$(L)Cl], has been obtained by similar reaction of ligand **1** with [Ir(PPh$_3$)$_3$Cl]. The observed elemental (C, H, N) analytical data of the two complexes are consistent with their compositions. For unambiguous characterization of these complexes, with reference to their stereochemistry and the coordination mode of ligand **1**, structures of both the complexes have been determined by X-ray crystallography. These are shown in figures 1 and 2, and some selected bond parameters are listed in table 2. Both structures are very similar. In each complex the ligand **1** is coordinated to the metal centre, via dissociation of both the pyrrole N–H and phenolic O–H protons, as a dianionic tridentate N,N,O-donor (**2**). Two triphenylphosphines and a chloride are also coordinated to the metal centre in both the complexes. The central metal ion is thus nested in a N$_2$OP$_2$Cl coordination sphere, which is distorted from ideal octahedral geometry, as reflected in all the bond parameters around the metal centres. The coordinated N,N,O-donor ligand (L) and chloride constitute one equatorial plane with the metal at the centre, and the two triphenylphosphines take up the remaining two axial positions, and hence they are mutually *trans*. The bond distances around the metal centre are all quite normal.[3]

Table 2. Selected bond lengths (Å) and angles (°) for [Rh(PPh$_3$)$_2$(L)Cl] and [Ir(PPh$_3$)$_2$(L)Cl].

[Rh(PPh$_3$)$_2$(L)Cl]		[Ir(PPh$_3$)$_2$(L)Cl]	
Bond lengths (Å)			
Rh–N1	1·950(9)	Ir–N1	1·972(6)
Rh–N2	2·064(9)	Ir–N2	1·985(6)
Rh–O	2·064(9)	Ir–O	2·191(11)
Rh–P	2·3726(15)	Ir–P	2·3673(11)
Rh–Pa	2·3726(15)	Ir–Pa	2·3673(11)
Rh–Cl	2·371(3)	Ir–Cl	2·4163(19)
Bond angles (°)			
N1–Rh–Cl	180·0(3)	N1–Ir–Cl	171·13(8)
N2–Rh–O	158·2(7)	N2–Ir–O	161·0(3)
P–Rh–Pa	175·83(7)	P–Ir–Pa	175·84(5)

Figure 2. View of the [Ir(PPh$_3$)$_2$(L)Cl] complex.

3.2 ^{1}H NMR spectra

Magnetic susceptibility measurements show that the [M(PPh$_3$)$_2$(L)Cl] (M = Rh and Ir) complexes are diamagnetic, which corresponds to the +3 state of rhodium and iridium (low-spin d^6, $S = 0$) in these complexes. ^{1}H NMR spectra of both the complexes have been recorded in CDCl$_3$ solution. Each complex shows broad signals within 7·03–7·60 ppm due to the coordinated PPh$_3$ ligands. The azomethine proton signal for the coordinated N,N,O-donor ligand (L) is observed at 5·82 and 5·73 ppm in the rhodium and iridium complexes respectively. Most of the expected aromatic proton signals for the coordinated L ligand have been observed within 5·5–6·6 ppm, while a few signals could not be detected due to their overlap with the broad signals of the PPh$_3$ ligands.

3.3 IR spectra

Infrared spectra of both the [M(PPh$_3$)$_2$(L)Cl] complexes are very similar. Each complex shows several sharp bands of different intensities in the 1700–400 cm^{-1} region. Assignment of each individual band to a specific vibration has not been attempted. N–H and O–H stretching frequencies, observed within 3300–3400 cm^{-1} in the uncoordinated N-(2′-hydroxyphenyl)pyrrole-2-aldimine ligand (**1**), are absent in the spectra of both the complexes. Three strong bands near 518, 696 and 743 cm^{-1} are observed in both the complexes, which are attributable to the coordinated PPh$_3$ ligands.[3] A few sharp bands are also displayed by both complexes near 1460, 1387, 1298 and 1035 cm^{-1}, which are absent in the spectra of the corresponding [M(PPh$_3$)$_3$Cl] complexes, and hence these are attributable to the coordinated N,N,O-donor ligand (L).

3.4 Electronic absorption spectra

[M(PPh$_3$)$_2$(L)Cl] complexes are soluble in dichloromethane, chloroform, acetone, acetonitrile, etc. producing orange solutions. Electronic spectra of these complexes have been recorded in dichloromethane solution. Each complex shows several intense absorptions in the visible and ultraviolet regions.

Table 3. Electronic spectral and cyclic voltammetric data.

Compound	Electronic spectral data[a] l_{max} (nm) (e/M^{-1} cm^{-1})	Cyclic voltammetric data[b] $E_{1/2}$/V (ΔEp/mV)
[Rh(PPh$_3$)$_2$(L)Cl]	512 (7300), 482 (8600), 450[c] (6100), 338 (14300), 290 (23200)	0.49(60) 1.14(60)
[Ir(PPh$_3$)$_2$(L)Cl]	526 (9100), 494 (8800), 464[c] (5200), 396 (5600), 360 (8000), 286 (17100), 254 (33600)	0.46(60) 1.07(60)

[a]In dichloromethane solution. [b]Solvent, 1 : 9 dichloromethane–acetonitrile; supporting electrolyte, TBAP; scan rate 50 mVs^{-1}. [c]Shoulder

Table 4. Composition of molecular orbitals.

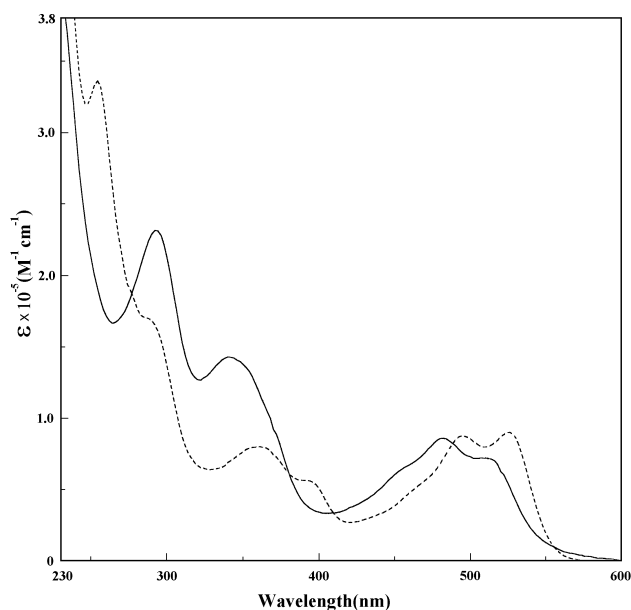| Compound	Contributing fragments	% Contribution of fragments to				
		HOMO	HOMO-1	HOMO-2	LUMO	LUMO + 1
[Rh(PPh$_3$)$_2$(L)Cl]	Rh	77	38	66	6	0
	L	10	56	28	93	94
[Ir(PPh$_3$)$_2$(L)Cl]	Ir	83	41	73	6	0
	L	4	52	24	93	96

Figure 3. Electronic spectra of the [Rh(PPh$_3$)$_2$(L)Cl] complex (———) and the [Ir(PPh$_3$)$_2$(L)Cl] complex (------) in dichloromethane solution.

Spectral data are given in table 3 and the spectra are shown in figure 3. Absorptions in the ultraviolet region are assignable to transitions within the ligand orbitals and those in the visible region are probably due to metal-to-ligand charge-transfer transitions. To give some insight into the nature of the absorptions in the visible region, qualitative EHMO calculations have been performed[12] on computer-generated models of both the complexes, where the phenyl rings of the triphenylphosphines have been replaced by hydrogens. The results are similar for both the complexes. Compositions of selected molecular orbitals are given in table 4. A partial MO diagram for the [Rh(PPh$_3$)$_2$(L)Cl] complex is shown in figure 4. The highest occupied molecular orbital (HOMO) and the next two filled orbitals (HOMO-1 and HOMO-2) have major contributions from the metal d_{xy}, d_{yz} and d_{zx} orbitals. However, HOMO-1 has slightly less metal character compared to HOMO and HOMO-2. These three occupied orbitals may therefore be regarded as the metal t_2 orbitals. The lowest unoccupied molecular orbital (LUMO) is localized almost entirely on the N,N,O-donor ligand (L) and is concentrated largely on the imine (C=N) fragment. LUMO + 1 is localized mostly on the phenyl ring of the L ligand. The lowest energy absorption in the visible region is therefore assignable to an allowed transition from the filled metal t_2-orbital (HOMO) to the vacant p^*(imine)-orbital of the L ligand (LUMO). The other absorptions in the visible region may be assigned to similar charge-transfer transitions from the filled metal t_2-orbitals to the vacant ligand (L) p^*-orbitals.

3.5 *Cyclic voltammetric study*

Electrochemical properties of both the complexes have been studied by cyclic voltammetry. The volt-
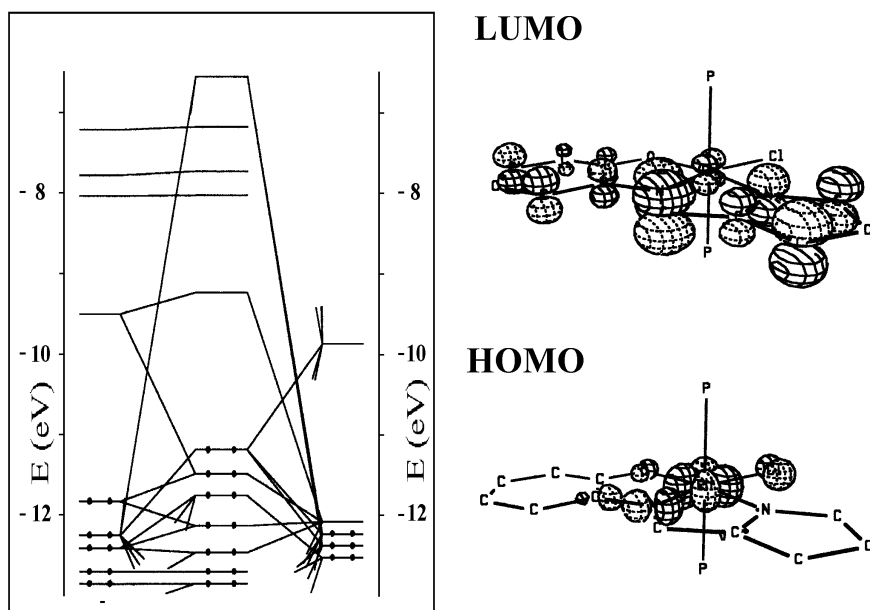
LUMO

HOMO

Figure 4. Partial molecular orbital diagram of the [Rh(PPh$_3$)$_2$(L)Cl] complex.

ammetric data are given in table 3. Both the complexes show two oxidative responses on the positive side of SCE. The first oxidative response is assigned to M(III)–M(IV) oxidation. This oxidation is reversible, characterized by a peak-to-peak separation (ΔE_p) of 60 mV and the anodic peak-current (i_{pa}) is equal to the cathodic peak-current (i_{pc}), as expected for a reversible electron-transfer process. The second oxidative response is quasi-reversible ($\Delta E_p = 60$ mV, but $i_{pa} \neq i_{pc}$) and is tentatively assigned to oxidation of the coordinated L ligand. One-electron stoichiometry of both the responses has been established by comparing their current heights with those of standard ferrocene/ferrocenium couple under identical experimental conditions.

4. Conclusions

The present study shows that coordination by N-(2′-hydroxyphenyl)pyrrole-2-aldimine (H$_2$L, **1**) in the tridentate N,N,O-fashion (**2**) can stabilize the higher oxidation states of a transition metal, which is manifested in the stabilization of the trivalent state of rhodium and iridium in the [M(PPh$_3$)$_2$(L)Cl] (M = Rh and Ir) complexes. Attempts to stabilize the higher oxidation states of other heavier transition metals by binding them to ligand **1** in the same tridentate fashion (**2**) are currently in progress.

5. Supplementary material

Crystallographic data for the [Rh(PPh$_3$)$_2$(L)Cl] and [Ir(PPh$_3$)$_2$(L)Cl] complexes in the CIF format have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 255056 for the [Rh(PPh$_3$)$_2$(L)Cl] complex and 255057 for the [Ir(PPh$_3$)$_2$(L)Cl] complex.

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