

Syntheses, characterization, structure and redox properties of new Rh(III) cyclometallates incorporating azoimine ligands

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Abstract

The reaction of 2-(aryloxo) aniline, **1** (HL-NH₂) [where HL-NH₂ is 2-(ArN=N)C₆H₄-NH₂; Ar = C₆H₅ (for HL¹-NH₂), *p*-MeC₆H₄ (for HL²-NH₂) and *p*-ClC₆H₄ (for HL³-NH₂). H of HL stands for dissociable proton of Ar due to orthometallation], with Rh(PPh₃)₃Cl (Wilkinson's catalyst) furnished the cyclometallated azoimine complexes of composition (L-NH)Rh(PPh₃)₂Cl (**2**). All the complexes were characterized by spectroscopic technique and confirmed by X-ray structure determination of (L³-NH)-Rh(PPh₃)₂Cl as a representative one. The azoimine chelate ring size of **2** is five membered where the phenyl ring adjacent to the chelate ring is distorted with four longer and two shorter bonds. This structural feature has been attributed to the delocalization of negative charge of the anionic ligands that formed in situ from the precursor (HL-NH₂) due to dissociation of an amino proton. The (L-NH)Rh(PPh₃)₂Cl complexes display an one electron oxidative response in the range of 0.331 to 0.436 V vs. SCE.

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Keywords: Cyclometallation; 2-(Aryloxo) aniline; Wilkinson's catalyst; Rh(III); Redox

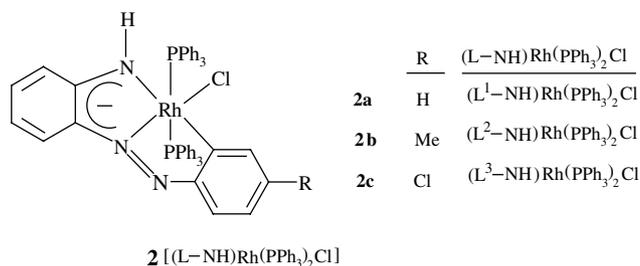
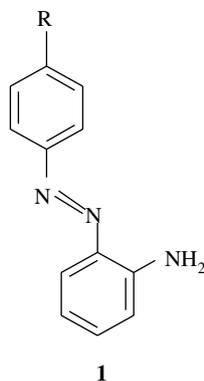
1. Introduction

Metal assisted C–H bond activation is of much interest in current chemical research. Metal–carbon bond formation reactions of transition metals are important in terms of C–H bond activation [1–3]. The metal mediated catalytic and stoichiometric organic transformations often involve transient organometallic species in the intermediate steps [4,5]. Orthometallation is one of the important routes to the synthesis of metal–carbon bond cleaving the C–H bond. Although chemistry of cyclometallated molecules is well developed, substantial literature lacks examples of cyclometallated complexes of Rh(III) incorporating azo ligands. We adopted the

strategy of oxidative addition of polydentate azo ligand into the tri-coordinated species Rh^I(PPh₃)₂Cl which is obtainable upon dissociation of a PPh₃ ligand of Wilkinson's catalyst Rh^I(PPh₃)₃Cl in solution [6]. Recently, it has been demonstrated that pre-coordination of sp² nitrogen donor leads the metal to undergo orthometallation at pendent phenyl ring [7] and thus azobenzene is an appropriate choice. A third anionic donor within the azobenzene moiety is prerequisite, apart from (N,C) coordination (of azobenzene), to satisfy the hexacoordination and residual positive charge of Rh(III) after oxidative addition. The 2-(aryloxo) aniline, **1**, ligands furnished azoimine (N, N) chelates of Pd(II), Pt(II), and Au(III) in its anionic form (HL-NH)[−], dissociating an amino proton [8–10]. Therefore, we planned to carry out reaction of Wilkinson's catalyst with **1**, which indeed, turn out to be successful since we could isolate the cyclometallated products of Rh(III) of the type **2**.

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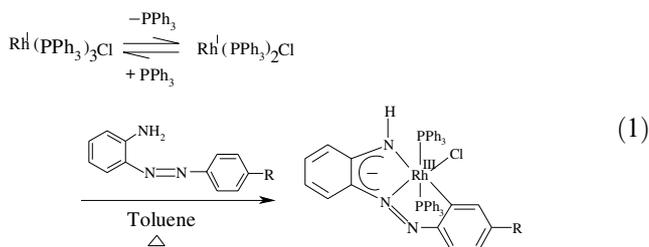


Herein, we describe the reaction of 2-(arylamino) aniline with Rh(PPh₃)₃Cl and formation of cyclometallated azoiminato chelates of Rh(III). The complex formations have been authenticated on the basis of X-ray structural data and ¹H NMR studies. The redox properties of the new Rh(III) cyclometallates have been studied electrochemically.

2. Results and discussion

2.1. Complex formation

The reaction of Rh(PPh₃)₃Cl with 2-(arylamino) aniline (HL-NH₂) in refluxing toluene in dinitrogen atmosphere afforded green complexes of composition [(L-NH)Rh(PPh₃)₂Cl] (**2**). These are a new family of orthometallated azoiminato (C, N, N) complexes of Rh(III) incorporating the dianionic (L-NH)²⁻ that formed in situ from the ligand precursor 2-(arylamino) aniline (HL-NH₂). It is believed that the reactions of Rh(PPh₃)₃Cl and (HL-NH₂) ligands proceeds according to Eq. (1), i.e., initial dissociation of PPh₃ from Rh(PPh₃)₃Cl followed by the oxidative addition of (L-NH)²⁻.



The diamagnetic (L-NH)Rh(PPh₃)₂Cl complexes were characterized on the basis of analytical (C, H, N) and spectral data and the structure was confirmed by X-ray structure determination of **2c** (see below).

2.2. Crystal and molecular structure of (L³-NH)Rh(PPh₃)₂Cl

Suitable crystals of (L³-NH)Rh(PPh₃)₂Cl were grown by slow diffusion of hexane into a dichloromethane solution. A perspective view of the molecule has been shown in Fig. 1 and selected bond distances and angles are collected in Table 1. The Rh(CNN)(P)₂Cl coordination sphere has distorted octahedral geometry. The dianionic (L³-NH)²⁻ ligand coordinates the Rh(III) in a tridentate (C, N, N) fashion along with two mutually *trans* PPh₃ and a chloride ligand. There is a CH₂Cl₂ solvent molecule per asymmetric unit in the crystal lattice. The Rh-C, Rh-Cl and Rh-P bond lengths of **2c** are within the normal range [6]. Rh-N(3) length is shorter than Rh-N(1) because of stronger dπ-pπ back bonding with the azo nitrogen, while the stronger *trans* influence of aryl carbon may be attributed to the longer Rh-N(1) distance [11]. Only one hydrogen [H(**4a**)] atom on N(1) could be located from difference Fourier mapping, signifying dissociation of the other amino proton consistent with the ¹H NMR data (see below). The C(12)-N(1) bond (1.336 Å) is shorter than C(6)-N(2) single bond (1.399 Å) in the same molecule and similar to an imine (>C=N-) length as a result of delocalization [8–10]. The rhodium center is closer to azo nitrogen N(3) (1.969 (1) Å) and the N(2)-N(3) distance (1.2875 (14) Å) is longer than the azo (-N=N-) distance (~1.25 Å) in free azo molecules [12].

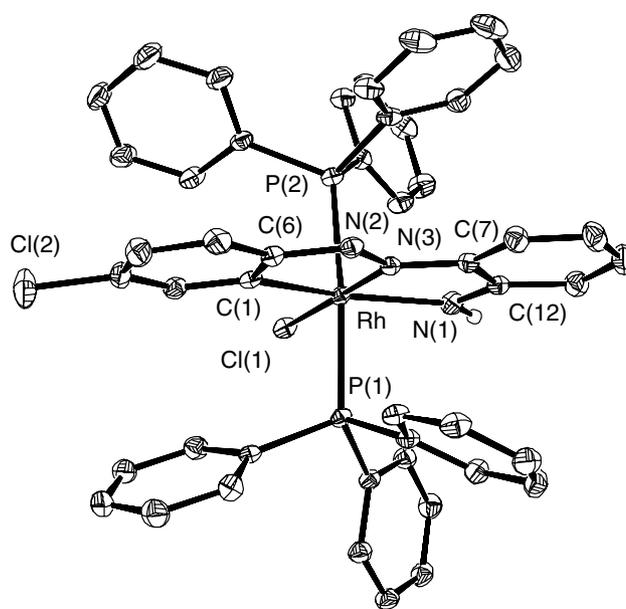


Fig. 1. ORTEP plot of **2c** with atom-numbering scheme. Hydrogen atoms, except that on N1, are omitted for clarity.

Table 1
Selected bond distances (Å) and angles (°) for **2c**

Distances (Å)	
Rh–N(1)	2.1489(14)
Rh–N(3)	1.9695(13)
Rh–Cl(1)	2.4029(4)
Rh–P(1)	2.3583(4)
Rh–P(2)	2.3709(4)
Rh–C(1)	2.0307(16)
N(2)–N(3)	1.2875(19)
N(1)–C(12)	1.337(2)
N(2)–C(6)	1.399(2)
N(3)–C(7)	1.383(2)
C(7)–C(12)	1.426(2)
C(7)–C(8)	1.410(2)
C(9)–C(10)	1.412(3)
C(10)–C(11)	1.368(3)
C(11)–C(12)	1.428(3)
C(8)–C(9)	1.362(3)
Angles (°)	
Cl(1)–Rh–P(1)	88.41(1)
Cl(1)–Rh–P(2)	89.76(1)
Cl(1)–Rh–N(3)	179.52(4)
Cl(1)–Rh–N(1)	100.90(4)
Cl(1)–Rh–C(1)	100.41(5)
P(1)–Rh–P(2)	176.04(1)
P(1)–Rh–N(3)	91.96(4)
P(1)–Rh–C(1)	88.93(5)
P(2)–Rh–N(3)	89.85(4)
P(2)–Rh–N(1)	93.73(4)
P(2)–Rh–C(1)	87.95(5)
N(3)–Rh–N(1)	79.40(5)
N(3)–Rh–C(1)	79.30(6)
C(1)–Rh–C(2)	133.36(12)
C(2)–C(1)–C(6)	117.54(15)

These observations are in support of backbone conjugation within the coordinated ligand [12]. The quinonoid distortion in the phenyl ring (C7, C8, C9, C10, C11, C12) adjacent to the five membered chelate with two shorter (av. ~ 1.365 Å) and four longer (av. ~ 1.415 Å) bonds is also in accordance with the delocalization and imine formation [8–10]. Thus, the formation of five-membered azoimine chelate has been inferred.

2.3. Spectral characterization and solution structure

The green complexes [(L-NH)Rh(PPh₃)₂Cl] displayed characteristic UV–Vis spectra. Data are collected in

Table 2
UV–Vis^a, IR^b and cyclic voltammetric data

Compound	λ_{\max}/nm ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$)	ν/cm^{-1}			$E_{1/2}/\text{V}^c$ ($\Delta E_p/\text{mV}$)
		$\nu_{\text{N-H}}$	$\nu_{\text{C=N}}$	$\nu_{\text{N=N}}$	
2a	780 (5350), 720 (6200), 290 (35900) 230 (54400)	3360	1599	1371	0.373(60)
2b	780 (5750), 720 (6500), 290 (37550) 230 (58100)	3344	1599	1359	0.331(65)
2c	780 (11500), 720 (13400), 290 (70800) 230 (103350)	3345	1601	1364	0.436(70)

^a In dichloromethane.

^b In KBr disc.

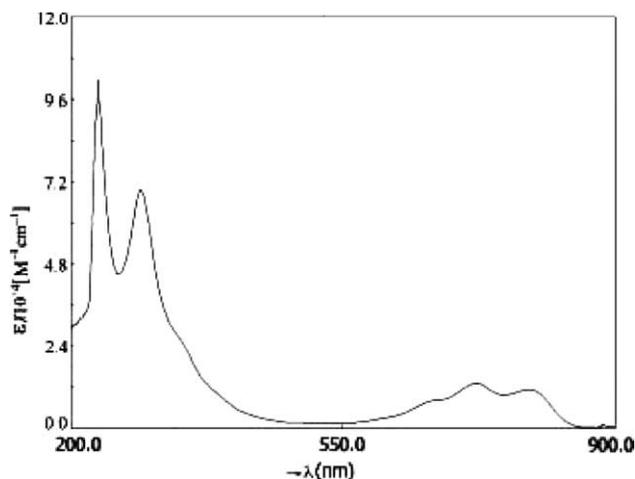
^c vs. SCE in dichloromethane solution using Bu₄NClO₄ supporting electrolyte.

Table 2. The spectrum of [(L³-NH)Rh(PPh₃)₂Cl] has been shown in Fig. 2. One of the important features in the UV–Vis spectra of the complexes is the high intensity absorption near considerably lower energy (~ 780 nm).

The IR spectra of [(L-NH)Rh(PPh₃)₂Cl] in solid KBr pellet displayed ν_{NH} as sharp single band in the range 3345–3360 cm^{-1} , in contrast to the ligands where ν_{NH_2} of NH₂ function appeared as split band in the range 3360–3458 cm^{-1} [8–10], indicating the proton dissociation from –NH₂ function of (HL-NH₂) upon coordination. The $\nu_{\text{N=N}}$ of (HL-NH₂) (1458–1474 cm^{-1}) were red shifted to 1359–1371 cm^{-1} in (L-NH)Rh(PPh₃)₂Cl signifying the coordination of azo nitrogen [8–10]. A new band, near 1600 cm^{-1} , in the IR spectra of the complexes unlike the ligands, has been attributed to imine formation [8–10]. The relevant IR data are collected in Table 2. The IR spectra of **2** are given in Supplementary materials (Figs. S1–S3).

The well resolved ¹H NMR spectra of (L-NH)Rh(PPh₃)₂Cl complexes are consistent with their structures. The aromatic proton resonances could be assigned on the basis of shielding and proton–proton interactions. The ¹H NMR spectra of the complexes have been compared and correlated with the corresponding spectra of the free ligands, HL-NH₂, a representative case for (L³-NH)Rh(PPh₃)₂Cl and HL³-NH₂ has been shown in Fig. 3 along with the numbering scheme in the inset. The significant features that have been taken into consideration to elucidate the structures in solution are as follows:

- The NH resonance of [(L-NH)Rh(PPh₃)₂Cl] appeared as a singlet in the range of δ 4.5–4.7 for one equivalent of proton, in contrast to two equivalent protons for the –NH₂ of free ligand, confirming the dissociation of one –NH₂ proton of the ligands upon complexation;
- the total count of aromatic protons matched well with the orthometallation (data are given in Section 3);
- the nature of spectra for **2a**, **2b** and **2c** (Figs. S4–S6) are similar in the up field segment (δ 5.4–6.4) of the aromatic region and were assigned to the four protons of C8, C9, C10, C11 in ring B (Fig. 3), while the resonances in the downfield

Fig. 2. UV-Vis spectra of **2c**.

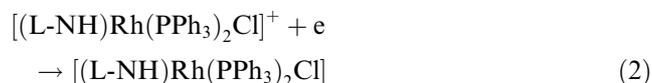
sector of aromatic region (δ 6.4–7.1) have been assigned to the aromatic protons of C2–C5 of ring A, since the spectral nature, in this region, varied significantly depending on R;

- (iv) a singlet near δ 7.0 for the **2b** and **2c** (where R = CH₃ or Cl) is for none other than C3 proton, diagnostic to orthometallation at C2 of ring A;
- (v) two multiplets ($\sim\delta$ 7.16 and $\sim\delta$ 7.5) of 12 protons each and another multiplet ($\delta \sim 7.26$) for six protons are in agreement with the two *trans* PPh₃ ligands.

2.4. Electrochemistry

(L-NH)Rh(PPh₃)₂Cl complexes exhibit one electron reversible oxidative cyclic voltammetric response in the range of 0.331–0.436 V vs. SCE in dichloromethane solution. Data are collected in Table 3 and a representative cyclic voltammogram for **2c** has been shown in Fig. 4.

The oxidation has been assigned according to the couple of Eq. (2) where [(L-NH)Rh(PPh₃)₂Cl]⁺ was believed to be the Rh(IV) analogue of [(L-NH)Rh(PPh₃)₂Cl]. The coulomb count, during



coulometric oxidation of [(L-NH)Rh(PPh₃)₂Cl] at $\sim+0.6$ V, matched with one electron transfer process (Section 3). The cyclic voltammogram of the electrogenerated [(L-NH)Rh(PPh₃)₂Cl]⁺ did not display any voltammetric response identical to that of the original complex, indicating a transformation upon oxidation. Therefore, the oxidative response of [(L-NH)Rh(PPh₃)₂Cl] has been assigned by comparing the assignment of analogous azophenolato complexes of Rh(III) [6]. The oxidation potential ($E_{1/2}$) of [(L-NH)Rh(PPh₃)₂Cl] was found to be sensitive to the nature of the substituent (R) present in the (HL-NH)⁻ ligand increasing linearly (Fig. 4) with increasing electron-withdrawing character of the substituent. The plot of $E_{1/2}$

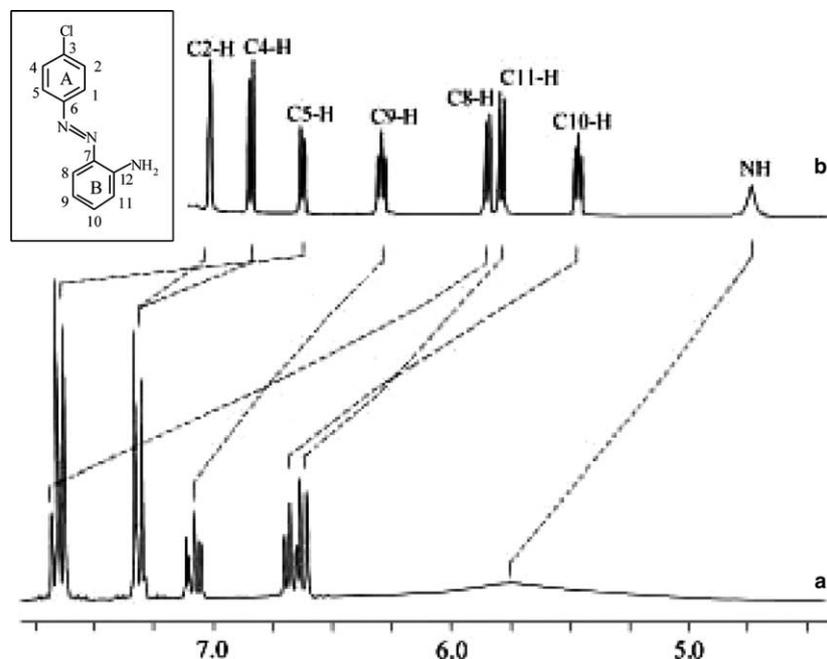
Fig. 3. A correlation of aromatic proton resonances of free (a) HL³-NH₂ and (b) **2c**. The numbering scheme is shown in the inset.

Table 3
Crystallographic data for **2c**

Chemical formula	C ₄₈ H ₃₈ Cl ₂ N ₃ P ₂ Rh · CH ₂ Cl ₂
Formula weight	977.49
Space group	Monoclinic <i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	13.641(3)
<i>b</i> (Å)	17.793(4)
<i>c</i> (Å)	17.962(4)
β (°)	94.533(1)
λ (Å)	0.71073
<i>V</i> (Å ³)	4346.37(17)
<i>Z</i>	4
Temperature (K)	293(2)
ρ (Mg/m ⁻³)	1.494
μ (mm ⁻¹)	0.752
<i>R</i> ^a (all data)	0.0277
<i>wR</i> ₂ ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0706
GOF ^c	1.08

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}, \text{ where } w = 1/\sigma^2(F_o^2) + (aP)^2 + bP, P = (F_o^2 + 2F_c^2)/3.$$

$$^c \text{GOF} = [\sum [w(F_o^2 - F_c^2)^2] / (n - p)]^{1/2}.$$

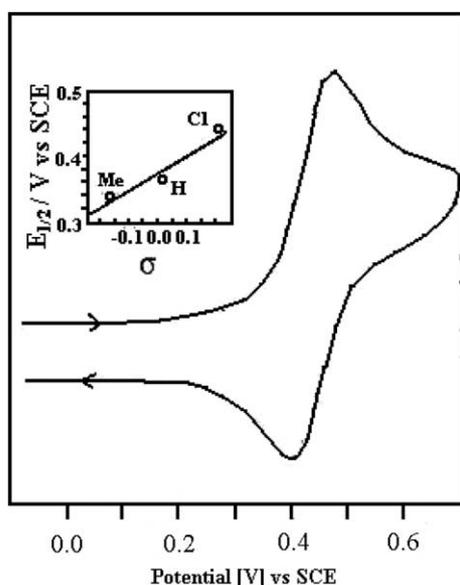


Fig. 4. Cyclic voltammogram of **2c** in dichloromethane solution (0.1 M NBu₄ClO₄) scan rate 50 mV s⁻¹ at 298 K. A least-squares plot of *E*_{1/2} values of the rhodium (III)–rhodium (IV) couple vs. σ (Hammett substituent constant) is shown in the inset.

values vs. Hammett substituent constant is linear as shown in inset in Fig. 4.

3. Experimental

3.1. Materials

All starting materials were used as received from commercial sources; the solvents were purchased from E. Merck, Kolkata, India, and purified and dried by

reported procedure [8–10]. *o*-Phenylenediamine, nitrobenzene, *p*-methyl and *p*-chloro nitrobenzene, triphenylphosphine were purchased from Loba, Kolkata, India. Rhodium trichloride was purchased from Arora Matthey, India. Rh(PPh₃)₃Cl were synthesized following a reported procedure [13]. The ligand 2-(phenylazo) aniline, 2-(*p*-tolylazo) aniline and 2-(*p*-chlorophenylazo) aniline were prepared following the reported procedure [8–10].

3.2. Physical measurements

Microanalysis (C, H, N) was performed using a Perkin–Elmer 240C elemental analyzer. Infrared spectra were recorded on a Perkin–Elmer L120-00A FT-IR spectrometer with the samples prepared with KBr pellets. Electronic spectra were recorded on a Shimadzu UV-2401 PC spectrophotometer. ¹H NMR spectra were obtained on Bruker RPX 500 NMR spectrometers in CDCl₃ using TMS as the internal standard. Electrochemical measurements were made under dinitrogen atmosphere using a PAR model VERSASTAT-II potentiostat. A platinum disc working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. All electrochemical data were collected at 298 K and are uncorrected for junction potentials.

3.3. Synthesis of complexes

3.3.1. (*L*¹-NH)Rh(PPh₃)₂Cl

Rh(PPh₃)₃Cl (200 mg, 0.22 mmol) was added to a solution of HL¹-NH₂ (44 mg, 0.22 mmol) in toluene. The mixture was then refluxed under a dinitrogen atmosphere for 4 h, when a green solution was obtained. Evaporation of this solution afforded a dark solid which was purified by thin layer chromatography on silica plate with toluene as the eluent. A green band separated and the complex was extracted from it with acetonitrile. The green solid, obtained upon evaporation of the solvent, was recrystallized from dichloromethane–hexane to afford (L¹-NH)Rh(PPh₃)₂Cl as a crystalline green solid. Yield: 126 mg, (67%). Anal. Found: C, 67.16; H, 4.56; N, 4.91. Calc. for RhC₄₈H₃₉ClN₃P₂: C, 67.13; H, 4.54; N 4.89%. ¹H NMR (CDCl₃): δ = 7.54 (d, PPh₃, 12H), 7.26 (t, PPh₃, 6H), 7.16 (t, PPh₃, C3-H, 13H), 6.93 (d, C2-H, 1H), 6.70 (t, C3-H, 1H), 6.42 (t, C4-H, 1H), 6.31 (t, C9-H, 1H), 5.85 (d, C8-H, 1H), 5.78 (d, C11-H, 1H), 5.46 (t, C5-H, 1H), 4.68 (s, NH, 1H).

3.3.2. (*L*²-NH)Rh(PPh₃)₂Cl

This complex was prepared and purified following a similar procedure as described for (L¹-NH)Rh(PPh₃)₂Cl using ligand HL²-NH₂ in place of HL¹-NH₂. Yield: 108 mg, (60%). Anal. Found: C, 67.47; H, 4.67; N, 4.

85. Calc. for $\text{RhC}_{49}\text{H}_{41}\text{ClN}_3\text{P}_2$: C, 67.43; H, 4.70; N, 4.81%. ^1H NMR (CDCl_3): $\delta = 7.54$ (m, PPh_3 , 12H), 7.26 (t, PPh_3 , 6H), 7.16 (t, PPh_3 , 12H), 6.90 (d, C2-H, C4-H, 2H), 6.52 (d, C5-H, 1H), 6.31 (t, C9-H, 1H), 5.87–5.76 (m, C8-H, C11-H, 2H), 5.45 (t, C10-H, 1H), 4.60 (s, NH, 1H), 1.94 (s, *p*- CH_3 , 3H).

3.3.3. $(L^3\text{-NH})\text{Rh}(\text{PPh}_3)_2\text{Cl}$

This complex was prepared and purified following a similar procedure as described above using ligand $\text{HL}^3\text{-NH}_2$. Yield: 112 mg, (60%). Anal. Found: C, 64.58; H, 4.30; N, 4.65. Calc. for $\text{RhC}_{48}\text{H}_{38}\text{Cl}_2\text{N}_3\text{P}_2$: C, 64.53; H, 4.25; N, 4.70%. ^1H NMR (CDCl_3): $\delta = 7.54$ (d, PPh_3 , 12H), 7.26 (t, PPh_3 , 6H), 7.17 (t, PPh_3 , 12H), 7.04 (s, C2-H, 1H), 6.86 (d, C4-H, 1H), 6.64 (d, C5-H, 1H), 6.31 (t, C9-H, 1H), 5.86 (d, C8-H, 2H), 5.80 (d, C11-H, 1H), 5.47 (t, C10-H, 1H), 4.75 (s, NH, 1H).

3.4. Electrochemical measurement

Twenty milligram of **2c** in 10 mL dichloromethane were electrolyzed by controlled potential coulometry using Bu_4NClO_4 supporting electrolyte at +0.6 V vs. SCE, respectively. The coulomb counts 2.39 C matched with the calculated values for 1 equiv. electron transfer.

4. Crystallography

Crystal data were collected by the ω -scan technique on a Bruker SMART CCD diffractometer using $\text{Mo K}\alpha$ monochromator ($\lambda = 0.71043$). The structure solution was done by direct method with SHELXS-97 program. Full-matrix least-square refinements were performed using the SHELXL-97 program (PC version). All non-hydrogen atoms were refined anisotropically using reflections $I > 2\sigma(I)$. Hydrogen atoms excepting H(4a) were included at the calculated positions. The crystal data and data collection parameters are listed in Table 3, Figs. S1–S6 supplementary materials and CCDC 269666 containing the crystallographic details for complex **2c** in CIF format are available free of charge from The Cambridge Crystallographic Data Centre via e-mail: www.ccdc.cam.ac.uk/data_request/cif.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2005.07.076](https://doi.org/10.1016/j.jorganchem.2005.07.076).

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