



# Mixed-ligand 1,3-diaryltriazenide complexes of ruthenium: Synthesis, structure and catalytic properties



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## ABSTRACT

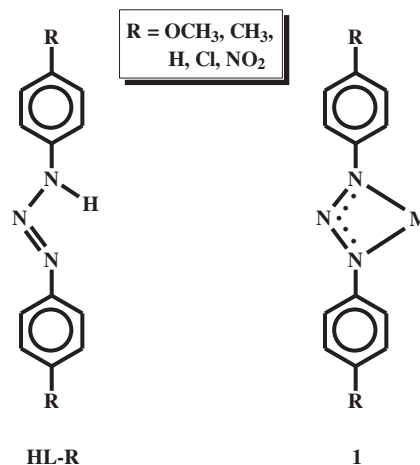
Reaction of 1,3-diaryltriazenes (abbreviated in general as HL-R, where H represents the dissociable N–H proton and R is the *para* substituent (R = OCH<sub>3</sub>, CH<sub>3</sub>, H, Cl, NO<sub>2</sub>) on the aryl fragment) with [Ru(PPh<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Cl<sub>2</sub>] in 2-methoxyethanol in the presence of a base (NEt<sub>3</sub>) affords a family of yellow complexes of the type [Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)(H)], where the 1,3-diaryltriazenes are coordinated as monoanionic bidentate NN-donors. Two triphenylphosphines, a hydride and a carbonyl are also coordinated to ruthenium. The triphenylphosphines are mutually *trans*, and the hydride and carbonyl are mutually *cis*. Structure of the [Ru(PPh<sub>3</sub>)<sub>2</sub>(L-H)(CO)(H)] complex has been determined by X-ray crystallography. All the complexes show intense absorptions in the visible region, which are assigned, based on DFT calculations, to transitions within orbitals of the triazenide ligand. The complexes exhibit an irreversible oxidation on the positive side of SCE and an irreversible reduction on the negative side. All the complexes are found to efficiently catalyze transfer hydrogenation reactions.

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## 1. Introduction

There has been considerable current attention on the coordination chemistry of the 1,3-diaryltriazenes primarily because of their varied modes of binding [1–3]. The 1,3-diaryltriazenide anion, formed *in situ* via loss of the acidic N–H proton, is a short-bite ligand, which is known to serve as monodentate ligand [1], chelating bidentate ligand [2], and also as bridging ligand [3]. However, in most of the cases it usually coordinates to a metal center as bidentate NN-donor forming a four-membered chelate ring (1) [2]. It is also worth mentioning that the 1,3-diaryltriazenes find important applications in biological field [4]. We have recently explored the chemistry of two groups of 1,3-diaryltriazenide complexes of rhodium [5], and the present work has originated from our continued interest in the triazenide complexes of other platinum group of metals. For the present study we have chosen a family of five 1,3-diaryltriazenes (HL-R) differing in the *para*-substituent R on the aryl fragment, and selected ruthenium as the metal center. The chosen ligands are abbreviated in general as HL-R, where H stands for the dissociable N–H hydrogen and R for the *para*-substituent. As the ruthenium starting material [Ru(PPh<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Cl<sub>2</sub>] has been selected, because of its demonstrated ability to readily accommodate ligands of different types via displacement of some of the pre-coordinated ligands [6]. The primary objective of the

undertaken study has been to synthesize a series of mixed-ligand ruthenium complexes of 1,3-diaryltriazenes, and find out the coordination mode of the triazenes in the complexes. Reaction of the selected 1,3-diaryltriazenes (HL-R) with [Ru(PPh<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Cl<sub>2</sub>] has indeed afforded a group of interesting mixed-ligand complexes, and herein we describe the chemistry of these complexes, with special reference to their formation, structure, spectral and electrochemical properties, and catalytic activity.



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## 2. Experimental

### 2.1. Materials

Commercial ruthenium trichloride, purchased from Arora Matthey, Kolkata, India, was converted to  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  by repeated evaporation with concentrated hydrochloric acid. Triphenylphosphine was purchased from Loba Chemie, Mumbai, India. The *para*-substituted anilines were obtained from S.D. Fine-Chem, Mumbai, India.  $[\text{Ru}(\text{PPh}_3)_2(\text{CO})_2\text{Cl}_2]$  and the 1,3-diaryltriazenes were prepared by following reported procedures [7,8]. Tetrabutylammonium hexafluorophosphate (TBHP), obtained from Sigma–Aldrich, was used for electrochemical work. Purification of dichloromethane and acetonitrile for electrochemical work was performed as reported in the literature [9]. All other chemicals and solvents were reagent grade commercial materials and were used as received.

### 2.2. Synthesis of the complexes

All the  $[\text{Ru}(\text{PPh}_3)_2(\text{L-R})(\text{CO})(\text{H})]$  complexes were synthesized by following a general procedure. Specific details are given below for a particular complex.

**$[\text{Ru}(\text{PPh}_3)_2(\text{L-OCH}_3)(\text{CO})(\text{H})]$ .** To a solution of  $\text{HL-OCH}_3$  (33 mg, 0.13 mmol) in 2-methoxyethanol (40 mL) was added triethylamine (13 mg, 0.13 mmol), followed by  $[\text{Ru}(\text{PPh}_3)_2(\text{CO})_2\text{Cl}_2]$  (100 mg, 0.13 mmol). The mixture was refluxed for 24 h, which yielded a yellow solution. The solution was evaporated in air to afford a yellow solid, which was purified by thin layer chromatography on a silica plate. With 1:1 hexane–benzene as eluant a yellow band separated, which was extracted by acetonitrile. Evaporation of this acetonitrile extract yielded  $[\text{Ru}(\text{PPh}_3)_2(\text{L-OCH}_3)(\text{CO})(\text{H})]$  as a yellow crystalline solid. Yield: 67%. *Anal.* Calc. for  $\text{C}_{51}\text{H}_{45}\text{N}_3\text{O}_3\text{P}_2\text{Ru}$ : C, 67.25; H, 4.95; N, 4.62. Found: C, 67.47; H, 4.91; N, 4.67%. Mass: 934,  $[\text{M}+\text{Na}]^+$ .  $^1\text{H}$  NMR in  $\text{CDCl}_3$ ,  $\delta$  ppm<sup>1</sup>: –12.90 (t, hydride,  $J = 20.6$ ); 3.46 (s,  $\text{OCH}_3$ ); 3.51 (s,  $\text{OCH}_3$ ); 6.64 (d, 2H,  $J = 8.9$ ); 6.76 (d, 2H,  $J = 9.0$ ); 6.90 (d, 2H,  $J = 8.9$ ); 7.01 (d, 2H,  $J = 9.3$ ); 7.14–7.70 (30H\*). IR,  $\bar{\nu}$  cm<sup>–1</sup>: 1926, 1634, 1501, 1438, 1280, 1098, 818, 745, 694 and 518.

**$[\text{Ru}(\text{PPh}_3)_2(\text{L-CH}_3)(\text{CO})(\text{H})]$ .** Yield: 72%. *Anal.* Calc. for  $\text{C}_{51}\text{H}_{45}\text{N}_3\text{O}_1\text{P}_2\text{Ru}$ : C, 69.70; H, 5.13; N, 4.78. Found: C, 69.67; H, 5.02; N, 4.80%. Mass: 902,  $[\text{M}+\text{Na}]^+$ .  $^1\text{H}$  NMR in  $\text{CDCl}_3$ ,  $\delta$  ppm: –12.87 (t, hydride,  $J = 20.6$ ); 2.17 (s,  $\text{CH}_3$ ); 2.23 (s,  $\text{CH}_3$ ); 6.33 (d, 2H,  $J = 7.2$ ); 6.46 (d, 2H,  $J = 7.4$ ); 6.79 (d, 2H,  $J = 7.3$ ); 6.87 (d, 2H,  $J = 7.6$ ); 6.95–7.70 (30H\*). IR,  $\bar{\nu}$  cm<sup>–1</sup>: 1928, 1636, 1502, 1436, 1279, 1094, 819, 746, 694 and 516.

**$[\text{Ru}(\text{PPh}_3)_2(\text{L-H})(\text{CO})(\text{H})]$ .** Yield: 70%. *Anal.* Calc. for  $\text{C}_{49}\text{H}_{41}\text{N}_3\text{O}_1\text{P}_2\text{Ru}$ : C, 69.18; H, 4.82; N, 4.94. Found: C, 69.46; H, 4.74; N, 4.98%. Mass: 874,  $[\text{M}+\text{Na}]^+$ .  $^1\text{H}$  NMR in  $\text{CDCl}_3$ ,  $\delta$  ppm: –12.85 (t, hydride,  $J = 20.6$ ); 6.94 (t, 1H,  $J = 6.8$ ); 7.04 (t, 1H,  $J = 7.3$ ); 7.36 (d, 2H,  $J = 7.5$ ); 7.26 (d, 2H,  $J = 7.2$ ); 7.20–7.70 (34H\*). IR,  $\bar{\nu}$  cm<sup>–1</sup>: 1928, 1636, 1500, 1435, 1280, 1097, 817, 745, 695 and 517.

**$[\text{Ru}(\text{PPh}_3)_2(\text{L-Cl})(\text{CO})(\text{H})]$ .** Yield: 72%. *Anal.* Calc. for  $\text{C}_{49}\text{H}_{39}\text{N}_3\text{O}_1\text{P}_2\text{Ru}$ : C, 63.98; H, 4.24; N, 4.57. Found: C, 64.10; H, 4.16; N, 4.63%. Mass: 943,  $[\text{M}+\text{Na}]^+$ .  $^1\text{H}$  NMR in  $\text{CDCl}_3$ ,  $\delta$  ppm: –12.93 (t, hydride,  $J = 20.6$ ); 6.75 (d, 2H,  $J = 7.4$ ); 7.00 (d, 2H,  $J = 8.6$ ); 7.22–7.70 (34H\*). IR,  $\bar{\nu}$  cm<sup>–1</sup>: 1929, 1634, 1502, 1436, 1279, 1096, 816, 746, 695 and 516.

**$[\text{Ru}(\text{PPh}_3)_2(\text{L-NO}_2)(\text{CO})(\text{H})]$ .** Yield: 69%. *Anal.* Calc. for  $\text{C}_{49}\text{H}_{39}\text{N}_5\text{O}_5\text{P}_2\text{Ru}$ : C, 62.55; H, 4.15; N, 7.45. Found: C, 62.61; H, 4.09; N, 7.49%. Mass: 964,  $[\text{M}+\text{Na}]^+$ .  $^1\text{H}$  NMR in  $\text{CDCl}_3$ ,  $\delta$  ppm: –12.95 (t, hydride,  $J = 20.6$ ); 7.03 (d, 2H,  $J = 8.2$ ); 7.54 (d, 2H,  $J = 8.3$ ); 7.20–7.89 (34H\*). IR,  $\bar{\nu}$  cm<sup>–1</sup>: 1930, 1635, 1503, 1438, 1278, 1094, 820, 744, 694 and 515.

### 2.3. Physical measurements

Microanalyses (C, H and N) were performed using a Heraeus Carlo Erba 1108 elemental analyzer. Mass spectra were recorded with a Micromass LCT electrospray (Qtof Micro YA263) mass spectrometer by electrospray ionization method. Magnetic susceptibilities were measured using a Sherwood MK-1 balance.  $^1\text{H}$  NMR spectra were recorded in  $\text{CDCl}_3$  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. Optimization of ground-state structures and energy calculations for all the complexes were carried out by density functional theory (DFT) method using the GAUSSIAN 03 package [10], where B3LYP was chosen as the basis function and 631g(d,p) basis set was taken for H, C and N, and SDD basis set for Ru and P. 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. GC–MS analyses were performed using a Perkin Elmer CLARUS 680 instrument.

### 2.4. Crystallography

Single crystals of  $[\text{Ru}(\text{PPh}_3)_2(\text{L-H})(\text{CO})(\text{H})]$  were obtained by slow diffusion of hexane into a solution of the complex in dichloromethane. Selected crystal data and data collection parameters are given in Table 1. Data were collected on a Bruker SMART Apex CCD area detector using graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). X-ray data reduction, structure solution and refinement were done using SHELXS-97 and SHELXL-97 programs [11]. The structure was solved by the direct methods.

### 2.5. Catalysis: general procedure for the transfer hydrogenation reactions

A mixture of ketone (1 mmol), a known mole percent of the catalyst and KOH (0.06 mmol) was dissolved in 2-propanol (5 mL),

**Table 1**  
Crystallographic data for  $[\text{Ru}(\text{PPh}_3)_2(\text{L-H})(\text{CO})(\text{H})]$ .

Empirical formula	$\text{C}_{49}\text{H}_{41}\text{N}_3\text{O}_1\text{P}_2\text{Ru}_1$
Formula weight	850.86
Crystal system	triclinic
Space group	$P\bar{1}$
<i>a</i> (Å)	11.8767(17)
<i>b</i> (Å)	14.0894(15)
<i>c</i> (Å)	14.9356(15)
$\alpha$ (°)	66.122(10)
$\beta$ (°)	69.210(11)
$\gamma$ (°)	65.226(12)
<i>V</i> (Å <sup>3</sup> )	2022.7(5)
<i>Z</i>	2
$\lambda$ (Å)	0.71073
Crystal size (mm)	$0.23 \times 0.36 \times 0.39$
<i>T</i> (K)	203
$\mu$ (mm <sup>–1</sup> )	0.508
<i>R</i> <sub>1</sub> <sup>a</sup>	0.0369
<i>wR</i> <sub>2</sub> <sup>b</sup>	0.1074
Goodness-of-fit <sup>c</sup>	1.04

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ .

<sup>b</sup>  $wR_2 = [\sum \{w(F_o^2 - F_c^2)^2\} / \sum \{w(F_o^2)\}]^{1/2}$ .

<sup>c</sup> Goodness-of-fit =  $[\sum \{w(F_o^2 - F_c^2)^2\} / (M - N)]^{1/2}$ , where *M* is the number of reflections and *N* is the number of parameters refined.

<sup>1</sup> Chemical shifts are given in ppm and multiplicity of the signals along with the associated coupling constants (*J* in Hz) are given in parentheses. Overlapping signals are marked with an asterisk.

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