Tris-(1,3-diaryltriazenide) complexes of rhodium – Synthesis, structure and, spectral and electrochemical properties

CHHANDASI GUHAROY,[a] MICHAEL G B DREW[b] and SAMARESH BHATTACHARYA[a,*]

[a]Department of Chemistry, Inorganic Chemistry Section, Jadavpur University, Kolkata 700 032
[b]Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK
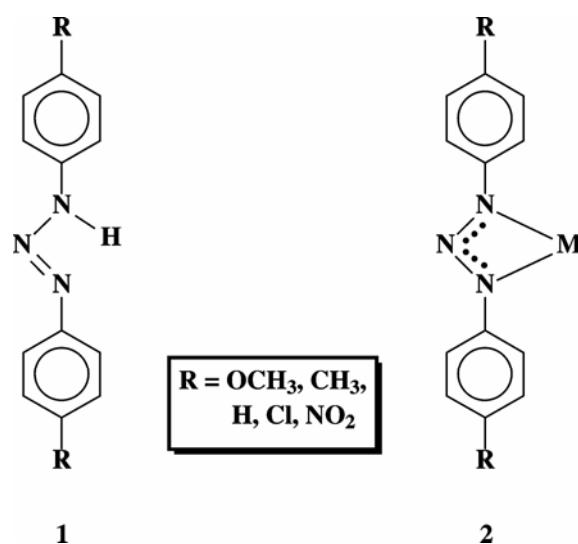e-mail: sbhattacharya@chemistry.jdvu.ac.in

Abstract. Reaction of 1,3-diaryltriazenes (abbreviated in general as HL-R, where R stands for the *para*-substituent in the aryl fragment and H stands for the dissociable hydrogen atom, R = OCH$_3$, CH$_3$, H, Cl, NO$_2$) with [Rh(PPh$_3$)$_2$(CO)Cl] in ethanol in the presence of NEt$_3$ produces a series of *tris*-diaryltriazenide complexes of rhodium of type [Rh(L-R)$_3$], where the triazenes are coordinated to rhodium as monoanionic, bidentate N,N-donors. Structure of the [Rh(L-OCH$_3$)$_3$] complex has been determined by X-ray crystallography. The complexes are diamagnetic, and show characteristic ^{1}H NMR signals and intense MLCT transitions in the visible region. They also fluoresce in the visible region under ambient condition while excited at around 400 nm. Cyclic voltammetry on these complexes shows a Rh(III)–Rh(IV) oxidation (within 0·84–1·67 V vs SCE), followed by an oxidation of the coordinated triazene ligand (except the R = NO$_2$ complex). An irreversible reduction of the coordinated triazene is also observed for all the complexes below –1·03 V vs SCE.

Keywords. 1,3-Diaryltriazenes; rhodium; *tris* complexes; N,N coordination; crystal structure; spectral and electrochemical properties.

1. Introduction

The chemistry of the 1,3-diaryltriazenes (**1**) has been receiving considerable interest in the research field because of its varied binding modes viz. monodentate,[1] chelating[2] and bridging.[3] It is a 'short bite' ligand that normally coordinates to a metal center via dissociation of the acidic N–H proton, as monoanionic, bidentate N,N-donor forming a four-membered chelate ring (**2**).[2] The triazene ligands also has significant biological applications.[4] In our laboratory, we have recently explored reaction of the 1,3-diaryltriazenes (**1**) with the Wilkinson's catalyst, viz. [Rh(PPh$_3$)$_3$Cl], which brought about interesting C–N and N–N bond cleavage of the 1,3-diaryltriazenes leading to formation of a series η^1-aryl complexes.[5] This observation prompted us to explore the reactivity of these triazene ligands with another rhodium(I) complex, viz. [Rh(PPh$_3$)$_2$(CO)Cl]. The primary objective of the present study was to find out whether the [Rh(PPh$_3$)$_2$(CO)Cl] complex can also

induce similar N–N and C–N bond cleavage of the triazene ligands (**1**). Reaction of the selected 1,3-diaryltriazenes (**1**) with [Rh(PPh$_3$)$_2$(CO)Cl] did not

R = OCH$_3$, CH$_3$, H, Cl, NO$_2$

1   **2**

cause any bond cleavage of the triazene ligands, but instead afforded a family of *tris*-triazenide com-

plexes of rhodium(III). The present report deals with the chemistry of these *tris*-triazenide complexes with special reference to their formation, structure and, spectral and electrochemical properties.

2. Experimental

2.1 *Materials*

Commercial rhodium trichloride was purchased from Arora Matthey, Kolkata, India. The *para*-substituted anilines were obtained from M/s S.D., India. All other chemicals and solvents were reagent grade commercial materials and were used as received. [Rh(PPh$_3$)$_2$(CO)Cl] was prepared following a reported procedure.[6] The 1,3-diaryltriazenes (1) were prepared by following a literature method.[7] Purification of acetonitrile and dichloromethane, and preparation of tetrabutylammonium perchlorate (TBAP) for electrochemical work were performed as reported in the literature.[8]

2.2 *Synthesis of the [Rh(L-R)$_3$] complexes*

The [Rh(L-R)$_3$] complexes were synthesized by following a general procedure. Specific details are given below for a particular complex.

[Rh(L-OCH$_3$)$_3$]: 1,3-Di(4′-methoxyphenyl)triazene (112 mg, 0·43 mmol) was dissolved in ethanol (40 mL) and triethylamine (45 mg, 0·45 mmol) was added to it.[9] To the solution was then added [Rh(PPh$_3$)$_2$(CO)Cl] (100 mg, 0·14 mmol). The resulting mixture was then heated to reflux for 24 h, whereby an orange solution was produced. Evaporation of this solution gave an orange solid, which was subjected to purification by thin layer chromatography on a silica plate. Using benzene as the eluant an orangish-yellow band separated. This band was extracted with acetonitrile. On evaporation of the acetonitrile extract complex [Rh(L-OCH$_3$)$_3$] was obtained as an orange crystalline solid. Yield: 75%. Analysis: Calc for C$_{42}$H$_{42}$N$_9$O$_6$Rh: C, 57·87; H, 4·82; N, 14·46%. Found: C, 57·81; H, 4·80; N, 14·49%. ^{1}H NMR:[10] 3·75 (6OCH$_3$); 6·74 (*d*, 12H, *J* = 9·0); 7·20 (*d*, 12H, *J* = 9·0).

[Rh(L-CH$_3$)$_3$]: Yield: 74%. Calc for C$_{42}$H$_{42}$N$_9$Rh: C, 65·04; H, 5·42; N, 16·26%. Found: C, 65·01; H,

5·42; N, 16·30%. ^{1}H NMR: 2·26 (6CH$_3$); 6·99 (*d*, 12H, *J* = 8·6); 7·16 (*d*, 12H, *J* = 8·1).

[Rh(L-H)$_3$]: Yield: 72%. Calc for C$_{36}$H$_{30}$N$_9$Rh: C, 62·53; H, 4·34; N, 18·24%. Found: C, 62·46; H, 4·33; N, 18·29%. ^{1}H NMR: 7·31 (*d*, 12H, *J* = 6·7); 7·18 (*t*, 12H, *J* = 8·9) 7·61 (*t*, 6H, *J* = 9·2).

[Rh(L-Cl)$_3$]: Yield: 75%. Calc. for C$_{36}$H$_{24}$N$_9$Cl$_6$Rh: C, 48·11; H, 2·67; N, 14·03%. Found: C, 48·09; H, 2·64; N, 14·08%. ^{1}H NMR: 7·12–7·21 (24H)*

[Rh(L-NO$_2$)$_3$]: Yield: 76%. Calc for C$_{36}$H$_{24}$N$_{15}$O$_{12}$Rh: C, 44·96; H, 2·50; N, 21·85%. Found: C, 44·94; H, 2·47; N, 21·89%. ^{1}H NMR: 6·62 (*d*, 12H, *J* = 8·7); 8·07 (*d*, 12H, *J* = 8·7).

2.3 *Physical measurements*

Microanalyses (C, H, N) were done using a Heraeus Carlo Erba 1108 elemental analyzer. ^{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. Emission spectra were recorded in a Jobin Yvon Horiba FluoroMax 3 Luminescence Spectrometer. 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.

2.4 *X-ray crystallographic analysis*

Single crystals of [Rh(L-OCH$_3$)$_3$] were obtained by slow diffusion of acetonitrile into a dichloromethane solution of the complex. Selected crystal data and data collection parameters are given in table 1. Data were collected on a Marresearch Image Plate system using graphite monochromated MoKα radiation. X-ray data reduction and, structure solution and refinement were done using SHELXS-97 and SHELXL-97 programs.[11] The structure was solved by the direct methods.

3. Results and discussion

3.1 *Synthesis and structure*

Reaction of 1,3-diaryltriazenes (**1**, abbreviated in general as HL-R, where R stands for the *para*-substituent in the aryl fragment and H stands for the dissociable hydrogen atom, R = OCH_3, CH_3, H, Cl, NO_2) with [Rh(PPh$_3$)$_2$(CO)Cl] in approximately 3 : 1 mole ratio proceeds smoothly in refluxing ethanol in the presence of triethylamine (NEt$_3$) to afford a family of orange complexes in decent yields. It is worth mentioning here that similar reaction between the 1,3-diaryltriazenes and [Rh(PPh$_3$)$_2$(CO)Cl] in 1 : 1 mole ratio affords the same orange complexes but in poor (~ 15%) yields. Preliminary (microanalytical and spectroscopic) characterizations on these complexes indicate absence of any CO or PPh$_3$ in them.

Table 1. Summary of structure determination of [Rh(L-OCH$_3$)$_3$].

Formula	C$_{42}$H$_{42}$N$_9$O$_6$Rh
Formula weight	871·76
Crystal system	Trigonal
Space group	$R\bar{3}$
Z	6
a (Å)	19·5498(7)
b (Å)	19·5498(7)
c (Å)	18·4370(7)
α (°)	90
β (°)	90
γ (°)	120
v (Å^3)	6102·5(4)
μ (mm^{-1})	0·479
Crystal size (mm^3)	0·03 × 0·04 × 0·22
T (K)	150
D_{calc} (g/cm^3)	1·423
λ (Å)	0·71073
No. of reflections measured	13929
No. of unique reflections	3943
R_1 indices[a,b] ($F > 4\sigma(F)$)	0·0862
wR_2	0·2307
GOF[c]	1·05

Table 2. Selected bond lengths (Å) and angles (°) for [Rh(L-OCH$_3$)$_3$].

Bond lengths (Å)			
Rh1–N1	2·033(4)	C11–N1	1·392(6)
Rh1–N3	2·026(6)	N1–N2	1·317(7)
		N2–N3	1·306(8)
		N3–C31	1·398(9)
Bond angles (°)			
N1–Rh1–N3b	162·6(2)	N1–Rh1–N3	61·0(19)

For an unambiguous characterization of these complexes, with regard to composition, stereochemistry and binding mode of the triazene ligands, structure of a representative member of the family, viz. the complex obtained from the reaction with HL-OCH$_3$, has been determined by X-ray crystallography. The structure is shown in figure 1 and selected bond parameters are listed in table 2. The structure shows that in this complex three triazene ligands are coordinated to rhodium as monoanionic bidentate N,N-donors, via dissociation of the N–H proton, forming four-membered chelate rings (**2**). In this complex rhodium is therefore sitting in a N$_6$ coordination en-
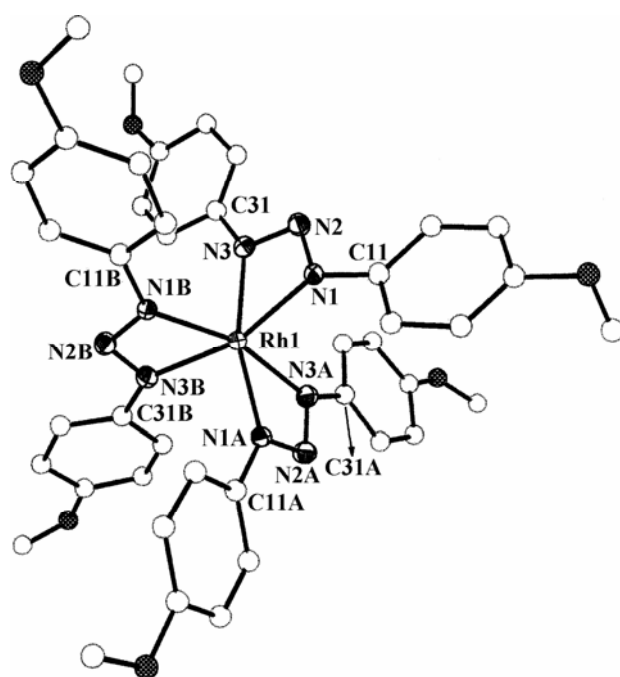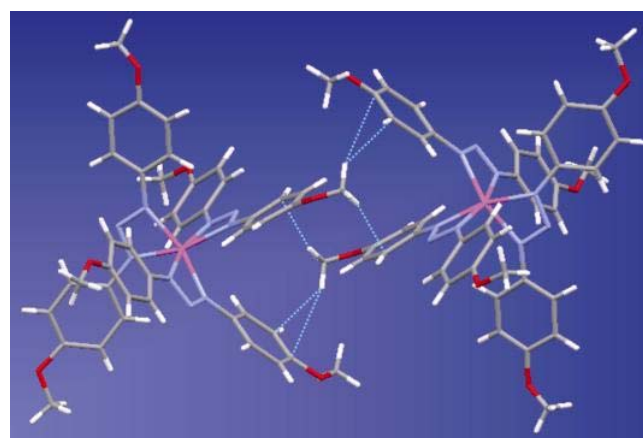

Figure 1. View of the [Rh(L-OCH$_3$)$_3$] complex.

Figure 2. C–H⋯π interactions in the lattice of the [Rh(L-OCH$_3$)$_3$] complex.

vironment, which is distorted significantly from ideal octahedral geometry, as reflected in the bond parameters around rhodium. This distortion is particularly attributable to the strain imposed by formation of the four-membered chelate rings with relatively small bite angles (61·0(19)°) by the triazene ligands. The Rh–N distances and the bond lengths within the coordinated ligands are quite normal.[2] This orange complex and the other four complexes of this family are therefore formulated in general as [Rh(L-R)₃]. It may be mentioned here that synthesis of such *tris*-(1,3-diaryltriazenide) complexes of rhodium has precedence in the literature.[2f,12]

The absence of any solvent of crystallization in the lattice of [Rh(L-OCH₃)₃] indicates possible existence of non-covalent interaction(s) between the individual complex molecules. An examination of the packing pattern in the lattice reveals that C–H---π interactions of two types, involving methoxy C–H's and π-clouds over the aryl rings, are active in the lattice (figure 2). Each individual complex molecule is thus linked with its neighbouring molecules through such C–H---π interactions, and these extended intermolecular interactions seem to be responsible for holding the crystal together. It may be relevant to note here that such non-covalent interactions are of significant importance in crystal engineering and biology.[13] As all the [Rh(L-R)₃] complexes have been synthesized similarly and they show similar properties (*vide infra*), the other four [Rh(L-R)₃] (R ≠ OCH₃) complexes are assumed to have similar structures as [Rh(L-OCH₃)₃].

Formation of the *tris*-triazenide complexes of rhodium(III) starting from a mixed ligand complex of rhodium(I) via displacement of all the coordinated ligands, viz. two triphenylphosphines, a carbonyl and a chloride, was quite intriguing. Though the exact sequences behind formation of these [Rh(L-R)₃] complexes are not completely clear, the speculated steps shown in scheme 1 seem probable. In the initial step, a 1,3-diaryltriazene reacts with the metal center in [Rh(PPh₃)₂(CO)Cl], whereby oxidative insertion of rhodium into the N–H bond takes place with simultaneous and usual dissociation of a PPh₃ from the metal center, affording a mono-hydride species. The Rh–Cl bond is also believed to get converted into a Rh–H bond under the prevailing reaction condition generating a di-hydride intermediate. Such conversion of M–Cl into M–H in alcoholic medium in the presence of a base is well documented in the literature.[14] This di-hydride intermediate then reacts with a second triazene ligand, which
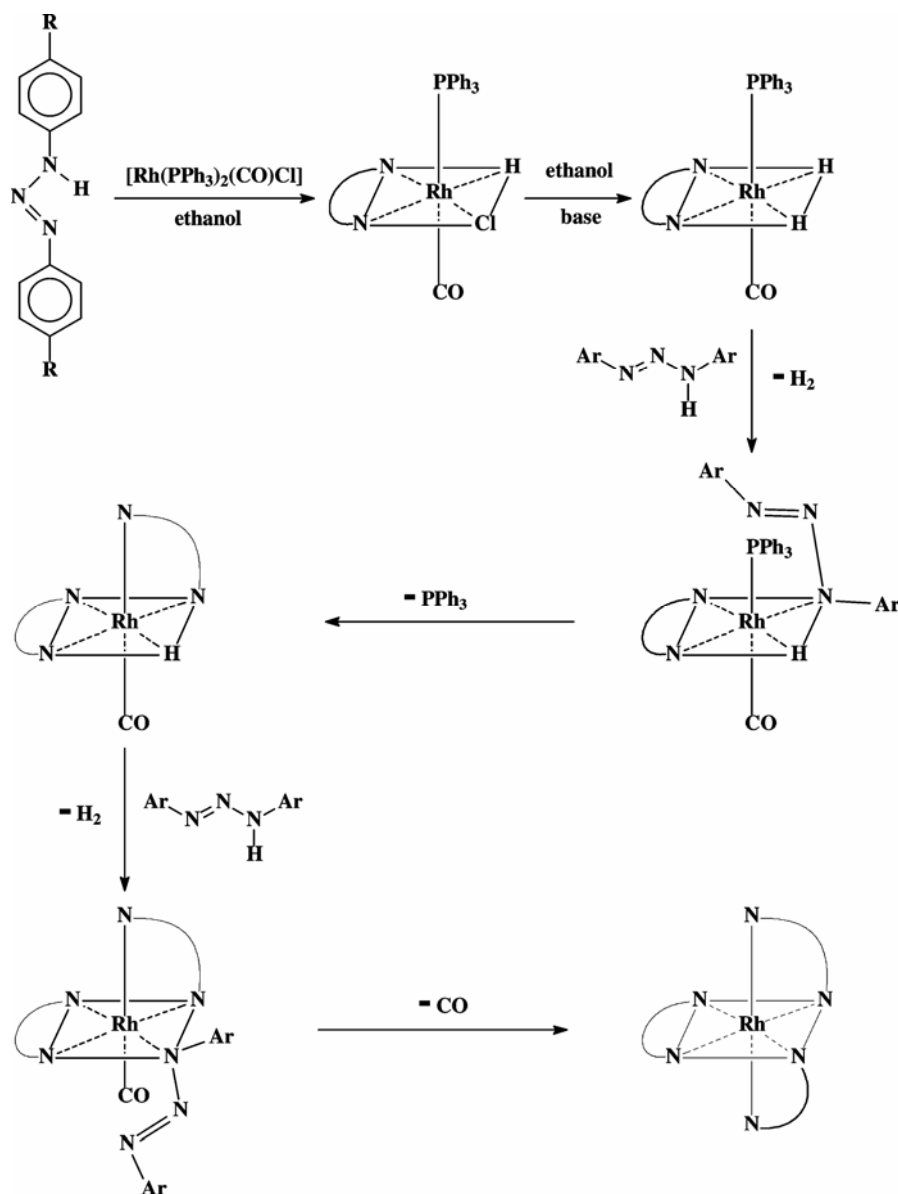
links itself to the metal center as a N,N-donor, probably via initial acid–base reaction between the N–H proton of the triazene ligand and the metal-bound hydride, followed by displacement of another PPh₃, probably favoured by the chelate effect. Chelation of the third 1,3-diaryltriazene takes place similarly, first via elimination of H₂ followed by displacement of CO, to yield the [Rh(L-R)₃] complexes. Elimination of molecular hydrogen or carbon monoxide during the course of the synthetic reaction could not be experimentally verified. In an attempt to isolate the mono-hydride species formed initially, reaction of the 1,3-diaryltriazenes was carried out with equimolar quantity of [Rh(PPh₃)₂(CO)Cl], which (as stated earlier) also afforded the same [Rh(L-R)₃] complexes in much lower yields.

3.2 *¹H NMR spectra*

All the [Rh(L-R)₃] complexes are diamagnetic, which corresponds to the trivalent state of rhodium (low-spin d^6, $S = 0$) in them. ¹H NMR spectra of these complexes have been recorded in CDCl₃ solution. The spectra are in well agreement with the highly symmetric nature of these complexes. The characteristic signals for the methoxy and methyl groups in the [Rh(L-OCH₃)₃] and [Rh(L-CH₃)₃] complexes appear at 3·75 and 2·26 ppm respectively. In the aromatic region, only two distinct doublets could be observed for the three [Rh(L-R)₃] complexes with R = OCH₃, CH₃ and NO₂, ≠ H. The more deshielded doublet is assigned to the ortho (with respect to the triazene function) protons and the less deshielded one to the meta ones. In the [Rh(L-Cl)₃] complex these doublets could not be distinctly recognized due to overlap problem. In [Rh(L-H)₃] one doublet at 7·31 ppm (due to the ortho protons) and two triplets at 7·18 ppm (due to the meta protons) and at 7·61 ppm (due to the para protons) are observed as expected. The ¹H NMR spectral data of the [Rh(L-R)₃] complexes are therefore consistent with their composition and stereochemistry.

3.3 *IR spectra*

Infrared spectra of the [Rh(L-R)₃] complexes show many bands of varying intensities within 4000–400 cm⁻¹. Assignment of each individual band to a specific vibration has not been attempted. However, the N–H stretch observed in the spectra of the uncoordinated triazene ligands around 3205 cm⁻¹ is

Scheme 1.

found to be absent in the spectra of the complexes, supporting loss of this N–H proton upon complexation. The $\nu(NN)$ bands arising from the triazene fragment appear around 1242 and 1500 cm^{-1} for all the complexes.[2f]

3.4 *Electronic absorption spectra*

Electronic spectra of all the complexes have been recorded in dichloromethane solution. Spectral data are presented in table 3. Spectrum of a selected complex is shown in figure 3. The complexes show several intense absorptions in the visible and ultraviolet region.[15] The absorptions in the ultraviolet re-

gion are believed to be due to transitions within the ligand orbitals. To have an insight into the nature of absorptions in the visible region, semi-empirical EHMO calculations by the CACAO package programs[16] have been performed on computer-generated models of all the complexes. The results are found to be qualitatively similar for all the complexes.[17] Compositions of some selected molecular orbitals are given in table 4 and partial MO diagram of a representative complex is shown in figure 4. The calculations show that in the [Rh(L-R)$_3$] complexes the highest occupied molecular orbital (HOMO) has major (> 50%) contribution from the metal d-orbitals. The next two filled molecular orbitals

Table 3. Electronic spectral and cyclic voltammetric data of the [Rh(L-R)$_3$] complexes.

Compounds	Electronic spectral data[a] λ_{max} (nm) (ε/M^{-1} cm^{-1})	Cyclic voltammetric data[b] E, V vs SCE	
		Oxidative responses	Reductive response
[Rh(L-OCH$_3$)$_3$]	252 (9400), 316[c] (4400), 418 (6800)	0·84[d], 1·01[d]	−1·03[e]
[Rh(L-CH$_3$)$_3$]	252 (8600), 306[c] (3700), 414 (5800)	1·08[d], 1·33[d]	−1·10[e]
[Rh(L-H)$_3$]	250 (10100), 300[c] (2500), 406 (6340)	1·29[d], 1·51[d]	−1·08[e]
[Rh(L-Cl)$_3$]	250[c] (12100), 306[c] (4200), 412 (7100)	1·31[d], 1·67[d]	−1·09[e]
[Rh(L-NO$_2$)$_3$]	230 (3700), 350 (8200)	1·46[d]	−1·13[e]

[a]In dichloromethane solution
[b]Solvent: 1 : 9 dichloromethane-acetonitrile; supporting electrolyte: TBAP; scan rate: 50 mVs^{-1}
[c]Shoulder; [d]E_{pa} value, where E_{pa} is the anodic peak potential; [e]E_{pc} value, where E_{pc} is the cathodic peak potential

Table 4. Composition of molecular orbitals.

Compounds	Contributing fragments	% Contribution of fragments to					
		HOMO	HOMO-1	HOMO-2	LUMO	LUMO + 1	LUMO + 2
[Rh(L-OCH$_3$)$_3$]	Rh	51	40	32	–	17	37
	Triazene	46	56	67	97 (N–N–N = 48)	78	59
[Rh(L-CH$_3$)$_3$]	Rh	50	40	33	–	18	33
	Triazene	47	57	64	97 (N–N–N = 47)	78	59
[Rh(L-H)$_3$]	Rh	50	38	34	–	17	21
	Triazene	49	53	60	95 (N–N–N = 40)	76	73
[Rh(L-Cl)$_3$]	Rh	44	30	15	–	17	20
	Triazene	52	63	82	97 (N–N–N = 46)	79	77
[Rh(L-NO$_2$)$_3$]	Rh	52	43	37	–	5	2
	Triazene	39	49	56	98 (N–N–N = 32) (NO$_2$ = 18)	96	94

Table 5. Emission spectral data for the [Rh(L-R)$_3$] complexes.

Compound	Emission data		
	λ_{max} (nm)		
	Excitation	Emission	Quantum yield (ϕ)
[Rh(L-OCH$_3$)$_3$]	418	466	0·007
[Rh(L-CH$_3$)$_3$]	414	461	0·016
[Rh(L-H)$_3$]	406	454	0·012
[Rh(L-Cl)$_3$]	412	453	0·007
[Rh(L-NO$_2$)$_3$]	350	390	0·050

(HOMO-1 and HOMO-2) also have significant contribution from rhodium. The lowest unoccupied molecular orbital (LUMO) is localized almost entirely on one 1,3-diaryltriazenide ligand and is concentrated mostly (> 40%) on the triazene fragment.[17] The next two vacant molecular orbitals (LUMO + 1 and LUMO + 2) are localized on the two other coordinated 1,3-diaryltriazene ligands. Hence the lowest energy absorption near 400 nm may be assigned to an electronic transition from the filled rhodium orbital (HOMO) to the vacant π^*-orbital (LUMO) localized on the triazene fragment of a coordinated 1,3-diaryltriazene ligand. The relatively high intensities of the charge-transfer transitions in the visible region tempted us to explore the luminescence properties of these complexes. In ethanol solution at ambient temperature (298 K) all the complexes have been found to display emission in the visible region
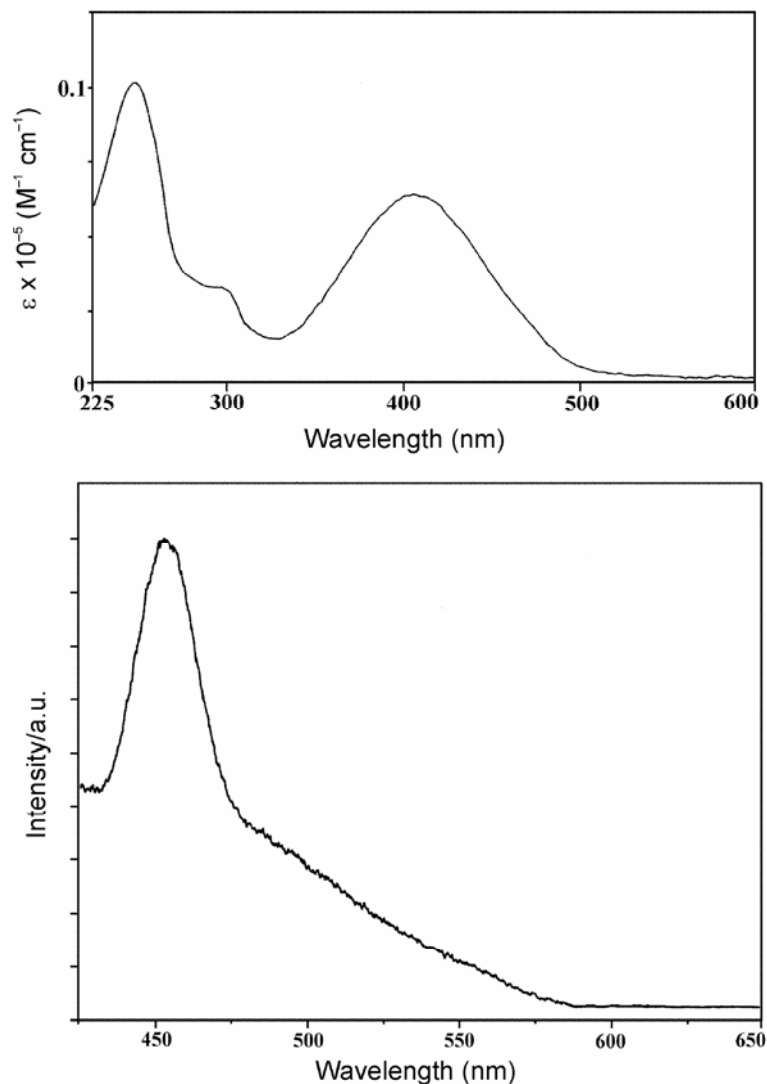
Figure 3. Absorption (top) emission (bottom) spectra of the [Rh(L-H)₃] complex.

using an excitation wavelength of ~400 nm[18] (figure 3). Quantum yields (ϕ) of these emissions have been evaluated (table 5) with reference to [Ru(bpy)₃]Cl₂ ($\phi = 0.028$ at 298 K),[19] which shows that these complexes are fairly good emitters under ambient conditions.

3.5 *Electrochemical properties*

Electrochemical properties of the [Rh(L-R)₃] complexes have been studied by cyclic voltammetry in 1 : 9 dichloromethane-acetonitrile solution (0·1 M TBAP).[20] Voltammetric data are presented in table 3 and a representative voltammogram is deposited as figure 5. The complexes show two irreversible oxidative responses on the positive side of SCE[21] and a reductive response on the negative side. In view of the composition of the HOMO (*vide infra*) the first oxidation is assigned to Rh(III)-Rh(IV) oxidation. The second oxidation is tentatively attributed to the oxidation of a coordinated triazene ligand. The reductive response is irreversible and, based on the composition of the LUMO, is assigned to reduction of the triazene fragment in the coordinated ligand. It may be mentioned here that, though the Rh(III)-Rh(IV) oxidation potential increases with increasing σ value of substituent R in the [Rh(L-R)₃] complexes, no linear correlation has been found to exist between oxidation potentials and 6σ.

4. Conclusions

The present study shows that the 1,3-diaryltriazenes (HL-R, **1**) can readily react with [Rh(PPh₃)₂(CO)Cl],

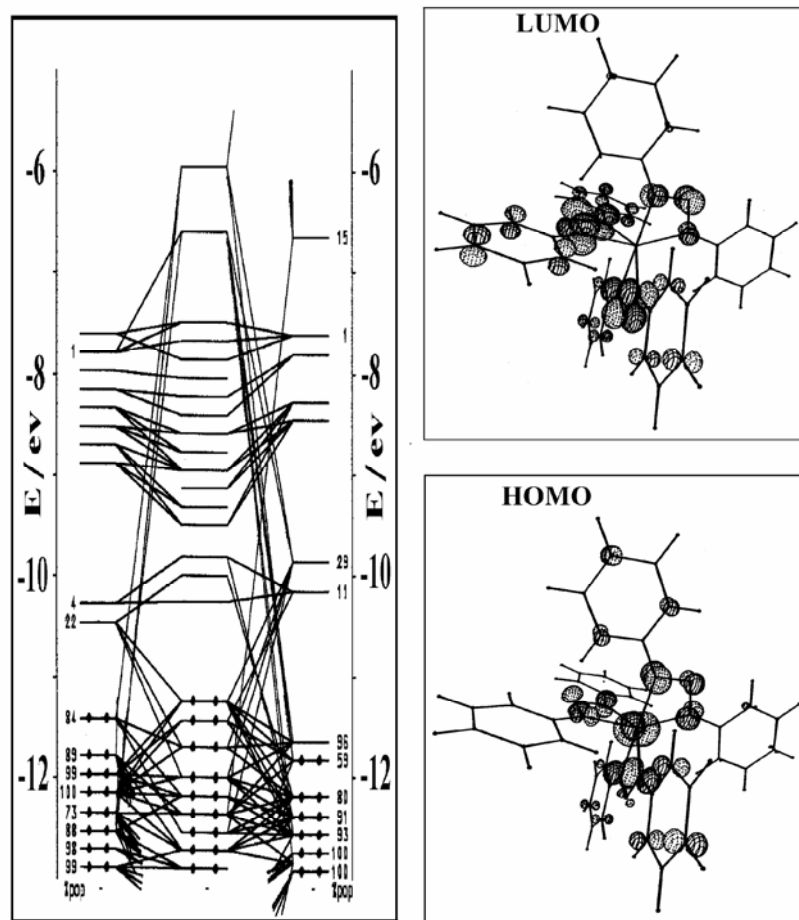**Figure 4.** Partial molecular orbital diagram of the [Rh(L-H)$_3$] complex.

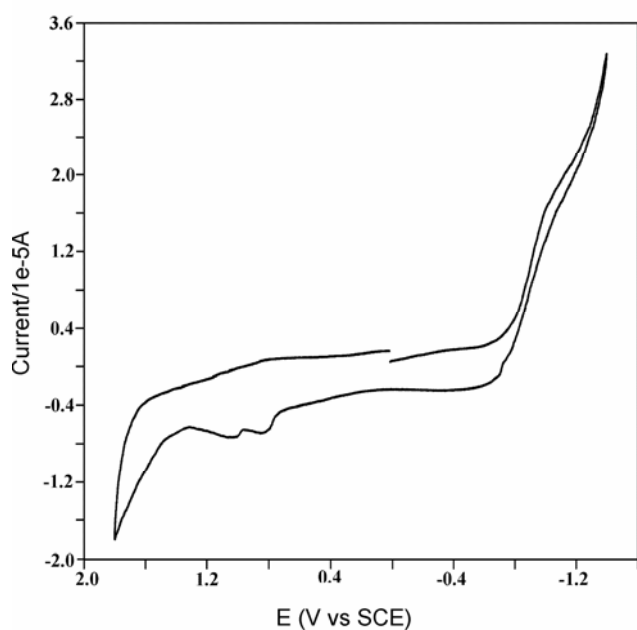**Figure 5.** Cyclic voltammogram of [Rh(L-OCH$_3$)$_3$] complex in 1:9 dichloromethane-acetonitrile solution (0·1 M TBAP) at a scan rate of 50 mV s^{-1}.

whereby initial N–H activation of a triazene ligand takes place generating a reactive hydride intermediate of rhodium. Further acid–base reactions between this hydride intermediate and two more triazene ligands finally affords the *tris*-triazenide complexes of rhodium(III). Interaction of these triazene ligands (**1**) with other reactive complexes of the platinum metals, expecting some interesting bond activation and/or bond cleavage reactions, are currently under exploration.

5. Supplementary material

Crystallographic data for the [Rh(L-OCH$_3$)$_3$] complexes in the CIF format have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 698648.

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9. The reaction does not occur in the absence of base (NEt$_3$).

10. 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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20. A little dichloromethane was necessary to take the complex into solution. Addition of large excess of acetonitrile was necessary to record the redox responses in proper shape

21. For the [Rh(L-NO$_2$)$_3$] complexes only one oxidation have been observed, probably because the other oxidation occurs beyond the voltage window