

Rhodium complexes of 3,5-di-*tert*-butylcatechol : synthesis, structure and, spectral and electrochemical properties

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Manuscript received online 11 April 2012, revised 23 April 2012, accepted 23 April 2012

Abstract : Reaction of $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ with 3,5-di-*tert*-butylcatechol (H_2DBC) in dry benzene affords a bis-semiquinonato rhodium(III) complex, $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})_2\text{Cl}]$. A similar reaction of $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ with a mixture of H_2DBC and quinolin-8-ol (Hq) in 1 : 1 : 1 mole ratio affords a mixed-bis complex of rhodium(III), $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})(\text{q})\text{Cl}]$. Formation of complexes $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})_2\text{Cl}]$ and $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})(\text{q})\text{Cl}]$ is believed to proceed through the intermediacy of a reactive hydrido complex, generated in the initial step via oxidative insertion of rhodium into the acidic O-H fragment of the ligand. Reaction of H_2DBC with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in ethanol yields a tris-semiquinonato complex of rhodium(III), $[\text{Rh}(\text{DBSQ})_3]$. Formation of this $[\text{Rh}(\text{DBSQ})_3]$ complex proceeds through simple displacement reaction. Structures of all the three complexes have been determined by X-ray crystallography. The $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})_2\text{Cl}]$ complex is diamagnetic and shows characteristic ^1H NMR spectrum, while complexes $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})(\text{q})\text{Cl}]$ and $[\text{Rh}(\text{DBSQ})_3]$ are one-electron paramagnetic, and show sharp ESR signal with $g \sim 2.0$. All the complexes show intense absorptions in the visible and ultraviolet regions. Cyclic voltammetry on all the three complexes shows an oxidation on the positive side of SCE and a reduction on the negative side, both of which are irreversible and ligand (DBSQ/q)-based.

Keywords : 3,5-Di-*tert*-butyl catechol, rhodium complexes, formation, crystal structures, spectral and electrochemical properties.

Introduction

The present work has originated from our interest in the chemistry of the rhodium complexes with organic ligands of different types¹. The coordination complexes of rhodium have been receiving considerable current attention², particularly because of their application in catalysis. For the present study 3,5-di-*tert*-butylcatechol (H_2DBC) has been selected as the principal ligand. The chosen ligand belongs to a class of redox non-innocent ligands, the transition metal coordination chemistry of which has developed over several years³. Studies on the coordination properties of 3,5-di-*tert*-butylcatechol have shown that it is capable of chelating to metals (i) as dianionic bidentate O,O-donor, in the form of catecholate, (ii) as monoanionic bidentate O,O-donor, in the form of semiquinonate, or (iii) as neutral bidentate O,O-donor, in the form of *ortho*-benzoquinone, forming stable five-membered chelate rings $\text{M}(\text{DBCat})$, $\text{M}(\text{DBSQ})$ and $\text{M}(\text{DBQ})$ respectively³. All these modes of coordination, shown in Chart 1, are directed primarily by the hardness of the

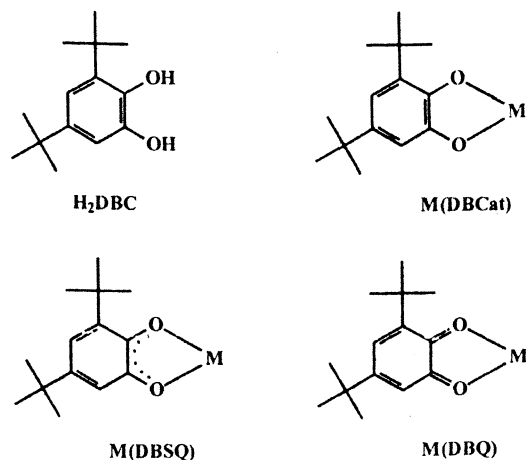


Chart 1

metal center. It is worth mentioning here that while coordination chemistry of the H_2DBC and related ligands is well studied with many transition metal ions⁴, including most of the platinum group of metals⁵, that with rhodium is relatively less explored⁶. To interact with the chosen H_2DBC ligand, we have selected two different rhodium

compounds, a rhodium(I) compound, viz. $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$, and a rhodium(III) compound, viz. $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$. Reactions between H_2DBC and the selected rhodium starting materials have resulted in the formation of interesting rhodium(III) complexes, and herein we describe the chemistry of these complexes, with special emphasis on their formation, structures and, spectral and electrochemical properties.

Experimental

Materials :

Rhodium trichloride was purchased from Arora Matthey, Kolkata, India. $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ was prepared by following a published procedure⁷. 3,5-Di-*tert*-butylcatechol (H_2DBC) and quinolin-8-ol (Hq) were obtained respectively from Sigma Aldrich and Loba Chemie, Mumbai, India. All other chemicals and solvents were reagent grade commercial materials and were used as received. Tetrabutylammonium hexafluorophosphate (TBHP), obtained from Sigma-Aldrich, was used for electrochemical work. Purification of dichloromethane and acetonitrile was performed as reported in the literature⁸.

Preparation of the complexes :

$[\text{Rh}(\text{PPh}_3)(\text{DBSQ})_2\text{Cl}]$: H_2DBC (48 mg, 0.22 mmol) was dissolved in dry benzene (40 ml) and the solution was purged with a stream of dinitrogen for 5 min. Then $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ (100 mg, 0.11 mmol) was added to it and the solution was stirred under a dinitrogen atmosphere for 4 h. Evaporation of the resulting brown solution afforded a solid mass, which was subjected to purification by thin layer chromatography on a silica plate. With benzene as the eluant a brown band separated as the major band, which was extracted with acetonitrile. Evaporation of the extract gave the $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})_2\text{Cl}]$ complex as a crystalline solid. Yield : 60%. Anal. Calcd. for $\text{C}_{46}\text{H}_{55}\text{O}_4\text{PClRh}$: C, 65.68; H, 6.54. Found : C, 65.70; H, 6.51%.

$[\text{Rh}(\text{PPh}_3)(\text{DBSQ})(\text{q})\text{Cl}]$: H_2DBC (24 mg, 0.11 mmol) and Hq (16 mg, 0.11 mmol) were dissolved in dry benzene (40 ml), and the solution was purged with a stream of dinitrogen for 5 min. Then $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ (100 mg, 0.11 mmol) was added to it and the solution was stirred under a dinitrogen atmosphere for 6 h. Evaporation of the resulting brown solution afforded a solid mass, which was subjected to purification by thin layer chromatogra-

phy on a silica plate. With benzene as the eluant a yellowish-brown band separated as the major band, which was extracted with acetonitrile. Evaporation of the extract gave the $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})(\text{q})\text{Cl}]$ complex as a crystalline solid. Yield : 55%. Anal. Calcd. for $\text{C}_{41}\text{H}_{42}\text{O}_3\text{NPClRh}$: C, 64.36; H, 5.49; N, 1.83. Found : C, 64.43; H, 5.50; N, 1.81%.

$[\text{Rh}(\text{DBSQ})_3]$: H_2DBC (126 mg, 0.57 mmol) was dissolved in ethanol (15 ml), and to it triethylamine was added dropwise till the solution was mildly basic. $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (50 mg, 0.19 mmol) was then added to this solution and it was allowed to stir for 24 h. Evaporation of the resulting brown solution afforded a solid mass, which was subjected to purification by thin layer chromatography on a silica plate. With 1 : 10 hexane : benzene as the eluant a brown band separated as the major band, which was extracted with acetonitrile. Evaporation of the extract gave the $[\text{Rh}(\text{DBSQ})_3]$ complex as a crystalline solid. Yield : 54%. Anal. Calcd. for $\text{C}_{42}\text{H}_{60}\text{O}_6\text{Rh}$: C, 66.06; H, 7.86. Found : C, 66.05; H, 7.93%.

Physical measurements :

Microanalyses (C, H, N) were performed using a Heraeus Carlo Erba 1108 elemental analyzer. IR spectra were obtained on a Perkin-Elmer Spectrum RX1 spectrometer with samples prepared as KBr pellets. Electronic spectra were recorded on a JASCO V-570 spectrophotometer. Magnetic susceptibilities were measured using a Sherwood MK-1 balance. ^1H NMR spectrum was recorded in CDCl_3 solution on a Bruker Avance DPX 300 NMR spectrometer using TMS as the internal standard. ESR spectra were recorded with a JEOL JES-FA 200 instrument fitted with a quartz Dewar for measurements at 77 K (liquid dinitrogen). All ESR spectra were calibrated with the aid of DPPH ($g = 2.0037$). Cyclic voltammetric studies were done on a CH Instruments model 600A electrochemical analyzer 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, and the data were collected at 298 K and are uncorrected for junction potentials. Calculation of ground state structures and energy for the complexes were carried out by density functional theory (DFT) method using the GAUSSIAN 03 (B3LYP/SDD-6-31G) package⁹. In all the DFT calculations phenyl rings of the

triphenylphosphine were replaced by hydrogens for simplification.

Crystallography :

Single crystals of complexes $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})_2\text{Cl}]$, $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})(\text{q})\text{Cl}]$ and $[\text{Rh}(\text{DBSQ})_3]$ were obtained by slow evaporation of solvent from acetonitrile solutions of the respective complexes. Selected crystal data and data collection parameters are given in Table 1. Data were collected on a Bruker SMART APEX CCD diffractometer using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). X-Ray data reduction, structure solution and refinement were done using SHELXS-97 and SHELXL-97 programs¹⁰. The structures were solved by the direct methods. CCDC 875258, 875259 and 875260 contain the supplementary crystallographic data.

Results and discussion

Synthesis and structure :

As delineated in the introduction, this work was undertaken to explore the feasibility of synthesizing rhodium complexes of 3,5-di-*tert*-butylcatechol (H_2DBC). This ex-

ploration was initiated with a reaction between H_2DBC and $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$, taken as the rhodium starting material, in 1 : 1 mole ratio in dry benzene. The expectation was to have a mono-catecholate complex of rhodium. The reaction proceeded smoothly at ambient temperature (25°C) under stirring condition, and afforded a mixed-ligand bis-semiquinonate complex of type $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})_2\text{Cl}]$ in a rather low yield¹¹. The low yield of this complex is attributable to the low H_2DBC : Rh mole ratio (1 : 1) used for its synthesis. On increasing the H_2DBC : Rh mole ratio to 2 : 1, yield of the $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})_2\text{Cl}]$ complex increased expectedly. In order to find out the relative disposition of the different ligands around the metal center in this $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})_2\text{Cl}]$ complex, its structure was determined by X-ray crystallography. A selected view of the complex molecule is shown in Fig. 1 and some relevant bond parameters are listed in Table 2. The structure shows that two 3,5-di-*tert*-butylcatechol fragments are coordinated to the rhodium center in a mutually *cis* fashion, and the C–O bond distances in these two ligands clearly indi-

Table 1. Crystallographic data for the complexes

Empirical formula	$[\text{Rh}(\text{PPh}_3)(\text{DBSQ})_2\text{Cl}]$ $\text{C}_{46}\text{H}_{55}\text{ClO}_4\text{PRh}$	$[\text{Rh}(\text{PPh}_3)(\text{DBSQ})(\text{q})\text{Cl}]$ $2(\text{C}_{41}\text{H}_{41}\text{ClINO}_3\text{PRh})$ CH_3CN	$[\text{Rh}(\text{DBSQ})_3]$ $\text{C}_{42}\text{H}_{60}\text{O}_6\text{Rh}$
Formula mass	841.23	1571.21	763.81
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$\text{P}2_1/\text{c}$	$\text{C}2/\text{c}$	Cc
a (Å)	20.7867(17)	29.7657(10)	11.2499(16)
b (Å)	11.4074(10)	13.6072(5)	33.145(5)
c (Å)	18.7352(16)	39.7070(13)	24.000(3)
β (°)	94.512(6)	108.416(2)	102.819(6)
V (Å ³)	4428.8(7)	15258.8(9)	8726.0(2)
Z	4	8	8
λ (Å)	0.71073	0.71073	0.71073
Crystal size (mm ³)	$0.12 \times 0.19 \times 0.24$	$0.16 \times 0.22 \times 0.32$	$0.13 \times 0.17 \times 0.29$
T (K)	296	296	296
μ (mm ⁻¹)	0.521	0.599	0.431
$R1^a$	0.0587	0.0548	0.0821
$wR2^b$	0.1811	0.1736	0.2167
GOF ^c	0.88	0.92	1.03

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR2 = [\sum \{w(F_o^2 - F_c^2)^2\} / \sum \{w(F_o^2)\}]^{1/2}.$$

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

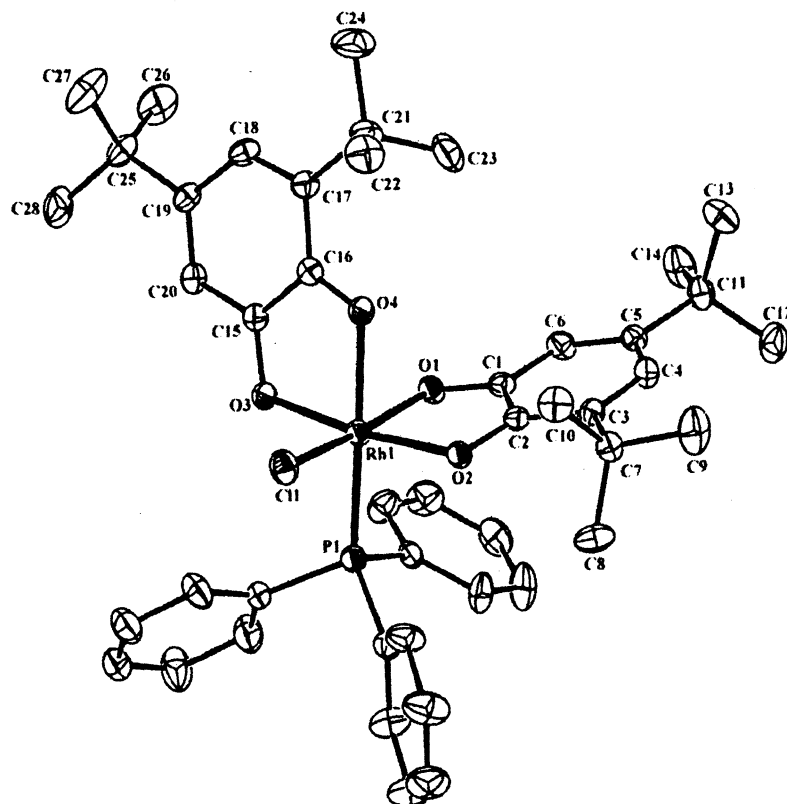
Fig. 1. Structure of the $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})_2\text{Cl}]$ complex.

Table 2. Selected bond distances and bond angles of the complexes

$[\text{Rh}(\text{PPh}_3)(\text{DBSQ})_2\text{Cl}]$			
Bond distances (Å)			
Rh1-C11	2.311(2)	O1-C1	1.296(5)
Rh1-P1	2.269(1)	O2-C2	1.293(5)
Rh1-O1	2.017(3)	O3-C15	1.301(5)
Rh1-O2	2.010(3)	O4-C16	1.283(5)
Rh1-O3	2.002(3)		
Rh1-O4	2.079(3)		
Bond angles (°)			
C11-Rh1-O1	171.09(10)	O1-Rh1-O2	81.72(12)
O2-Rh1-O3	171.85(12)	O3-Rh1-O4	81.74(12)
P1-Rh1-O4	172.18(8)		
$[\text{Rh}(\text{PPh}_3)(\text{DBSQ})(\text{q})\text{Cl}]$			
Bond distances (Å)			
Rh1-C11	2.334(1)	O2-C2	1.279(5)
Rh1-P1	2.273(1)	O3-C20	1.311(5)
Rh1-O1	2.021(3)		
Rh1-O2	2.079(3)		
Rh1-O3	2.030(1)		
Rh1-N1	2.015(3)		

Table-2 (contd.)

Bond angles (°)			
C11-Rh1-O3	174.53(8)	O1-Rh1-O2	81.61(10)
N1-Rh1-O1	169.25(12)	O3-Rh1-N1	82.31(12)
P1-Rh1-O2	174.65(8)		
$[\text{Rh}(\text{DBSQ})_3]$			
Bond distances (Å)			
Rh1-O1	1.955(18)	O1-C1	1.279(15)
Rh1-O2	1.931(14)	O2-C2	1.330(17)
Rh1-O3	2.001(13)	O3-C15	1.303(15)
Rh1-O4	1.996(18)	O4-C16	1.339(18)
Rh1-O5	1.987(15)	O5-C29	1.300(20)
Rh1-O6	1.985(13)	O6-C30	1.305(19)
Bond angles (°)			
O1-Rh1-O4	173.6(6)	O1-Rh1-O2	84.4(6)
O2-Rh1-O5	175.0(6)	O3-Rh1-O4	84.0(6)
O3-Rh1-O6	175.3(6)	O5-Rh1-O6	82.7(6)

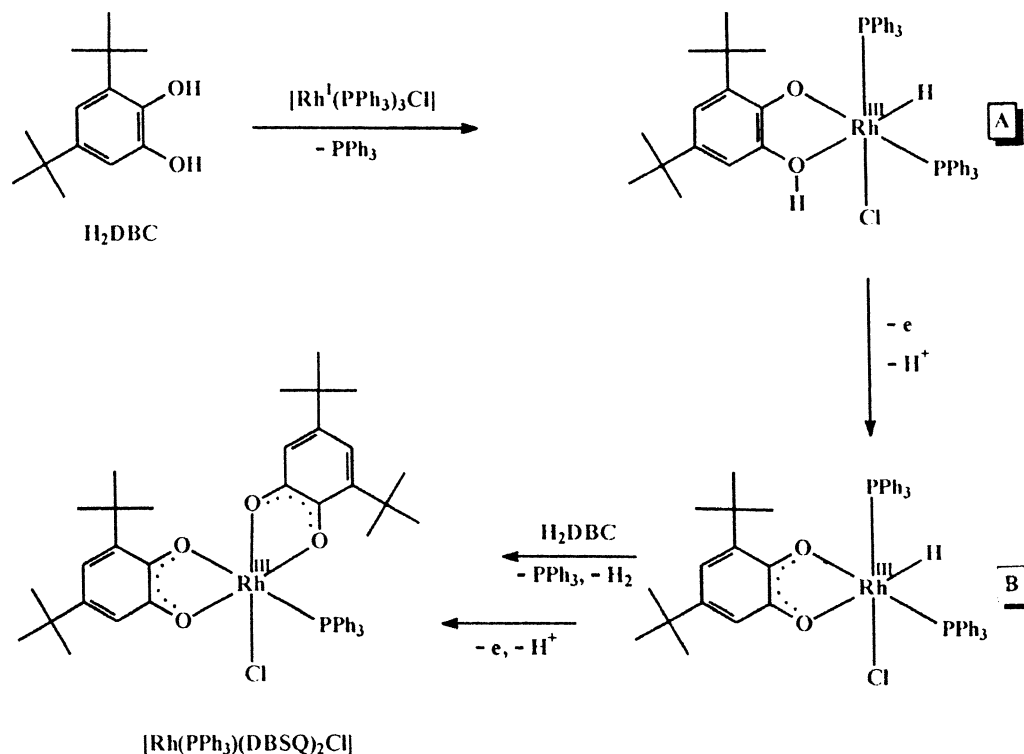
cate that both of them are existing in the semi-quinonate form. A triphenylphosphine and a chloride are also coordinated to the metal center, which are mutually *cis*. All four rhodium-oxygen bond lengths compare well with the

reported values^{6d}. The Rh-P and Rh-Cl bond distances are also found to be normal¹. Hence in this complex rhodium is nested in a O₄PCl coordination sphere, which is significantly distorted from ideal octahedral geometry, as reflected in all the bond parameters around rhodium.

Formation of the bis-semiquinonate complex, even with a metal-H₂DBC mole ratio of 1 : 1, has been quite intriguing. The probable steps behind formation of the bis-complex are outlined in Scheme 1. On interaction of H₂DBC with the rhodium(I) center in [Rh(PPh₃)₃Cl], activation of one of the phenolic O–H bonds in H₂DBC

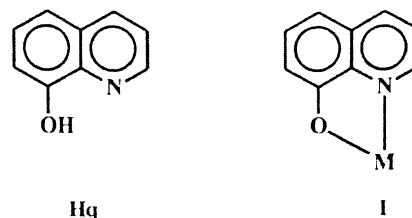
tion of molecular hydrogen and PPh₃, and then electron and proton loss takes place from the newly coordinated HDBC ligand yielding the [Rh(PPh₃)(DBSQ)₂Cl] complex as the final product.

Formation of a highly reactive hydrido-intermediate via activation of a phenolic O–H bond of H₂DBC by the rhodium(I) center in [Rh(PPh₃)₃Cl] and its subsequent rapid reaction with a second molecule of the same ligand (Scheme 1) prompted us to attempt a reaction of [Rh(PPh₃)₃Cl] with a 1 : 1 mixture of two phenolic ligands, viz. 3,5-di-*tert*-butylcatechol (H₂DBC) and quinolin-8-ol



Scheme 1. Probable steps behind formation of the [Rh(PPh₃)(DBSQ)₂Cl] complex.

seems to take place in the initial step, whereby rhodium inserts oxidatively into the phenolic O–H bond producing a hydrido-complex of type [Rh(PPh₃)₂(HDBC)(H)Cl] as the active intermediate (**A**). The coordinated HDBC ligand in this hydrido species (**A**) then undergoes a one-electron aerial oxidation, associated with dissociation of the remaining phenolic OH proton, producing a second hydrido-intermediate of type [Rh(PPh₃)₂(DBSQ)(H)Cl] (**B**). In the following steps, another molecule of H₂DBC reacts with **B**, whereby it binds to rhodium via elimina-



(Hq) with an aim and expectation of obtaining a mixed-ligand complex of type [Rh(PPh₃)(DBSQ)(q)Cl]. This reaction was carried out in a similar way as before, and

as anticipated, it indeed afforded the targeted complex in reasonable yield¹². Identity of this $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})(\text{q})\text{Cl}]$ complex has been authenticated by its crystal structure determination, which (Fig. 2) shows that both the bidentate ligands are coordinated to rhodium in the usual manner and, a PPh_3 and a chloride are coordinated to the metal center. The observed bond parameters (Table 2) are all found to be quite usual¹. The probable steps behind formation of this mixed-bis complex is illustrated in Scheme 2. As in the earlier reaction (Scheme 1), two hydrido-intermediates (**A** and **B**) are believed to be formed sequentially, and thereafter reaction with Hq takes place yielding $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})(\text{q})\text{Cl}]$. It needs to be noted here that an alternative scheme, where initial reaction of Hq with $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ may take place generating a different hydrido-intermediate of type $[\text{Rh}(\text{PPh}_3)_2(\text{q})(\text{H})\text{Cl}]$, cannot, in principle, be ruled out. It is relevant to mention in this context that well-characterized rhodium hydrido complexes are scarce in the literature¹³.

Formation of both the above two complexes, viz. $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})_2\text{Cl}]$ and $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})(\text{q})\text{Cl}]$, proceeded through an initial redox reaction whereby a phenolic O–H bond activation was brought about by the rhodium(I) center in the starting $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ complex. In order to avoid this redox step in the beginning, and to see its consequences on the nature of product, reaction of H_2DBC was planned with a rhodium(III) center, viz. rhodium trichloride. The reaction proceeded smoothly in slightly basic medium, and afforded the tris-semiquinonate complex, $[\text{Rh}(\text{DBSQ})_3]$, in decent yield. As the DBSQ ligand is unsymmetric bidentate in nature, the $[\text{Rh}(\text{DBSQ})_3]$ complex may, in principle, exist in two geometries, viz. facial and meridional. In order to find out the stereochemistry of the $[\text{Rh}(\text{DBSQ})_3]$ complex, its structure was determined by X-ray crystallography. The structure (Fig. 3) shows that this $[\text{Rh}(\text{DBSQ})_3]$ complex has the facial geometry. Though quality of the structure is relatively poor, all six carbon-oxygen bond lengths are simi-

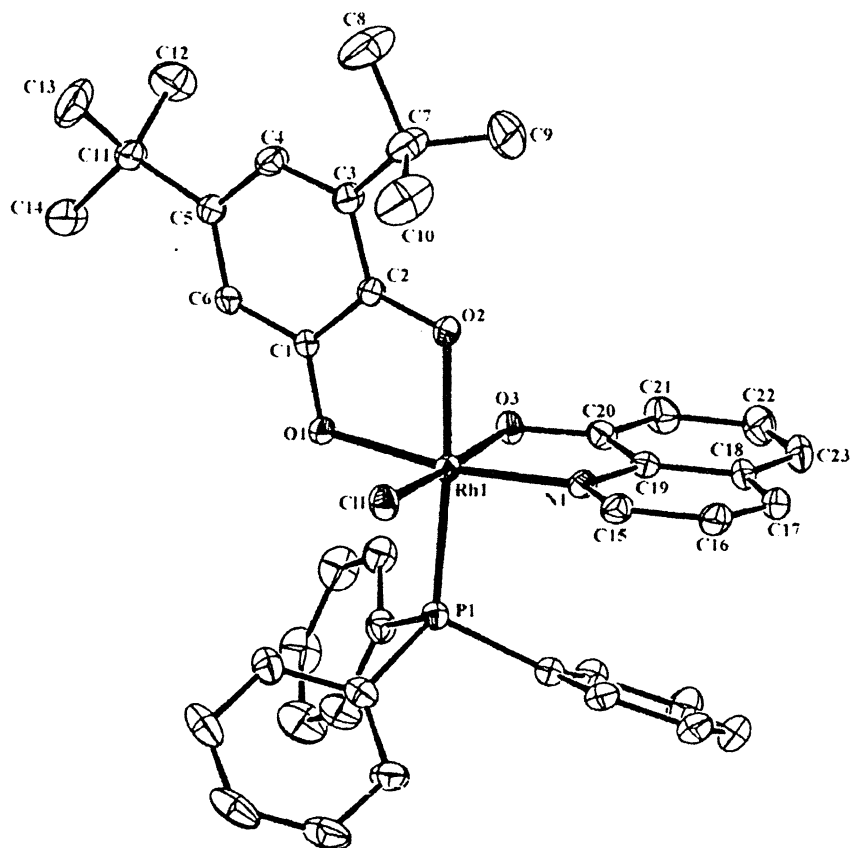
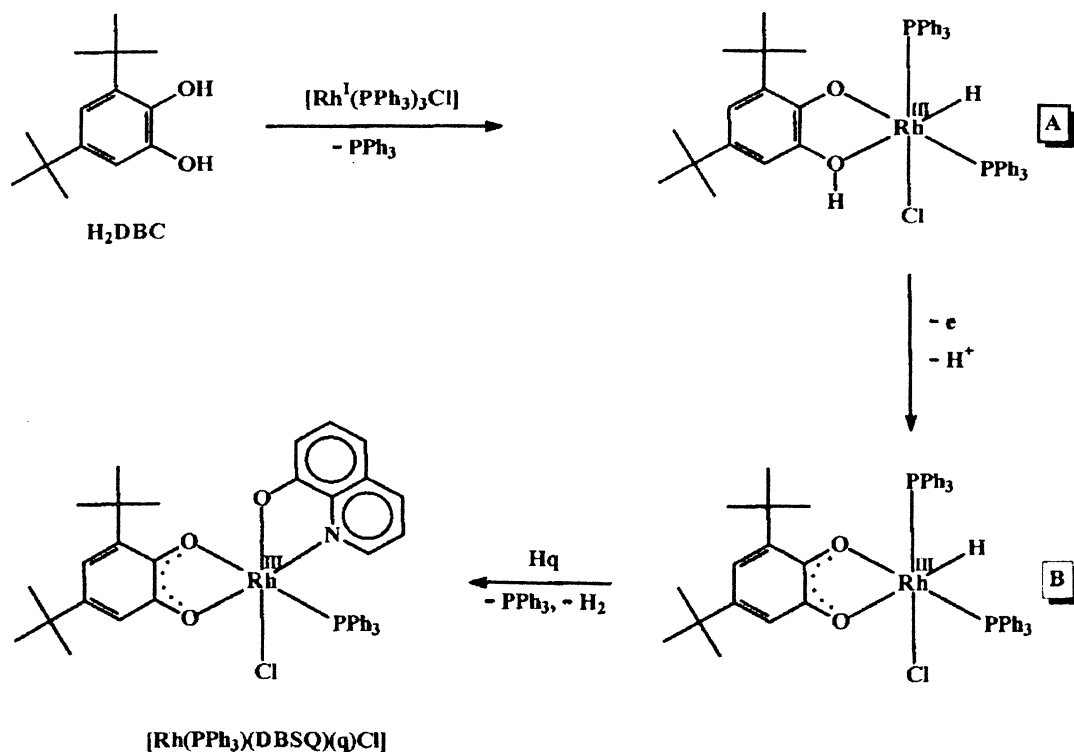


Fig. 2. Structure of the $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})(\text{q})\text{Cl}]$ complex.



Scheme 2. Probable steps behind formation of the $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})(\text{q})\text{Cl}]$ complex.

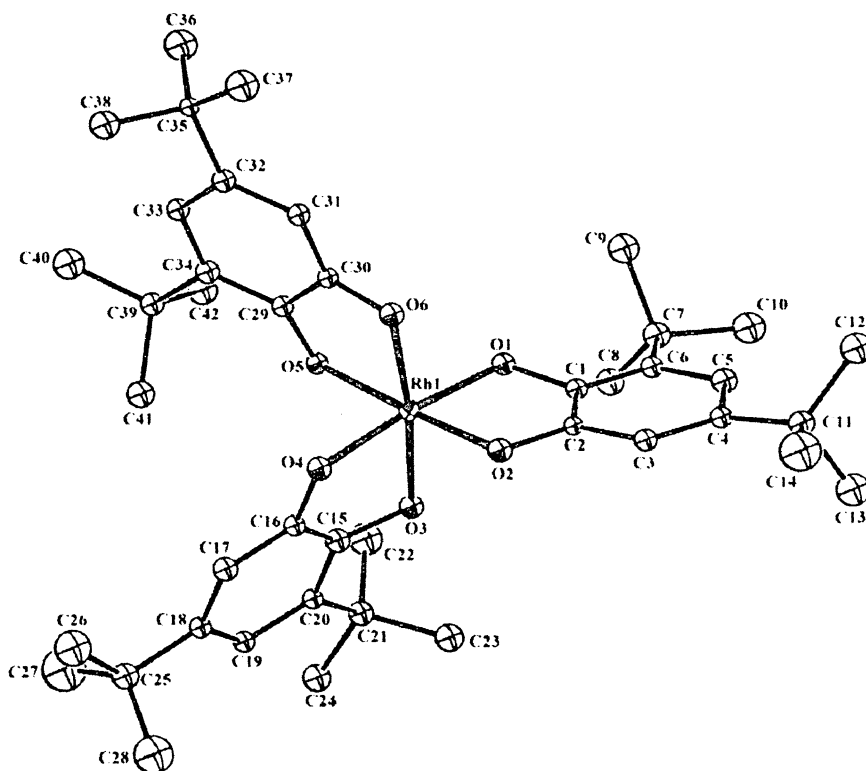


Fig. 3. Structure of the $[\text{Rh}(\text{DBSQ})_3]$ complex.

lar (Table 2) and are indicative of semiquinonate ligand. Also, all six rhodium-oxygen bond lengths (Table 2) are consistent with rhodium-oxygen bond distances in rhodium-semiquinone complex^{6d}. Formation of this tris-complex was not associated with any metal-centered redox changes in the initial step. However, the overall reaction was associated with elimination of three equivalents of HCl (facilitated by the basic medium) and, proton and electron transfer from initially coordinated HDBC ligands.

Spectral properties :

In the $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})_2\text{Cl}]$ complex, the trivalent rhodium center is diamagnetic (low-spin d^6 , $S = 0$), but it is linked to two one-electron paramagnetic semiquinonate radical ligands. However, magnetic susceptibility measurements show that the $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})_2\text{Cl}]$ complex is diamagnetic, and this observed diamagnetism is attributable to antiferromagnetic coupling between the two coordinated semiquinonate radical ligands. ^1H NMR spectrum of this complex has been recorded in CDCl_3 solution, which shows broad signals within 7.46–7.82 ppm due to the phenyl protons of the PPh_3 ligand. In addition, most of the expected signals from the coordinated DBSQ ligands are also clearly observed. For example, sharp signals at 1.22 ppm and 1.25 ppm are observed for the *tert*-butyl groups. Out of the four expected singlets for the aromatic protons, two are distinctly observed at 6.20 ppm and 6.93 ppm, while the other two singlets could not be identified, probably due to their overlap with the PPh_3 signals.

In the $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})(\text{q})\text{Cl}]$ complex, the same diamagnetic metal center is linked to one semiquinonate radical ligand, and as expected, this complex is found to be one-electron paramagnetic ($\mu_{\text{eff}} = 1.87 \mu_{\text{B}}$). Similarly in the $[\text{Rh}(\text{DBSQ})_3]$ complex, three semiquinonate ligands are bound to the diamagnetic metal center, and this complex is also found to be one-electron paramagnetic ($\mu_{\text{eff}} = 1.79 \mu_{\text{B}}$), which is believed to result from antiferromagnetic coupling between two of the three radical ligands. ESR spectra of both the paramagnetic complexes, viz. $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})(\text{q})\text{Cl}]$ and $[\text{Rh}(\text{DBSQ})_3]$, have been recorded in acetonitrile solution, at 77 K. Spectra of both the complexes (Fig. 4) show a single sharp signal at $g \sim 2.0$, and thus testify presence of the uncoupled semiquinonate radical spin in these two complexes.

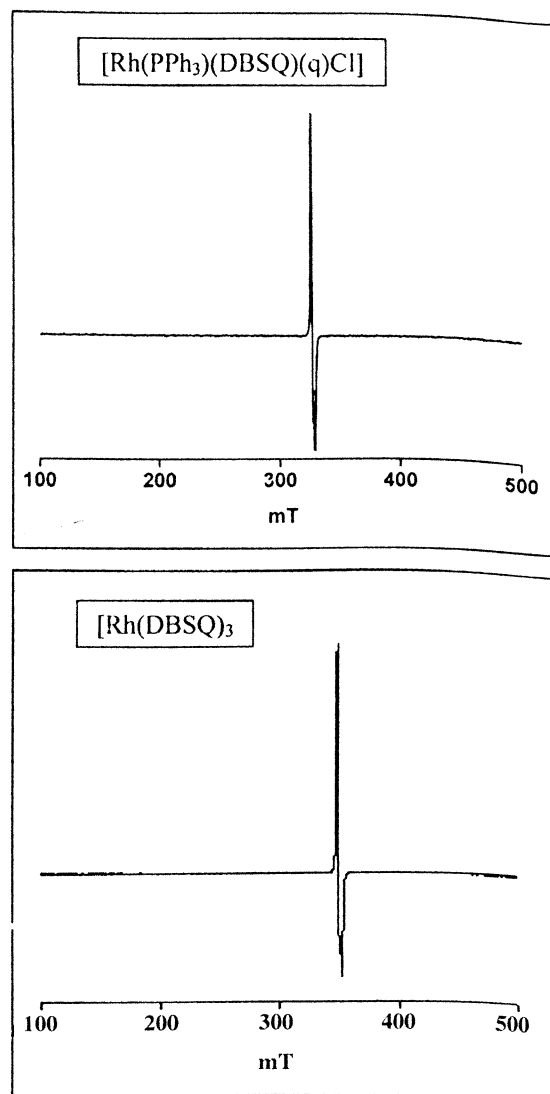


Fig. 4. ESR spectra of the $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})(\text{q})\text{Cl}]$ and $[\text{Rh}(\text{DBSQ})_3]$ complexes in acetonitrile solution at 77 K.

Infrared spectra of all the complexes show many vibrations of different intensities in the region 4000–400 cm^{-1} . Assignment of each individual band to a specific vibration has not been attempted. In complexes $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})_2\text{Cl}]$ and $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})(\text{q})\text{Cl}]$ three strong bands are observed near 535, 693 and 749 cm^{-1} , which are attributed to the coordinated PPh_3 ligand. Comparison with the spectrum of $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ shows the presence of several new bands in $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})_2\text{Cl}]$, such as bands at 1638, 1360, 1271, 1265, 1207, 1138 cm^{-1} , which must be due to the coordinated DBSQ ligands. Of these, the bands at 1360, 1265, 1207, 1138 cm^{-1} are attributable to the *tert*-butyl groups^{6d}. In $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})(\text{q})\text{Cl}]$, besides bands due to PPh_3 and

DBSQ ligands, new bands are observed at 820, 1095, 1318, 1374, 1437, 1462, 1500 and 1573 cm^{-1} , due to the coordinated quinolinolate ligand. In $[\text{Rh}(\text{DBSQ})_3]$, bands due to the coordinated DBSQ ligands are only observed, as expected. The IR and NMR/ESR spectral data of the $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})_2\text{Cl}]$, $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})(\text{q})\text{Cl}]$ and $[\text{Rh}(\text{DBSQ})_3]$ complexes are therefore consistent with their composition.

All the complexes are found to be soluble in common organic solvents like methanol, ethanol, acetone, acetonitrile, dichloromethane, chloroform, etc., producing brown solutions for $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})_2\text{Cl}]$ and $[\text{Rh}(\text{DBSQ})_3]$, and brown-yellow solution for $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})(\text{q})\text{Cl}]$. Electronic spectra of these complexes have been recorded in dichloromethane solution and spectral data are presented in Table 3. The spectra show several absorptions in the

visible and ultraviolet regions. The intense absorptions in the ultraviolet region are believed to be due to allowed transitions within the ligand orbitals. To have an understanding of the origin of the absorptions in the visible region, DFT calculations have been performed on all three complexes. Composition of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are given in Table 4. In $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})_2\text{Cl}]$ the HOMO is mostly spread over the two DBSQ ligands with minor contribution coming from the metal center and the chloride. Similarly the LUMO also has major contribution from the two DBSQ ligands. Contour plots of the HOMO and LUMO of this complex is shown in Fig. 5. Hence the absorption observed at 463 nm in this complex is assignable to a transition from the HOMO to the LUMO, both of which are

Table 3. Electronic spectral and cyclic voltammetric data

Complex	Electronic spectral data ^a	Cyclic voltammetric data ^b
	λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$)	E_{pa}^c , E_{pc}^d V vs SCE
$[\text{Rh}(\text{PPh}_3)(\text{DBSQ})_2\text{Cl}]$	463(900), 387(1600), 269 ^s (17400), 224(62200)	0.93 ^c , -0.21 ^d
$[\text{Rh}(\text{PPh}_3)(\text{DBSQ})(\text{q})\text{Cl}]$	428(2600), 313(9500), 269(18800), 246 ^s (28500), 222 ^s (54000)	0.76 ^c , -0.27 ^d
$[\text{Rh}(\text{DBSQ})_3]$	485(3900), 300(16500), 281(19300), 221 ^s (86000)	1.10 ^c , -0.22 ^d

^aIn dichloromethane solution, ^sshoulder, ^bacetonitrile solution, supporting electrolyte TBHP, 50 mV/s, ^c E_{pa} value, where E_{pa} is anodic peak potential, ^d E_{pc} value, where E_{pc} is cathodic peak potential.

Table 4. Composition of selected molecular orbitals of the complexes

Complex	Contributing fragments	%Contribution of the fragments to	
		HOMO	LUMO
$[\text{Rh}(\text{PPh}_3)(\text{DBSQ})_2\text{Cl}]$	Rh	2.97	5.87
	Cl	0.68	0.60
	PPh ₃	0.0	0.00
	DBSQ ^x	53.92	53.04
	DBSQ ^y	42.43	40.49
$[\text{Rh}(\text{PPh}_3)(\text{DBSQ})(\text{q})\text{Cl}]$	Rh	8.18	6.64
	Cl	0.99	0.15
	PPh ₃	0.0	0.0
	DBSQ	69.34	18.20
	q	21.49	75.01
$[\text{Rh}(\text{DBSQ})_3]$	Rh	2.60	8.00
	DBSQ	50.14	29.01
	DBSQ	36.97	40.17
	DBSQ	10.29	22.82

^xThe DBSQ ligand which has one oxygen *trans* to the coordinated P1.

^yThe DBSQ ligand which has one oxygen *trans* to the coordinated C11.

delocalized almost entirely over the two semiquinonate ligands. In $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})(\text{q})\text{Cl}]$, the HOMO and LUMO are mostly spread over the DBSQ and quinolinolate ligands, and hence the absorption at 428 nm in this complex is assignable to a transition from the HOMO to the LUMO both of which have a mixed nature. In the $[\text{Rh}(\text{DBSQ})_3]$ complex, both the HOMO and LUMO are spread almost entirely over the coordinated semiquinonate ligands, and therefore the absorption at 485 nm is assignable to transitions within orbitals of the coordinated DBSQ ligands.

Electrochemical properties of the $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})_2\text{Cl}]$, $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})(\text{q})\text{Cl}]$ and $[\text{Rh}(\text{DBSQ})_3]$ complexes have been studied by cyclic voltammetry in acetonitrile solution (0.1 M TBHP). Voltammetric data are presented in Table 3. All three complexes show an irreversible oxidative response on the positive side of SCE and an irreversible reductive response on the negative side. In view of the composition of the HOMO and LUMO, in $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})_2\text{Cl}]$ complex, both the oxidative and reductive responses are assignable respec-

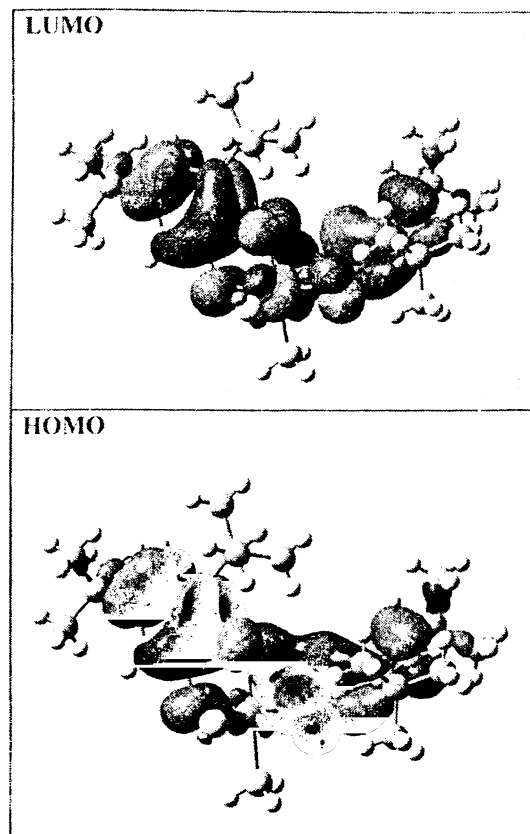


Fig. 5. Contour plot of HOMO and LUMO of the $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})_2\text{Cl}]$ complex.

tively to oxidation and reduction of the coordinated DBSQ ligand. In case of $[\text{Rh}(\text{PPh}_3)(\text{DBSQ})(\text{q})\text{Cl}]$ complex, based on composition of the HOMO and LUMO, the oxidative response is assigned to oxidation of the DBSQ ligand and the reductive response is assigned to reduction of the coordinated quinolinolate ligand. Similarly, in case of $[\text{Rh}(\text{DBSQ})_3]$ complex, both the oxidative and reductive responses are assigned to oxidation and reduction of the coordinated ligands.

Conclusion :

The present study shows that upon reaction of the rhodium(I) center in $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ with a bidentate chelating ligand (of type HL-L) containing a potentially dissociable acidic hydrogen, a rhodium(III) hydrido complex of type $[\text{Rh}(\text{PPh}_3)_2(\text{L-L})(\text{H})\text{Cl}]$ is formed in the initial step via oxidative addition of the metal center into the acidic fragment. The subsequent steps are dictated by this very reactive hydrido intermediate. This has been manifested in the reaction of 3,5-di-*tert*-butylcatechol (H_2DBC)

with $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$. The present study also demonstrates that, instead of rhodium(I), if rhodium(III) center is allowed to react with the same H_2DBC ligand, no metal-centered redox reaction takes place, and a tris-complex is obtained via simple ligand displacement reaction.

Acknowledgement

Financial assistance received from the Department of Science and Technology, New Delhi [Grant No. SR/S1/RFIC-01/2009] is gratefully acknowledged. The authors thank Dr. T. K. Paine of the Indian Association for the Cultivation of Science, Kolkata, for his help in recording the ESR spectra. Poulami Sengupta thanks the Council of Scientific and Industrial Research, New Delhi, for her fellowship [Grant No. 09/096(0583)/2007-EMR-I].

Appendix A

Supplementary data :

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC numbers 875258, 875259 and 875260.

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