Interaction of 2-(arylazo)phenols with rhodium. Usual coordination vs. C–H and C–C activation

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Abstract

Reaction of 2-(2′-hydroxyphenylazo)phenol with [Rh(PPh$_3$)$_3$Cl] in refluxing benzene in presence of triethylamine afforded a red complex in which the ligand is coordinated to rhodium as a tridentate O,N,O-donor. However, similar reaction of [Rh(PPh$_3$)$_3$Cl] with 2-(2′-carboxyphenylazo)-4-methylphenol yielded two complexes, viz. a blue one and a green one. In both the complexes the ligand is coordinated as C,N,O-donor. However, in the blue complex orthometallation takes place from the ortho-carbon atom, which bears –COOH group via decarboxylation and in green one orthometallation occurs from the other ortho-carbon. Structures of all the three complexes were determined by X-ray crystallography. In all the three complexes rhodium is sharing the equatorial plane with the tridentate ligand and a chloride, and the two triphenylphosphines are axially disposed. All of the complexes show intense MLCT transitions in the visible region. Cyclic voltammetry on these complexes shows a Rh(III)–Rh(IV) oxidation on the positive side of SCE and a reduction of the coordinated azophenolate ligand on the negative side.
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Keywords: 2-(Arylazo)phenols; Rhodium; Usual coordination; C–H and C–C activation

1. Introduction

There is considerable current interest in the reactions of transition metals with suitable organic ligands leading to the formation of metal–carbon bond(s) via C–H or C–C activation [1]. Formation of such organometallic complexes is of particular importance as they often serve as reactive intermediates in metal-mediated transformation of organic substrates [1,2]. The present work has originated from our interest in this area [3]. During our recent studies we have observed that 2-(arylazo)phenols (**1**) readily undergo cyclometallation (**2**) via platinum metal mediated C–H activation at one ortho-position of the phenyl ring in the arylazo fragment [3a,3c,3g,3j]. In the present study

we have selected two modified 2-(arylazo)phenols, viz. 2-(2′-hydroxyphenylazo)phenol (**3**) and 2-(2′-carboxyphenylazo)-4-methylphenol (**4**), in both of which one ortho-position of the phenyl ring in the arylazo fragment is strategically blocked by a hydroxy group and a carboxy group respectively. These two ligands are known to bind metal ions usually as dianionic tridentate O,N,O-donors forming stable chelates (**5** and **6**) [4]. However, in view of the possible free rotation of the phenyl ring in the arylazo fragment around the C–N bond, cylometallation of these ligands is also, in principle, possible (**7** and **8**). The present study was initiated to explore these possibilities in these two ligands (**3** and **4**), and rhodium has been chosen as the platinum metal to interact with these selected ligands. As the source of rhodium the Wilkinson's catalyst, [Rh(PPh$_3$)$_3$Cl], has been utilized. This particular complex has been picked up as the rhodium starting material

because of its recognized efficiency to undergo facile reaction with phenolic ligands and, more importantly, its demonstrated ability to accommodate tridentate ligands via dissociation of a triphenylphosphine [3a,3d,3k,3l]. Reaction of [Rh(PPh$_3$)$_3$Cl] with the ligands **3** and **4** has been found to afford complexes, where the ligands have displayed interesting modes of binding. Herein we wish to report the chemistry of all these complexes, with special reference to their formation, structure, and electrochemical properties.
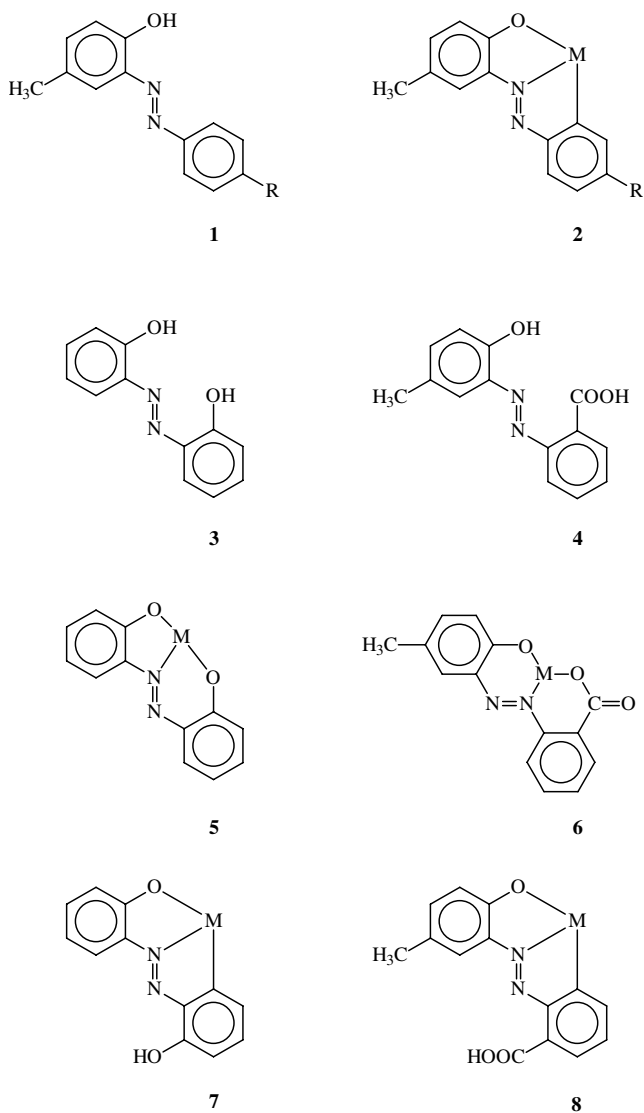
2. Results and discussion

2.1. Synthesis and characterization

Reaction of 2-(2′-hydroxyphenylazo)phenol (**3**) with [Rh(PPh$_3$)$_3$Cl] has been carried out in refluxing benzene in the presence of triethylamine to afford a red complex

(**9**) in a decent yield. Preliminary (microanalytical, magnetic, spectral, etc.) characterizations on complex **9** indicate that ligand **3** is probably coordinated to the metal center in the expected dianionic tridentate O,N,O-fashion (**5**) along with two triphenylphosphines and a chloride. To authenticate the structure of complex **9**, as well as the binding mode of ligand **3** in it, its structure has been determined by X-ray crystallography. The structure is shown in Fig. 1 and selected bond parameters are listed in Table 1. The structure shows that ligand **3** is indeed bound to rhodium in the expected dianionic tridentate fashion (**5**), forming two adjacent five- and six-membered rings with bite angles of 77.45° and 98.08°, respectively. The other three coordination sites are occupied by two triphenylphosphines and a chloride. The overall structure is a distorted octahedron with the O,N,O-donor ligand and the chloride occupying the equatorial plane with the metal at the center and two axially disposed PPh$_3$ ligands. The observed Rh–Cl, Rh–P, Rh–O, and Rh–N bond distances, as well as the C–O and N–N lengths in the O,N,O-chelate, are all quite normal [3a,5]. In complex **9** rhodium is existing in its +3 oxidation state, and hence its formation from the rhodium(I) starting material (Scheme 1) involves loss of two electrons from the metal center. In the presence of triethylamine ligand **3** also undergoes loss of two protons. So in effect the doubly deprotonated ligand **3** binds oxidatively to the metal center with simultaneous dissociation of a PPh$_3$ from [Rh(PPh$_3$)$_3$Cl] during the formation of complex **9**.

Reaction of the other chosen ligand, viz. 2-(2′-carboxyphenylazo)-4-methylphenol (**4**), with [Rh(PPh$_3$)$_3$Cl] also proceeds smoothly under similar experimental condition as before. This reaction, however, yielded two complexes
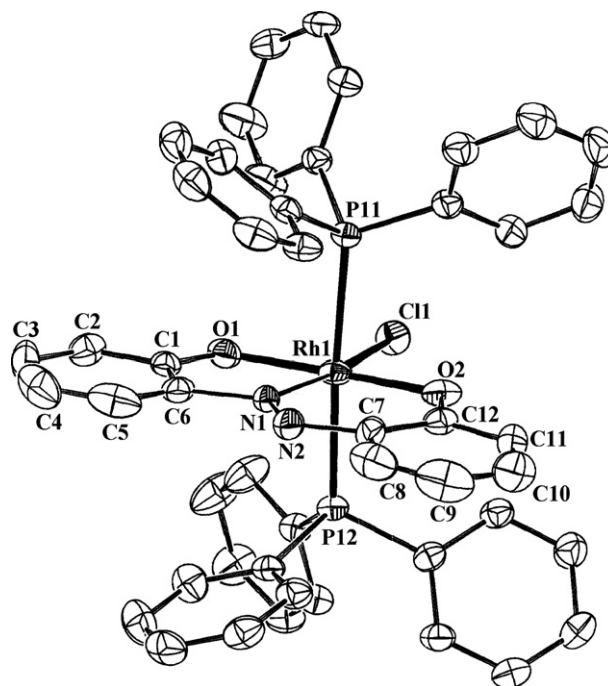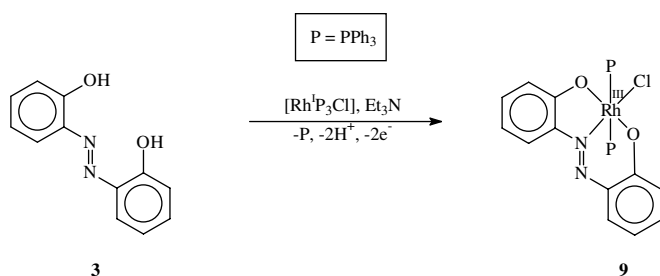

Fig. 1. View of complex **9**.

Table 1
Selected bond lengths (Å) and bond angles (°) for complexes 9–11

Complex 9		Complex 10		Complex 11	
Bond lengths (Å)					
Rh(1)–Cl(1)	2.3643(6)	Rh(1)–Cl(1)	2.398(3)	Rh–Cl(1)	2.3868(10)
Rh(1)–P(11)	2.3827(8)	Rh(1)–P(1)	2.371(3)	Rh–P(1)	2.3717(12)
Rh(1)–P(12)	2.3720(8)	Rh(1)–P(2)	2.389(3)	Rh–P(2)	2.3641(12)
Rh(1)–O(1)	2.0263(17)	Rh(1)–O(85)	2.209(4)	Rh–O(1)	2.195(3)
Rh(1)–N(1)	1.998(4)	Rh(1)–N(78)	1.960(4)	Rh–N(1)	1.956(3)
Rh(1)–O(2)	2.0119(17)	Rh(1)–C(71)	2.005(4)	Rh–C(12)	2.008(4)
C(1)–O(1)	1.325(3)	C(84)–O(85)	1.317(5)	C(1)–O(1)	1.294(5)
N(1)–N(2)	1.273(5)	N(77)–N(78)	1.296(4)	N(1)–N(2)	1.270(4)
C(6)–N(1)	1.499(4)	C(811)–N(77)	1.401(5)	C(6)–N(1)	1.380(5)
C(7)–N(2)	1.393(5)	C(79)–N(78)	1.394(5)	C(7)–N(2)	1.390(5)
C(12)–O(2)	1.300(3)	C(71)–C(811)	1.418(5)	C(7)–C(12)	1.417(5)
				C(8)–C(14)	1.498(5)
				C(14)–O(2)	1.338(6)
				C(14)–O(3)	1.204(6)
Bond angles (°)					
P(11)–Rh(1)–P(12)	175.96(3)	P(1)–Rh(1)–P(2)	173.72(4)	P(1)–Rh–P(2)	173.37(4)
O(1)–Rh(1)–O(2)	175.51(7)	O(85)–Rh(1)–C(71)	159.47(12)	O(1)–Rh–C(12)	159.39(13)
Cl(1)–Rh(1)–N(1)	168.98(11)	Cl(1)–Rh(1)–N(78)	178.67(9)	Cl–Rh–N(1)	174.78(10)
N(1)–Rh(1)–O(1)	77.45(12)	N(78)–Rh(1)–O(85)	80.07(11)	N(1)–Rh–O(1)	80.02(12)
N(1)–Rh(1)–O(2)	98.08(12)	N(78)–Rh(1)–C(71)	79.43(13)	N(1)–Rh–C(12)	79.38(14)
				O(2)–C(14)–O(3)	119.6(4)

with distinctly different colors, viz. a blue complex (10) and a green complex (11). The preliminary characterization data of these complexes have failed to indicate any definite coordination mode of ligand 4 in them. To find out the binding mode(s) of ligand 4 in these complexes, as well as their stereochemistries, structure of both the complexes has been determined by X-ray crystallography. The structures are shown in Fig. 2 (complex 10) and Fig. 3 (complex 11) and relevant bond parameters are given in Table 1. Structure of complex 10 (Fig. 2) shows that in it ligand 4 is coordinated to rhodium as a dianionic C,N,O-donor via decarboxylation, forming two adjacent five-membered rings with bite angles of 80.07° and 79.43°. Two triphenylphosphines and a chloride are also coordinated to the metal center as before. The C,N,O-coordinated ligand, rhodium and the chloride are sharing one equatorial plane and the two PPh$_3$ ligands are occupying the axial positions. The observed bond parameters compare well with those observed in complex 9. However, the Rh–O bond is significantly longer than the corresponding Rh–O bond in complex 9, which may be attributed to the strain developed due

to formation of two five-membered chelate rings by the C,N,O-bound ligand. Structure of the complex 11 (Fig. 3) shows that in it ligand 4 is again coordinated to rhodium as a C,N,O-donor, but in a different fashion. In this complex orthometallation has taken place from the other ortho-carbon, which does not bear the carboxy group. Besides presence of the –COOH group in the C,N,O-donor ligand, other structural features in this green complex are comparable to those observed in the complex 10.
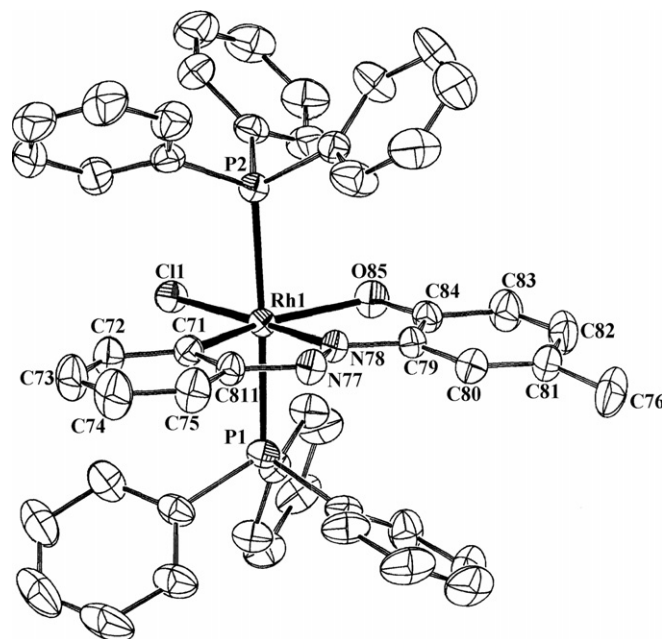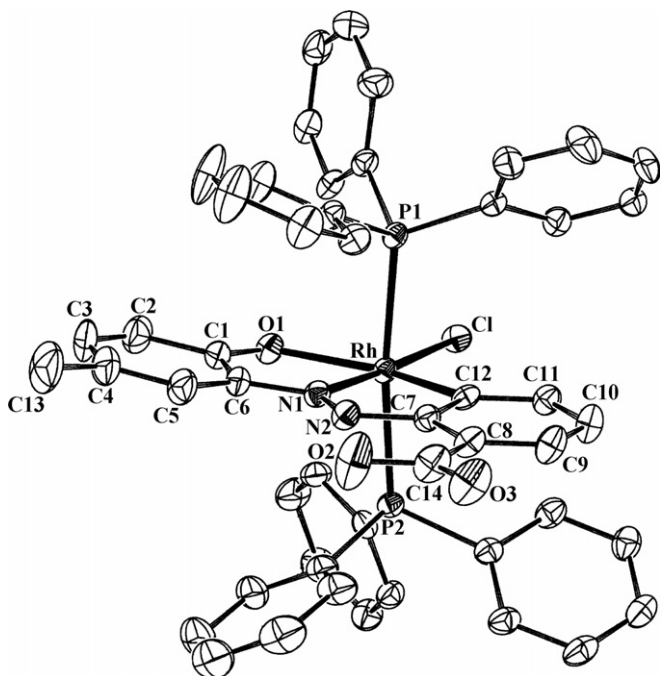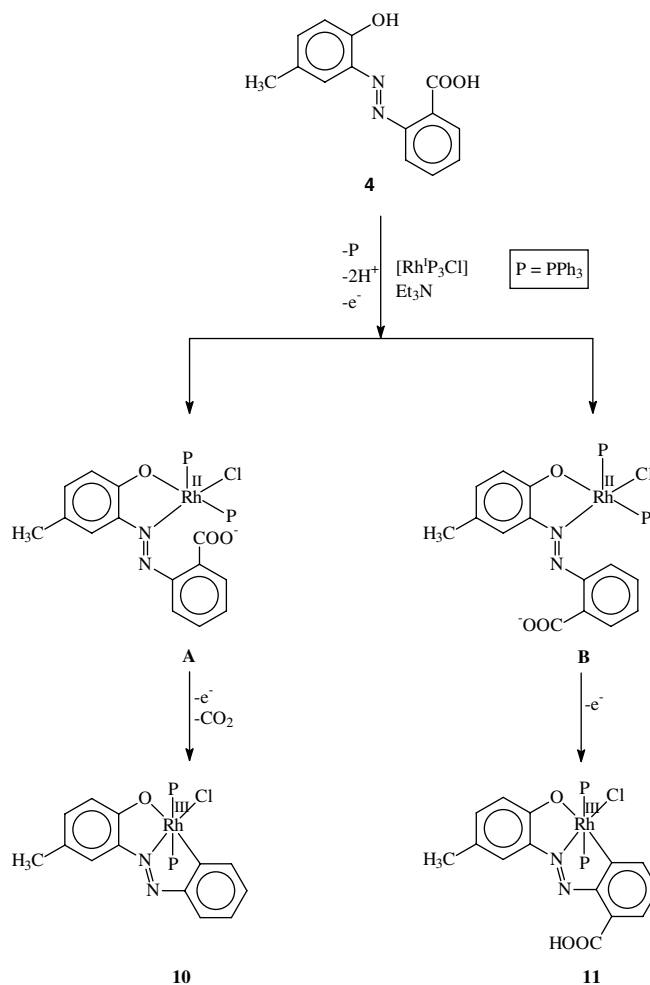

Fig. 2. View of complex 10.

Scheme 1. Formation of complex 9.

Fig. 3. View of complex **11**.

Scheme 2. Probable steps for the formation of complexes **10** and **11**.

Formation of these two complexes from the same reaction has been quite interesting, and the speculated steps involved in the synthetic reaction are illustrated in Scheme 2. In the presence of NEt$_3$ both the phenolic and carboxylic protons of ligand **4** are believed to get dissociated and the resulting dianionic ligand coordinates the metal center in [Rh(PPh$_3$)$_3$Cl] as a N,O-donor with loss of an electron from the metal center and dissociation of a PPh$_3$, to generate a reactive pentacoordinated rhodium(II) intermediate. During the free rotation of the pendent phenyl ring around the C–N bond the ortho-carbons come in close proximity to the metal center, facilitating either a C–C activation (in rotamer **A**) or a C–H activation (in rotamer **B**). It is interesting to note that in the rotamer **A** the carboxylate fragment, though may appear close to the metal center, is actually disposed so far away from the metal center that it cannot participate in coordination [6]. Thus complex **10** is believed to form from rotamer **A** via loss of carbondioxide [7] along with loss of an electron from the metal center, while complex **11** is formed from rotamer **B** via loss of a proton and a one-electron oxidation of the metal center. The free carboxylate fragment in complex **11** is likely to remain in the deprotonated form in the presence of NEt$_3$ (as the HNEt$_3^+$ salt). However, during the work-up the HNEt$_3^+$ salt probably undergoes usual hydrolysis to afford the free COOH fragment in complex **11**. It is interesting to note that similar cylometallation of some phenolic Schiff bases mediated by [Rh(PPh$_3$)$_3$Cl] has been observed before [3l,8]. It may also be noted here that in the first synthetic reaction between ligand **3** and [Rh(PPh$_3$)$_3$Cl] no orthometallated product (containing **7**) is obtained, probably due to the much higher acidity of the phenolic O–H compared to the phenyl C–H.

2.2. Spectral studies

Infrared spectra of all the complexes show many bands of varying intensities within 400–4000 cm^{-1}. Assignment of each individual band to a specific vibration has not been attempted. However, three strong bands observed around 746, 695, and 516 cm^{-1} are attributable to the coordinated PPh$_3$ ligands [3]. Spectrum of the complex **11** shows a strong band at 1730 cm^{-1}, which is absent in complex **10**, is due to the COOH fragment. Magnetic susceptibility measurements show that all the three complexes are diamagnetic, which corresponds to the trivalent state of rhodium (low-spin d^6, $S = 0$) in them. ^{1}H NMR spectra of complexes **9–11** have been recorded in CDCl$_3$ solution. The spectral data of each complex, given in experimental section, are found to be in good agreement with its composition. The methyl signals of the coordinated azo ligand in complexes **10** and **11** are observed around 2.00 ppm. In the spectrum of complex **11**, the carboxylic proton signal is observed clearly at 12.41 ppm.

All the three complexes (**9–11**) are found to be readily soluble in dichloromethane, sparingly soluble in acetonitrile and acetone, and poorly soluble in alcoholic solvents.

Table 2
Electronic spectral and cyclic voltammetric data of the complexes

Compound	Electronic spectral data[a] λ_{max}, nm (ε, M^{-1} cm^{-1})	Cyclic voltammetric data[c]
Complex 9	534(5600), 503(4800)[b], 339(7600)[b], 304(19000), 230(52000)	1.08[d] (70)[e], −1.31[f]
Complex 10	635(2500), 591(2200)[b], 341(4300)[b], 291(10900), 232(19000)	0.82[d] (75)[e], −1.30[f]
Complex 11	702(12300), 649(10600), 373(13700)[b], 346(16300)[b], 296(38900), 230(64700)	1.01[d] (81)[e], −1.00[f]

Where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively.
[a] In dichloromethane solution.
[b] Shoulder.
[c] Solvent: 1:9 dichloromethane–acetonitrile; supporting electrolyte, TBAP; reference electrode, SCE, scan rate, 50 mV s^{-1}.
[d] $E_{1/2} = 0.5(E_{pa} + E_{pc})$; where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively.
[e] $\Delta E_{p} = E_{pa} - E_{pc}$.
[f] E_{pc} value.

Table 3
Composition of selected molecular orbitals

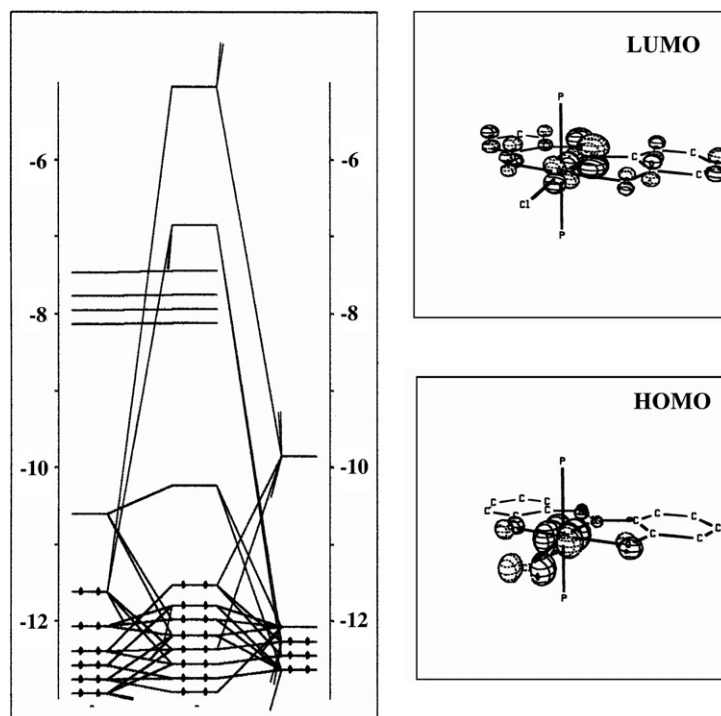| Compounds	Contributing fragments	% Contribution of fragments to					
		HOMO	HOMO − 1	HOMO − 2	LUMO	LUMO + 1	LUMO + 2
Complex 9	Rh	81	70	34	13	–	–
	Chloride	5	–	–	–	–	–
	Tridentate ligand (ONO)	7	20	60	81 (N=N, 54)	98	98
Complex 10	Rh	78	43	53	15	–	–
	Chloride	4	–	4	–	–	–
	Tridentate ligand (CNO)	8	52	33	81 (N=N, 48)	96	95
Complex 11	Rh	79	39	56	12	–	–
	Chloride	5	–	4	–	–	–
	Tridentate ligand (CNO)	8	57	33	83 (N=N, 41)	95	96

Fig. 4. Partial molecular orbital diagram of complex 9.

Electronic spectra of all the complexes have been recorded in dichloromethane solution. Each complex shows several intense absorptions in the visible and ultraviolet region (Table 2). The absorptions in the ultraviolet region are believed to be due to transitions within the ligand orbitals. To have an insight into the nature of absorptions

in the visible region, EHMO calculations have been performed [9] on computer generated models of the all the three complexes, where phenyl rings of the PPh$_3$ ligands have been replaced by hydrogens. Compositions of selected molecular orbitals are given in Table 3 and partial MO diagram of complex 9 is shown in Fig. 4. Partial MO diagrams of complexes 10 and 11 are deposited as Supplementary material (Figs. S1 and S2). The calculations reveal that the highest occupied molecular orbital (HOMO) has major ($\geqslant 78\%$) contribution from the metal d-orbitals, whereas the lowest unoccupied molecular orbital (LUMO) is primarily ($\geqslant 81\%$) delocalized over the coordinated O,N,O- or C,N,O-donor ligand and is concentrated heavily ($\geqslant 41\%$) on the azo fragment. Hence the lowest energy absorption in the visible region is assignable to a charge-transfer transition from the filled rhodium orbital (HOMO) to the π^*-(azo) orbital (LUMO) of the tridentate ligand. The other absorptions in the visible region are attributable to transitions occurring from the other filled orbitals to the higher energy vacant orbitals.

2.3. Electrochemical properties

Electrochemical properties of complexes 9–11 have been studied in 1:9 dichloromethane–acetonitrile solution (0.1 M TBAP) by cyclic voltammetry [10]. Voltammetric data are presented in Table 2 and a selected voltammogram is presented as Supplementary material (Fig. S3). Each complex shows an oxidative response on the positive side of SCE and a reductive response on the negative side. The oxidative response is reversible in nature, characterized by a peak-to-peak separation (ΔE_p) of ~75 mV and the anodic peak-current (i_{pa}) is almost equal to the cathodic peak-current (i_{pc}) as expected for a reversible response. In view of the composition of the HOMO, this oxidation is assigned to a Rh(III)–Rh(IV) oxidation. Similarly in view of the composition of the LUMO, the irreversible reductive response is attributed to reduction of the azo group of the tridentate ligand. One electron nature of the signals is established by comparing their current heights (i_{pa}) with those of the ferrocene–ferrocenium couple ($\Delta E_p = 76$ mV) under similar experimental conditions.

3. Conclusions

The present study shows that 2-(arylazo)phenols, having a suitable substituent in one ortho-position in the phenyl ring of the arylazo fragment, can undergo facile C–H or C–C activation mediated by transition metals. This is manifested in the reaction of 2-(2'-carboxyphenylazo)-4-methylphenol (4) with [Rh(PPh$_3$)$_3$Cl], where ligand 4 undergoes C–H as well as C–C activation. While 2-(2'-hydroxyphenylazo)phenol (3), upon similar reaction with [Rh(PPh$_3$)$_3$Cl], binds to rhodium only in the O,N,O-fashion (5) and no C–H activation of this ligand takes place.

4. Experimental

Rhodium trichloride was obtained from Arora Matthey, Kolkata, India. All other chemicals and solvents were reagent grade commercial materials and were used as received. [Rh(PPh$_3$)$_3$Cl] was synthesized by following a reported procedure [11]. The 2-(2'-hydroxyphenylazo)phenol and 2-(2'-carboxyphenylazo)-4-methylphenol were prepared following reported procedures [12]. Purification of dichloromethane and acetonitrile, and preparation of tetrabutylammonium perchlorate (TBAP) for electrochemical work were performed as before [13]. Microanalyses (C, H, N) were performed using a Heraeus Carlo Erba 1108 elemental analyzer. 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. Magnetic susceptibilities were measured using a PAR 155 vibrating sample magnetometer fitted with a Walker scientific L75FBAL magnet. ^{1}H NMR spectra were recorded in CDCl$_3$ solution on a Bruker Avance DPX 300 NMR spectrometer using TMS as the internal standard. Electrochemical measurements were made using a CH Instruments model 600 A electrochemical analyzer. 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 experiments were performed under a dinitrogen atmosphere. All electrochemical data were collected at 298 K and are uncorrected for junction potentials.

4.1. Synthesis of complexes

Complex 9. 2-(2'-Hydroxyphenylazo)phenol (23 mg, 0.11 mmol) was dissolved in benzene (30 mL) and to it was added triethylamine (25 mg, 0.25 mmol). Then [Rh(PPh$_3$)$_3$Cl] (100 mg, 0.11 mmol) was added and the mixture was heated at reflux under dinitrogen atmosphere, for 5 h to yield a deep red solution. Evaporation of this solution gave a dark red solid, which was subjected to purification by thin layer chromatography on a silica plate. With benzene as the eluant, a red band separated, which was extracted with acetonitrile. Upon evaporation of the acetonitrile extract complex 9 was obtained as a crystalline red solid. Yield: 88%. Anal. Calc. for C$_{48}$H$_{38}$N$_2$O$_2$P$_2$ClRh: C, 65.87; H, 4.35; N, 3.20. Found: C, 65.43; H, 4.37; N, 3.18%. ^{1}H NMR [14]: 6.18 (t, 1H, $J = 7.5$); 6.31 (t, 1H, $J = 7.5$); 6.60 (d, 1H, $J = 6.0$); 6.69 (d, 1H, $J = 9.0$); 6.87 (t, 1H, $J = 7.5$); 6.97 (d, 1H, $J = 9.0$); 7.06 (d, 1H, $J = 6.0$); 7.14–7.46 (2PPh$_3$).

Complex 10 and complex 11. 2-(2'-Carboxyphenylazo)-4-methylphenol (28 mg, 0.11 mmol) was dissolved in benzene (30 mL) and to it was added triethylamine (25 mg, 0.25 mmol). Then [Rh(PPh$_3$)$_3$Cl] (100 mg, 0.11 mmol) was added and the mixture was heated at reflux under dinitrogen atmosphere for 5 h to yield a bluish-green solution. Evaporation of this solution gave a dark green solid, which

was subjected to purification by thin layer chromatography on a silica plate. With 1:10 acetonitrile–benzene as the eluant, a blue band separated followed by a green one, which were extracted with acetonitrile. Upon evaporation of these extracts complex **10** and **11** were obtained as crystalline blue (yield: 35%) and green (yield: 55%) solids, respectively. Complex **10**: Anal. Calc. for complex $C_{49}H_{40}N_2OP_2ClRh$: C, 67.39; H, 4.58; N, 3.21. Found: C, 67.04; H, 4.56; N, 3.19%. ^{1}H NMR: 2.00 (CH_3); 5.80 (s, 1H); 6.19 (d, 1H, $J = 9.0$); 6.35 (t, 1H, $J = 7.5$); 6.46 (d, 1H, $J = 6.0$); 6.68 (t, 1H, $J = 7.5$); 6.99–7.48 ($2PPh_3$); 7.54–7.63 (2H). [ast] Complex **11**: Anal. Calc. for complex $C_{50}H_{40}N_2O_2P_2ClRh$: C, 65.18; H, 4.35; N, 3.04. Found: C, 65.61; H, 4.33; N, 3.07%. ^{1}H NMR: 1.82 (CH_3); 5.62 (s, 1H); 6.25 (d, 1H, $J = 9.0$); 6.54 (t, 1H, $J = 7.5$); 6.63 (d, 1H, $J = 9.0$); 7.17–7.58 ($2PPh_3$); 12.41 (COOH).

4.2. X-ray structure determination

Single crystals of complexes **9**–**11** were grown by slow diffusion of hexane into dichloromethane solutions of the respective complexes. Selected crystal data and data collection parameters are given in Table 4. Data on the crystals of the complexes **9** and **11** were collected on a Bruker SMART 1000 CCD diffractometer, while those on the crystal of complex **10** were collected on a Marresearch Image Plate system, using graphite monochromated Mo Kα radiation. X-ray data reduction, structure solution and refinement were done using the SHELXS-97 and SHELXL-97 packages [15]. The structures were solved by the direct methods. In the crystal of complex **9** disorder was identified in the central –N=N– unit of each azo ligand by unrealistic geometry and poor refinement as ordered groups. A split

atom model for each N atom was introduced and geometric restraints applied: N=N 1.28 Å, C···N 2.28 Å and similarity restraints on C–N distances. This model refined well, in one molecule the occupancies converged at 0.537(6) and 0.463(6), while in the other the values were 0.600(6) and 0.400(6). Such disorder typically extends to a lesser extent into the phenyl rings but no further modeling was deemed necessary in this case.

Acknowledgements

Appendix A. Supplementary material

CCDCs 613285, 613286, and 613287 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge via htpp://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Partial MO diagrams for complex **10** and **11** (Figs. S1 and S2), and cyclic voltammogram of complex **11** (Fig. S3). Supplementary data associated with

Table 4
Crystallographic data for complexes **9**–**11**

	Complex **9**	Complex **10**	Complex **11**
Empirical formula	$C_{48}H_{38}N_2O_2P_2ClRh$	$C_{49}H_{40}N_2OP_2ClRh$	$C_{50}H_{40}N_2O_3P_2ClRh, 0.5(CH_2Cl_2)$
F_w	875.10	868.65	959.60
Space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$
Unit cell dimensions			
a (Å)	23.4822(10)	12.346(14)	10.4131(9)
b (Å)	17.6758(8)	19.05(2)	11.9353(10)
c (Å)	20.9611(9)	18.65(2)	19.150(2)
α (°)	90	90	103.681(2)
β (°)	114.532	108.338(10)	91.955(2)
γ (°)	90	90	95.044(2)
V (Å³)	7914.9(6)	4164(8)	2299.8(4)
Z	8	4	2
λ (Å)	0.71073	0.71073	0.71073
Crystal size (mm)	$0.23 \times 0.27 \times 0.40$	$0.05 \times 0.05 \times 0.30$	$0.06 \times 0.15 \times 0.50$
T (K)	150	293	150
μ (mm⁻¹)	0.623	0.565	0.601
R_1[a]	0.0295	0.0473	0.0459
wR_2[b]	0.0794	0.1055	0.1560
GOF[c]	1.02	1.11	1.05

[a] $R_1 = \sum ||F_o| - |F_c||/\sum |F_o|$.

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

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

this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.10.063.

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