Iridium mediated phenolic O–H activation and cyclometalation of 2-(naphthyl-1′-azo)-4-methylphenol – Formation of organoiridium complexes

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Abstract.   Reaction of 2-(naphthyl-1′-azo)-4-methylphenol with [Ir(PPh$_3$)$_3$Cl] in refluxing ethanol in the presence of a base (NEt$_3$) affords an organoiridium complex of type [Ir(PPh$_3$)$_2$(L)(H)], where L represents the coordinated 2-(naphthyl-1′-azo)-4-methylphenolate ligand. A similar reaction carried out in toluene affords the [Ir(PPh$_3$)$_2$(L)(H)] complex along with a similar complex of type [Ir(PPh$_3$)$_2$(L)Cl]. Structures of both the [Ir(PPh$_3$)$_2$(L)(H)] and [Ir(PPh$_3$)$_2$(L)Cl] complexes have been determined by X-ray crystallography. In both the complexes, 2-(naphthyl-1′-azo)-4-methylphenol is coordinated to iridium, via C–H activation at the 2′ position of the naphthyl ring, as a dianionic tridentate C, N, O-donor and the two triphenylphosphines are *trans*. The organoiridium complexes show intense MLCT transitions in the visible region. Cyclic voltammetry on the [Ir(PPh$_3$)$_2$(L)(H)] and [Ir(PPh$_3$)$_2$(L)Cl] complexes shows a reversible Ir(III)–Ir(IV) oxidation respectively at 0·55 and 0·73 V vs SCE. An irreversible oxidation of the coordinated 2-(naphthyl-1′-azo)-4-methylphenolate ligand is observed above 1·0 V vs SCE and an irreversible reduction of the same is observed near −1·0 V vs SCE.

Keywords.   2-(Naphthyl-1′-azo)-4-methylphenol; iridium; C–H activation; structure; electrochemical properties.

1.   Introduction

There has been considerable current interest in metal mediated chemical transformations of organic molecules.[1] Such reactions often proceed via a C–H activation step leading to the formation of organometallic complexes as reactive intermediates,[2] which then undergo further reactions to yield the desired product. Metal mediated C–H activation of organic molecules has thus been an attractive field of chemical research and we have been active in this area for the past few years.[3] We have recently observed that upon reaction with [Ir(PPh$_3$)$_3$Cl] the 2-(arylazo)phenols (**1**) undergo both phenolic O–H and phenyl C–H activation, and afford organoiridium complexes where the 2-(arylazo)phenols coordinate iridium as tridentate C, N, O-donors (**2**).[3c] We have also observed that if both the *ortho* positions of the phenyl ring in the arylazo fragment are blocked by methyl groups then

C–H activation of one methyl group takes place.[3a] However, if only one *ortho* position is blocked by a methyl group keeping the other unsubstituted, then the methyl group remain unchanged and only phenyl C–H activation takes place.[3a] These observations have encouraged us to explore the interaction of [Ir(PPh$_3$)$_3$Cl] with other ligands of similar type, particularly with those which have potential to display ambivalence, and the present work has emerged out of this exploration. For the present study we selected 2-(naphthyl-1′-azo)-4-methylphenol (**3**) as the target ligand for C–H activation. In this ligand (**3**) one *ortho* position (9′) of the naphthyl ring is blocked while the other *ortho* position (2′) is still unsubstituted. Hence C–H activation of this ligand (**3**) can, in principle, take place at either 2′ or 8′ position to afford chelates **4** or **5**. A third linkage isomer **6** is also possible if the second azo-nitrogen participates in coordination and C–H activation takes place at the 8′ position. To find out the preference of binding of ligand **3**, it has been allowed to react with

[Ir(PPh₃)₃Cl] and such reactions afforded interesting organoiridium complexes where ligand **3** has been
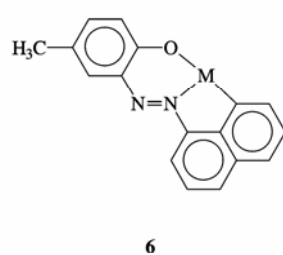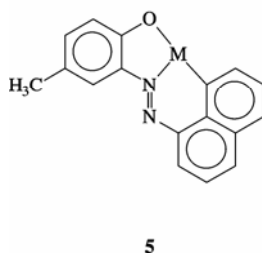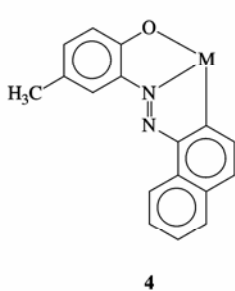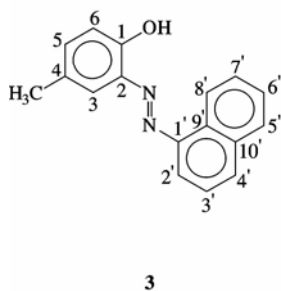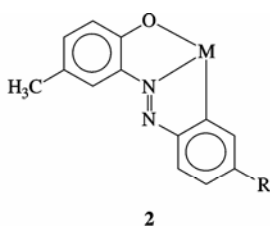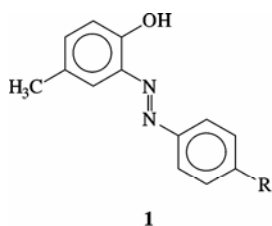
found to undergo C–H activation only at the 2′ position (**4**). An account of the chemistry of these organoiridium complexes is presented in this paper, with special reference to their synthesis, structure and spectral and electrochemical properties.

2. Experimental

2.1 *Materials*

Iridium trichloride was purchased from Arora Matthey, Kolkata, India. [Ir(PPh₃)₃Cl] was prepared as reported earlier.[2b] 1-Naphthylamine was obtained from M/s Loba, India, and *p*-cresol was purchased from M/s S.D., India. 2-(Naphthyl-1′-azo)-4-methylphenol was prepared by coupling diazotized 1-naphthylamine with *p*-cresol. Purification of acetonitrile, dichloromethane and preparation of tetrabutylammonium perchlorate (TBAP) for electrochemical work were performed as before.[4]

2.2 *Synthesis of complexes*

2.2a *[Ir(PPh₃)₂(L)(H)]:* 2-(Naphthyl-1′-azo)-4-methylphenol (26 mg, 0·10 mmol) was dissolved in

ethanol (50 mL) and the solution was purged with a stream of dinitrogen for 5 min. To the solution were added triethylamine (20 mg, 0·20 mmol) and [Ir(PPh₃)₃Cl] (100 mg, 0·10 mmol) successively. The mixture was refluxed under a dinitrogen atmosphere for 8 h, whereby greenish-blue solution was obtained. Evaporation of this solution afforded a dark solid, which was subjected to purification by thin layer chromatography on a silica plate. With benzene–acetonitrile (20 : 1) as the eluant, a blue band separated, which was extracted with acetonitrile. Upon evaporation of the acetonitrile extract [Ir(PPh₃)₂(L)(H)] was obtained as a crystalline blue solid. Yield: 65%. Analysis: Calc for C₅₃H₄₃N₂OP₂Ir: C, 65·09; H, 4·40; N, 2·87%. Found: C, 65·37; H, 4·43; N, 2·92%. ¹H-NMR:[5] –11·97 (*t*, hydride, *J* = 18·0), 1·95 (CH₃), 6·24 (*d*, 1H, *J* = 8·1), 6·42–6·55 (4H*), 6·92–7·03 (3H*), 7·06–7·56 (2PPh₃), 8·43 (*d*, 1H, *J* = 8·2).

2.2b *[Ir(PPh₃)₂(L)Cl]:* This complex was prepared by following the same above procedure using toluene instead of ethanol and the refluxing time was 20 h. Purification was achieved by thin layer chromatography on a silica plate with benzene–acetonitrile (20 : 1) as the eluant. Two blue bands separated, which were extracted with acetonitrile. Slow evaporation of the extract of the faster moving blue band gave [Ir(PPh₃)₂(L)(H)] (Yield: 35%) and that of the slower moving blue band gave [Ir(PPh₃)₂(L)Cl] (Yield: 30%) as crystalline solids. Analysis Calc. for C₅₃H₄₂N₂OP₂ClIr: C, 62·88; H, 4·15; N, 2·77%. C, 63·04; H, 4·11; N, 2·89. ¹H-NMR:[5] 1·73 (CH₃), 5·87 (*s*, 1H), 6·19 (*d*, 1H, *J* = 8·7), 6·34 (*d*, 1H, *J* = 9·4), 6·78 (*d*, 1H, *J* = 8·6), 6·91 (*t*, 1H, *J* = 7·5), 7·01–7·56 (2PPh₃), 8·26 (*d*, 1H, *J* = 8·1).

2.3 *Physical measurements*

Microanalyses (C, H, N) were done using a Heraeus Carlo Erba 1108 elemental analyzer. ¹H NMR spectra in CDCl₃ 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. 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 structure determination*

Single crystals of $[Ir(PPh_3)_2(L)(H)]$ were grown by slow diffusion of hexane into a dichloromethane solution of the complex and those of $[Ir(PPh_3)_2(L)Cl]$ were grown 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 Bruker Smart CCD diffractometer using graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å) by ω scans. X-ray data reduction and, structure solution and refinement were done using SHELXS-97 and SHELXL-97 programs.[6] The structures were solved by direct methods.

3. Results and discussion

3.1 *Synthesis and structure*

Reaction of 2-(naphthyl-1'-azo)-4-methylphenol with $[Ir(PPh_3)_3Cl]$ proceeds smoothly in refluxing ethanol in the presence of triethylamine to afford a blue

complex in a decent yield. Though the preliminary characterization data (microanalysis, ^{1}H NMR and IR) indicated the presence of a 2-(naphthyl-1'-azo)-4-methylphenolate ligand, two triphenylphosphines and a hydride in this complex, they could not point to any definite stereochemistry of the complex, as well as the coordination mode of 2-(naphthyl-1'-azo)-4-methylphenol in it. For an unambiguous characterization of this complex, its structure has been determined by X-ray crystallography. The structure is shown in figure 1 and some relevant bond parameters are listed in table 2. The structure shows that the 2-(naphthyl-1'-azo)-4-methylphenol is coordinated to iridium, via C-H activation at the 2' position, as a C, N, O-donor (**4**), with bite angles of 78.05 (14)° [N(1)–Ir–O(1)] and 77.49(16)° [C(8)–Ir–N(1)]. Two triphenylphosphines and a hydride are also coordinated to the metal center. This complex is therefore formulated as $[Ir(PPh_3)_2(L)(H)]$, where L refers to the 2-(naphthyl-1'-azo)-4-methylphenolate ligand coordinated as in **4**. The observed microanalytical data are also consistent with this composition. In this $[Ir(PPh_3)_2(L)(H)]$ complex iridium is sitting in a HCNOP$_2$ coordination sphere, which is significantly distorted from ideal octahedral geometry as reflected in the bond parameters around the metal center. The coordinated 2-(naphthyl-1'-azo)-4-methylphenolate

Table 1. Summary of structure determination of $[Ir(PPh_3)_2(L)(H)]$ and $[Ir(PPh_3)_2(L)Cl]$.

	$[Ir(PPh_3)_2(L)(H)]$	$[Ir(PPh_3)_2(L)Cl]$
Formula	$C_{53}H_{43}N_2OP_2Ir$	$C_{53}H_{42}N_2OP_2ClIr$
Formula weight	978.03	1012.48
Crystal system	Triclinic	Monoclinic
Space group	$P1$	$C2/c$
a (Å)	10.5915(6)	24.3644(9)
b (Å)	12.7197(7)	9.2310(4)
c (Å)	16.5346(9)	21.5454(9)
α (°)	88.347(1)	90
β (°)	87.910(1)	116.425(1)
γ (°)	78.179(1)	90
V (Å^3)	2178.3(2)	4339.4(3)
Z	2	4
T (K)	295(2)	295(2)
μ (mm^{-1})	3.179	3.254
$R1^a$	0.0353	0.0285
$WR2^b$	0.0890	0.0668
GOF^c	1.089	1.035

$^a R1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$; $^b wR2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)\}]^{1/2}$; ^{c}GOF $= [\Sigma(w(F_o^2 - F_c^2)^2)/(M - N)]^{1/2}$, where M is the number of reflections and N is the number of parameters refined
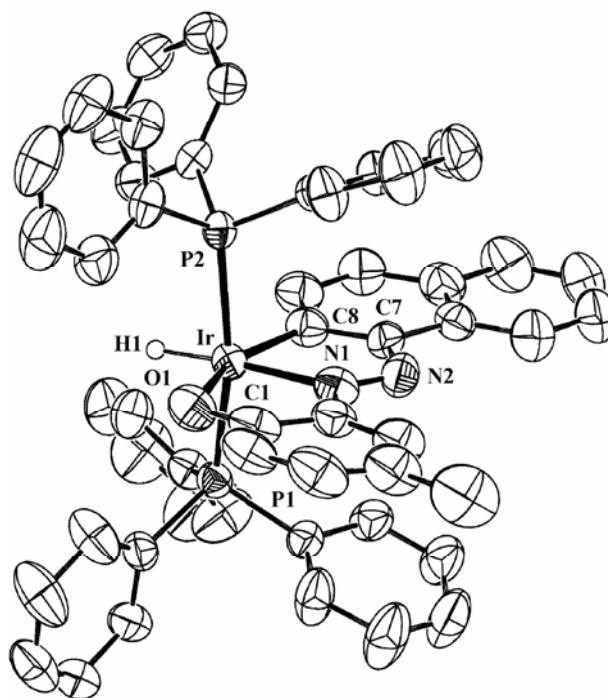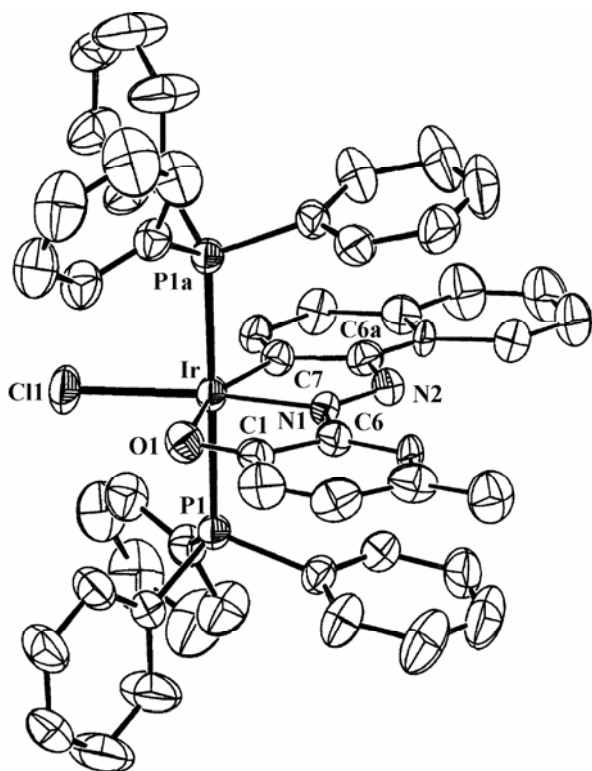

Figure 1. View of the $[Ir(PPh_3)_2(L)(H)]$ molecule.

Table 2. Selected bond lengths (Å) and bond angles (°) for [Ir(PPh$_3$)$_2$(L)(H)] and [Ir(PPh$_3$)$_2$(L)Cl].

[Ir(PPh$_3$)$_2$(L)(H)]

Bond lengths (Å)

Ir–H(1)	1·35(5)	Ir–P(2)	2·3053(10)
Ir–C(8)	2·010(4)	C(6)–N(1)	1·352(6)
Ir–N(1)	2·053(4)	C(7)–N(2)	1·452(6)
Ir–O(1)	2·213(3)	C(1)–O(1)	1·311(6)
Ir–P(1)	2·2991(10)	N(1)–N(2)	1·235(5)

Bond angles (°)

H(1)–Ir–N(1)	174(2)	C(8)–Ir–N(1)	77·49(16)
C(8)–Ir–O(1)	155·49(17)	N(1)–Ir–O(1)	78·05(14)
P(1)–Ir–P(2)	163·83(3)		

[Ir(PPh$_3$)$_2$(L)Cl]

Bond lengths (Å)

Ir–C(7)	1·919(6)	Ir–Cl(1)	2·3784(12)
Ir–N(1)	1·975(5)	C(6)–N(1)	1·294(5)
Ir–O(1)	2·264(6)	C(6a)–N(2)	1·498(5)
Ir–P(1)	2·3661(8)	C(1)–O(1)	1·308(8)
Ir–P(1a)	2·3661(8)	N(1)–N(2)	1·265(5)

Bond angles (°)

C(7)–Ir–O(1)	158·0(2)	C(7)–Ir–N(1)	80·0(2)
Cl(1)–Ir–N(1)	164·86(13)	N(1)–Ir–O(1)	78·02(18)
P(1)–Ir–P(1a)	179·25(4)		

Figure 2. View of the [Ir(PPh$_3$)$_2$(L)Cl] molecule.

ligand and the hydride are sharing the same equatorial plane with iridium at the center, and the two triphenylphosphines have occupied the remaining two axial positions. The Ir–H and Ir–P distances are quite normal, and so are the Ir–C, Ir–N, Ir–O, C–O and N–N bond lengths within the Ir(L) fragment.[2b,7]

The presence of a hydride in the [Ir(PPh$_3$)$_2$(L)(H)] complex has been quite interesting. Two sources of the hydride seem logical, the solvent (ethanol) used for its synthesis might have served as a source of the hydride, or oxidative insertion of iridium(I) into the phenolic O–H bond of 2-(naphthyl-1′-azo)-4-methylphenol might also have resulted in the formation of the hydride. To sort this out, reaction of 2-(naphthyl-1′-azo)-4-methylphenol with [Ir(PPh$_3$)$_3$Cl] has also been carried out in refluxing toluene in the presence of triethylamine. A mixture of two blue complexes has been obtained from this reaction, which have been separated by chromatography. The blue complex, which moves faster through the column, has been found to be the [Ir(PPh$_3$)$_2$(L)(H)] complex. The other blue complex, which moves relatively slowly through the column, has been found to be the chloride analogue of the [Ir(PPh$_3$)$_2$(L)(H)]

complex, viz. [Ir(PPh₃)₂(L)Cl]. The observed micro-analytical data of this [Ir(PPh₃)₂(L)Cl] complex agree well with its composition. To ascertain the coordination mode of 2-(naphthyl-1'-azo)-4-methyl-phenol in this [Ir(PPh₃)₂(L)Cl] complex, its structure has also been determined by X-ray crystallography. The structure (figure 2) shows that the [Ir(PPh₃)₂(L)Cl] complex has a similar structure as the [Ir(PPh₃)₂(L)(H)] complex, except that the position of hydride in the latter is occupied by a chloride in the former. The Ir–Cl distance is normal,[2b,7c,7e] and structural features in the rest of the complex mole-cule, i.e. within the Ir(PPh₃)₂(L) fragment, are found to be comparable to those observed in the same fragment of the [Ir(PPh₃)₂(L)(H)] complex.

Formation of the hydride complex, [Ir(PPh₃)₂(L)(H)], in addition to its chloride analogue, [Ir(PPh₃)₂(L)Cl], from the reaction carried out in toluene clearly shows that ethanol has not been the source of hydride in the earlier synthetic reaction. The exact mechanism of the synthetic reactions is not com-pletely clear to us. However, the sequences shown in scheme 1 seem probable. In the initial step 2-(naphthyl-1'-azo)-4-methylphenol binds to the metal center in [Ir(PPh₃)₃Cl] via oxidative insertion of iridium into the phenolic O–H bond, with simulta-neous dissociation of one triphenylphosphine, and thus affords two geometric isomers of a reactive in-termediate (complexes **7** and **8**). These intermediates then undergo cyclometalation via elimination of either HCl (in case of **7**) or H₂ (in case of **8**) afford-ing the [Ir(PPh₃)₂(L)(H)] and [Ir(PPh₃)₂(L)Cl] com-plexes respectively. In the ethanol reaction only the intermediate **7** is generated. Its isomerization to complex **8** could not take place in ethanol probably because of its low boiling point. Isolation of these speculated intermediates has not been possible probably because of their rapid transformation into the corresponding cyclometalated species.

3.2 ^{1}H NMR spectra

Magnetic susceptibility measurements show that both the [Ir(PPh₃)₂(L)(H)] and [Ir(PPh₃)₂(L)Cl] complexes are diamagnetic, which corresponds to the +3 oxidation state of iridium (low-spin d^6, $S = 0$) in these complexes. ^{1}H NMR spectrum of [Ir(PPh₃)₂(L)(H)] shows broad signals within 7·06–7·56 ppm, attributable to the two triphenylpho-sphines. The methyl signal of the coordinated 2-(naphthyl-1'-azo)-4-methylphenolate ligand is observed at 1·95 ppm and all the aromatic proton signals expected from it are also clearly observed in the expected region. The hydride signal is observed at −11·97 ppm as a distinct triplet, due to coupling with two magnetically equivalent phosphorus nuclei. Besides the absence of the hydride signal, ^{1}H NMR spectrum of the [Ir(PPh₃)₂(L)Cl] complex is very similar to that of the [Ir(PPh₃)₂(L)(H)] complex.

3.3 IR spectra

Infrared spectra of the [Ir(PPh₃)₂(L)(H)] and [Ir(PPh₃)₂(L)Cl] complexes are mostly similar. Each complex shows three strong bands near 515, 695 and 750 cm⁻¹, which are attributable to the coordinated PPh₃ ligands. Comparison with the spectrum of [Ir(PPh₃)₃Cl] shows that some additional bands (near
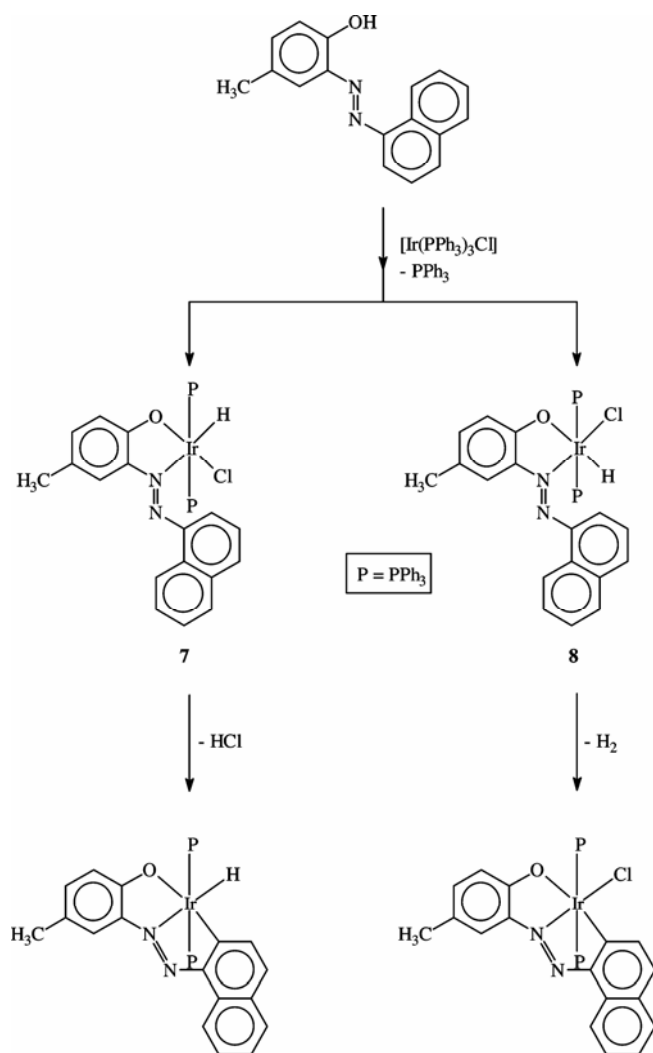
Scheme 1. Probable steps in the formation of [Ir(PPh₃)₂(L)(H)] and [Ir(PPh₃)₂(L)Cl].

Table 3. Electronic spectral data.

Compound	λ_{max}, nm (ε, M^{-1} cm^{-1})[a]
[Ir(PPh$_3$)$_2$(L)(H)]	658 (8700), 616[b] (7900), 404[b] (6500), 350 (11800), 268 (38300)
[Ir(PPh$_3$)$_2$(L)Cl]	696 (5900), 636[b] (5100), 402[b] (6200), 362 (8900), 308[b] (12200), 258 (39800)

[a]In dichloromethane; [b]Shoulder

Table 4. Composition of selected molecular orbitals.

Complex	Contributing fragments	% Contribution of fragments to					
		HOMO	HOMO − 1	HOMO − 2	LUMO	LUMO + 1	LUMO + 2
[Ir(PPh$_3$)$_2$(L)(H)]	Ir	78	36	14	9	–	53
	L	11	57	69	88	94	44
					(N = N 47)		
[Ir(PPh$_3$)$_2$(L)Cl]	Ir	83	36	74	9	–	57
	L	7	55	14	87	94	33
					(N = N 46)		
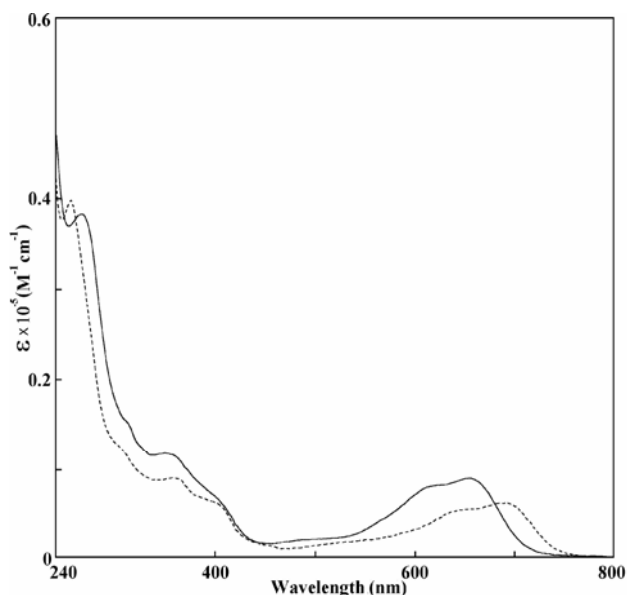
Figure 3. Electronic spectra of [Ir(PPh$_3$)$_2$(L)(H)] (——) and [Ir(PPh$_3$)$_2$(L)Cl] (-----) in dichloromethane solution.

1246, 1289 and 1321 cm^{-1}) are present in these two complexes, which must be due to the coordinated 2-(naphthyl-1′-azo)-4-methylphenolate ligand. In the [Ir(PPh$_3$)$_2$(L)(H)] complex the Ir–H stretch is observed as a sharp band at 2069 cm^{-1}. In the [Ir(PPh$_3$)$_2$(L)Cl] complex the Ir–Cl stretch is observed at 295 cm^{-1}.

3.4 *Electronic absorption spectra*

The [Ir(PPh$_3$)$_2$(L)(H)] and [Ir(PPh$_3$)$_2$(L)Cl] complexes are soluble in chloroform, dichloromethane,

acetonitrile, acetone, etc., producing intense blue solutions. Electronic spectra of both the complexes have been recorded in dichloromethane solution. Spectral data are presented in table 3 and the spectra are shown in figure 3. Each complex shows several intense absorptions in the visible and ultraviolet region. The absorptions in the ultraviolet region are believed to be due to transitions within the ligand orbitals, and those in the visible region are probably due to metal-to-ligand charge-transfer transitions. To have an insight into the nature of absorptions in the visible region, qualitative EHMO calculations by the CACAO package programs[8] have been performed on computer-generated models of both the complexes, where phenyl rings of the triphenylphosphines have been replaced by hydrogens. The results are found to be qualitatively similar for both the complexes.[9] Composition of selected molecular orbitals is given in table 4 and partial MO diagram of the [Ir(PPh$_3$)$_2$(L)(H)] complex is shown in figure 4. Partial MO diagram of the [Ir(PPh$_3$)$_2$(L)Cl] complex is deposited as supporting information (figure S1). The highest occupied molecular orbital (HOMO) and the next filled orbital (HOMO-1) are relatively close in energy and both have significant contribution from the metal t_2 orbitals. The lowest unoccupied molecular orbital (LUMO) has major ($\geq$ 87%) contribution from the 2-(naphthyl-1′-azo)-4-methylphenolate ligand and is concentrated mostly ($\geq$ 46%) on the azo fragment. The higher energy vacant orbitals (LUMO+1, LUMO+2, etc.) are rather distant from the LUMO and are delocalized over other parts of the 2-(naphthyl-1′-azo)-4-methyl-
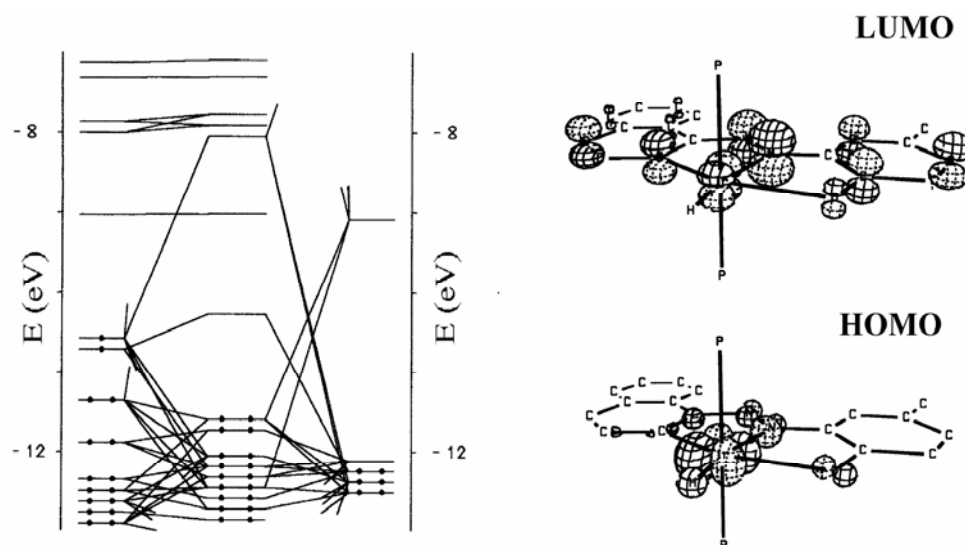
LUMO

HOMO

Figure 4.   Partial molecular orbital diagram of [Ir(PPh₃)₂(L)(H)].

Table 5.   Cyclic voltammetric data.[a]

Compound	E, V vs SCE	
	Ox	Red
[Ir(PPh₃)₂(L)(H)]	0·55 (72),[b] 1·15[c]	−1·05[d]
[Ir(PPh₃)₂(L)Cl]	0·73 (69),[b] 1·30[c]	−1·10[d]

[a]In 1 : 9 dichloromethane-acetonitrile; supporting electrolyte, TBAP; scan rate 50 mVs⁻¹
[b]$E_{1/2}$ value (ΔE_p value), where $E_{1/2} = 0.5\ (E_{pa} + E_{pc})$ and $\Delta E_p = E_{pa} - E_{pc}$, where E_{pa} and E_{pc} are anodic and cathodic peak-potentials respectively
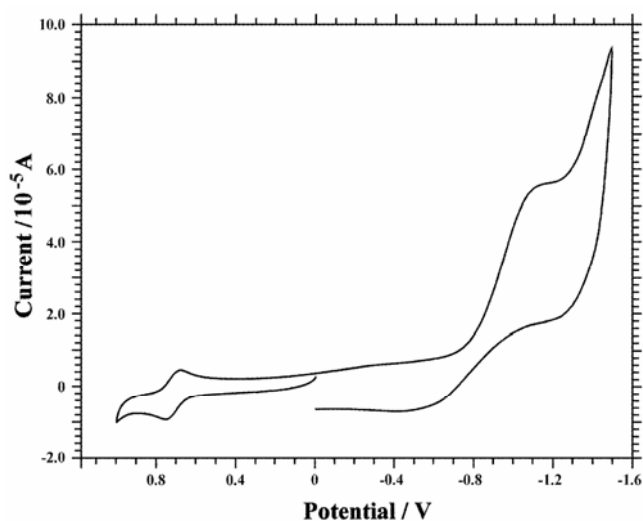[c]E_{pa} value; [d]E_{pc} value

Figure 5.   Cyclic voltammogram of [Ir(PPh₃)₂(L)Cl] in 1 : 9 dichloromethane-acetonitrile solution (0·1 M TBAP) at a scan rate of 50 mVs⁻¹.

phenolate ligand. The lowest energy absorption in the visible region is therefore assignable to an allowed charge-transfer transition from the filled iridium-t_2 orbital (HOMO) to the vacant π^*(azo)-orbital of the 2-(naphthyl-1′-azo)-4-methylphenolate ligand (LUMO). The next intense absorption in the visible region, which appears as a shoulder, may be assigned to the charge-transfer transitions from HOMO-1 to LUMO. The other absorptions in the visible region are assignable to transition from the filled orbitals to the higher energy vacant orbitals.

3.5   *Electrochemical properties*

Electrochemical properties of the complexes have been studied by cyclic voltammetry in 1 : 9 dichloromethane–acetonitrile solution (0·1 M TBAP).[10] Voltammetric data are given in table 5 and a representative voltammogram is shown in figure 5. Each complex shows two oxidative responses on the positive side of SCE and a reductive response on the negative side. In view of the results of the EHMO calculations, the first oxidative response is assigned to Ir(III)–Ir(IV) oxidation and the reductive response is assigned to reduction of the coordinated 2-(naphthyl-1′-azo)-4-methylphenolate ligand. The second oxidative response is tentatively assigned to oxidation of the coordinated 2-(naphthyl-1′-azo)-4-methylphenolate ligand. In both the complexes the Ir(III)–Ir(IV) oxidation has been found to be reversible, characterized by a peak-to-peak separation (ΔE_p) of about 70 mV, which remains unchanged

upon variation of scan rate, and the anodic peak-current (i_{pa}) is also found to be equal to the cathodic peak-current (i_{pc}), as expected for a reversible couple. The ligand oxidation and reduction have been found to be irreversible in both the complexes. One-electron nature of the Ir(III)–Ir(IV) oxidation has been established by comparing its current height (i_{pa}) with that of standard ferrocene-ferrocenium couple under identical experimental conditions. The irreversible responses show non-stoichiometric currents.

4. Conclusions

The present study shows that 2-(naphthyl-1′-azo)-4-methylphenol undergoes facile phenolic O–H and aryl C–H (at 2′ position) activation mediated by [Ir(PPh$_3$)$_3$Cl]. The present study also indicates that such activation of other organic molecules, which have structural similarity to 2-(naphthyl-1′-azo)-4-methylphenol, may be possible upon their reaction with [Ir(PPh$_3$)$_3$Cl], and such possibilities are currently under exploration.

Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC-249187 for [Ir(PPh$_3$)$_2$(L)(H)] and CCDC-249188 for [Ir(PPh$_3$)$_2$(L)Cl]. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax. (int code): +44(1223) 336-033] or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk. Partial molecular orbital diagrams of the [Ir(PPh$_3$)$_2$(L)Cl] complex (Figure S1) is available as supporting information.

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9. The HOMO-2 in $[Ir(PPh_3)_2(L)(H)]$ has less metal character

10. 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