

Full Length Research Paper

Palladium(II)-triphenylphosphine-arylaazoimidazole complexes: Synthesis and spectroscopic characterization

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Reaction of $[Pd(PPh_3)_2Cl_2/Br_2]$ with $AgOTf$ in dichloromethane followed by addition of ligand leads to $[Pd(PPh_3)_2(OSO_2CF_3)_2]$ and then $[Pd(PPh_3)_2(RaaiR)](OSO_2CF_3)_2$ [$RaaiR/ = p-R-C_6H_4-N=N-C_3H_2-NN-1-R/$, (1-3), abbreviated as N,N/-chelator, where N(imidazole) and N(azo) represent N and N/, respectively; R = H (a), Me (b), Cl (c) and R/ = Me (1), CH_2CH_3 (2), CH_2Ph (3), OSO_2CF_3 is the triflate anion]. ^{31}P { 1H } NMR confirm that due to the two phosphorus atoms interaction in the azoimine environment resulting sharp peaks. The 1H NMR spectral measurements suggest chelating proton with lot of phenyl protons in the aromatic region. In the 1H - 1H COSY spectrum of the present complexes and contour peaks in the 1H - ^{13}C HMQC spectrum, assign the solution structure in each complexes.

Key words: Palladium(II), arylazoimidazole, 1H ^{13}C (1H), ^{31}P (1H), 1H - 1H COSY, 1H - ^{13}C HMQC NMR, ESI mass, IR spectra, electrochemistry.

INTRODUCTION

Nonlinear optical (NLO) materials have attracted great interest because of their wide range of possible applications in several fields, such as laser technology, telecommunications, data storage, and optical switches (Hissler et al, 2000; Kubo et al, 2002; Lauterbach and Fabian, 1999; Makedonas and Mitsopoulou 2001). The above-mentioned complexes with the "noninnocent" dithiolene ligand represent a very promising class of compounds for NLO materials, in view of their peculiar electronic structure. This specific structure is dominated by the existence in the same molecule of the two different unsaturated chelating ligands, one of which is more easily reduced and the other more easily oxidized. These complexes generally absorb light in the visible and ultraviolet regions. Over the past decade, Eisenberg and co-workers have performed elaborate studies on the charge-transfer excited state of mixed-ligand Pt(II) complexes with diimine and dithiolate ligands. For most complexes, the excited state is considered to involve the

highest occupied molecular orbital (HOMO), which is a mixture of platinum and dithiolate orbital character, and the lowest unoccupied molecular orbital (LUMO)². The square planar geometry of platinum (II) complexes with diimine ligands makes it feasible to introduce selectively properly designed diimine ligands and suitable coligands in a coplanar arrangement and thus allows the tailoring of molecules for potential application as photosensitizers or photocatalysts. Electronic transitions in complexes span, is a broad range depending on both the diimine ligands and the coligands (Huertas et al., 2001). The charge transfer excited state of Pt(II) complexes is emissive, in contradiction to Pd(II), in fluid solution and undergoes electron-transfer quenching both oxidatively and reductively (Huertas et al., 2001). In 1985, Srivastava and co-workers suggested that, both complexes Pt(bpy)(tdt) and Pd(bpy)(tdt) act as photosensitizers for the formation of singlet oxygen, attributing this ability to a unique LL'CT-based excited state (Byabartta et al., 2001). More

recently, attention has again shifted to the mixed ligand complexes of Pd(II) and Pt(II) as they undergo photoinduced oxidation in the presence of atmospheric oxygen to yield monosulfenate, disulfenate, mixed sulfinate/sulfenate, monosulfinate, and disulfinate complexes. In the case, where coligands are no longer innocent, but provide high lying filled p or orbitals, the HOMO may have significant to dominating coligand contributions, admixed to metal nd orbitals, and the resulting lowest transition is assigned to a ligand-to-ligand charge transfer (LL'CT) (Byabartta et al., 2001). Since the HOMO has mixed metal/ligand character, it is also referred to as mixed metal/ligand to ligand charge transfer (MMLL'CT) (Huertas et al., 2001). From this point of view we can assign the main difference between the LL'CT and MMLL'CT transitions as the percentage of metal nd orbitals to HOMO. Since in the literature both assignments have been considered for the lowest energy transition of M(diimine)(dithiolate) complexes along with the nonspecific term "charge transfer to diimine" transition that has been employed by Eisenberg et al. More recently, 2 g,i, it seems that the knowledge of the nature of the frontier orbitals as well as the nature of the energy transitions would be unambiguously a helpful tool in synthesis or design of functional molecules and for a mechanistic analysis of their photochemistry and electrochemistry. An appropriate choice of diimine chelate ligand, metal, and coligand (dithiolene or dithiolate), should therefore allow predetermination of the character of the lowest energy transitions and lowest emitting states in such molecules. Up to now the assignments of their excited state are based mainly on the pioneering experimental work of Eisenberg,² as complemented by elementary theoretical work on frontier orbitals.² In this paper, the reaction of RaaIR/ on Palladium(II) PPh₃ derivatives was examined and the products, [Pd(PPh₃)₂(RaaIR/)](OTf)₃ [RaaIR/ = p-R-C₆H₄-N=N-C₃H₂-NN-1-R/, (1-3), abbreviated as N,N/-chelator, where N(imidazole) and N(azo) represent N and N/, respectively; R = H (a), Me (b), Cl (c) and R/ = Me (1), CH₂CH₃ (2), CH₂Ph (3), OSO₂CF₃ is the triflate anion] were isolated. The complexes were well characterized by IR, ¹H NMR (1D and 2D), mass spectrometry.

EXPERIMENTAL

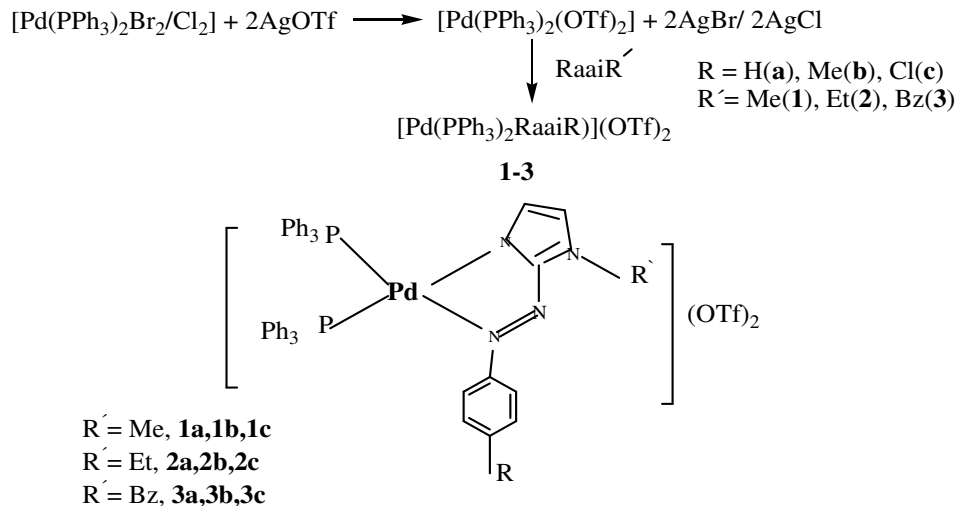
Published methods were used to prepare RaaIR', [PdII(PPh₃)₂(Cl)₂]_{1,2}. All other chemicals and organic solvents used for preparative work were of reagent grade (SRL, Sigma Alhrich). The purification of solvents was done with the following literature method. Microanalytical data (C, H, N) were collected using a Perkin Elmer 2400 CHN instrument. IR spectra were obtained using a JASCO 420 spectrophotometer (4000 - 200 cm⁻¹). The ¹H NMR spectra in CDCl₃ were obtained on a Bruker 500 MHz FT NMR spectrometer using SiMe₄ as internal reference, CFCl₃ (external 19 F). Solution electrical conductivities were measured using a Systronics 304 conductivity meter with solute concentration ~10⁻³ M

in acetonitrile. Mass spectra were recorded on VG Autospec ESI-mass spectrometer. Electrochemical work was carried out using an EG and G PARC Versastat computer controlled 250 electrochemical system. All experiments were performed under a N₂ atmosphere at 298 K using a Pt-disk milli working electrode at a scan rate of 50 mVs⁻¹. All results were referenced to a saturated calomel electrode (SCE).

Preparation of the complexes, bis-(triphenylphosphine){1-(ethyl)-2-(phenylazo)imidazole-(palladium (II))}, [Pd(PPh₃)₂(HaaiEt)](OTf)₂, (2a)

To a dichloromethane solution (15 cm³) of [Pd(PPh₃)₂Cl₂] (0.573 g, 0.1 mmol) was added stoichiometric amount of AgOTf (0.514 g, 0.2 mmol) and the AgCl formed was filtered off. To the filtrate a dichloromethane solution of 1-(ethyl)-2-(phenylazo)imidazole (0.190 g, 0.1 mmol) was added dropwise, and the mixture was stirred at 343 - 353 K for 4 h. The solution that resulted was concentrated (4 cm³) and kept in a refrigerator for 1 h. The addition of hexane to the above orange solution gave a precipitate which was collected by filtration, washed thoroughly with hexane to remove excess ligand and then dried in vacuo over pump overnight. Analytically pure complexes were obtained. The yield was 70 - 80%.

Analysis of [Pd(PPh₃)₂(HaaiEt)](OTf)₂, (2a), Found, C: 67.94, H: 5.1, N: 6.72, Calcd for [C₄₇H₄₂N₄PdP₂](OSO₂CF₃)₂: C: 67.9, H: 5.1, N: 6.73, IR (KBr disk) : v(C=C) 1610 cm⁻¹, v(N=N) 1300 cm⁻¹, v(C=N) 1560 cm⁻¹ v (PPh₃)₂, 1102,755,695 cm⁻¹; ESIMS: 830.5(M-OTf); ¹H NMR (CDCl₃): 7.5(d, 7 and 11H, J = 5Hz), 7.9(d, 8 and 10 H, J = 5 Hz), 7.19-7.27, 7.3-7.42 (Ph of (PPh₃)₂), 7.58(m, 4 and 5 H), 4.54(quetet, Et, J = 5 Hz), 1.59(s, Et); ³¹P {¹H}NMR (CDCl₃) : 28.66 ppm; ¹⁹F {¹H} NMR (CDCl₃) : -78 ppm; Analysis of [Pd(PPh₃)₂(MeaaiEt)](OTf)₂, (2b), Found, C: 68.2, H: 5.29, N: 6.9, Calcd for [C₄₈H₄₄N₄PdP₂](OSO₂CF₃)₂: C: 68.1, H: 5.29, N: 6.6, IR (KBr disk) : v(C=C) 1610 cm⁻¹, v(N=N) 1300 cm⁻¹, v(C=N) 1560 cm⁻¹ v(PPh₃)₂, 1102,755 cm⁻¹; ESIMS: 844.5(M-OTf); ¹H NMR (CDCl₃): 7.52(d, 7 and ¹¹H, J = 5Hz), 7.65(d, 8 and 10 H, J = 5 Hz), 7.19-7.27, 7.31-7.42 (Ph of (PPh₃)₂), 7.5(m, 4 and 5 H), 4.50(quetet, Et, J = 4.5 Hz), 1.5(s, Et); ³¹P {¹H} NMR (CDCl₃) : 28.66 ppm; ¹⁹F {¹H}NMR (CDCl₃) : -78 ppm; Analysis of [Pd(PPh₃)₂(ClaiiEt)](OTf)₂, (2c), Found, C: 65.24, H: 4.71, N: 6.57, Calcd for [C₄₇H₄₁N₄PdClP₂](OSO₂CF₃)₂: C: 65.24, H: 4.71, N: 6.7, IR (KBr disk) : v(C=C) 1612 cm⁻¹, v(N=N) 1305 cm⁻¹, v(C=N) 1566 cm⁻¹ v (PPh₃)₂, 1102,759,699 cm⁻¹; ESIMS: 865(M-OTf); ¹H NMR (CDCl₃): 7.5(d, 7 and 11H, J = 5 Hz), 7.49(d, 8 and 10 H, J = 5 Hz), 7.19-7.27, 7.31-7.42 (Ph of (PPh₃)₂), 7.5(m, 4 and 5 H), 4.54(quetet, Et, J = 5 Hz), 1.59(s, Et); ³¹P {¹H} NMR (CDCl₃) : 28.65 ppm; ¹⁹F {¹H} NMR (CDCl₃) : -78 ppm; Analysis of [Pd(PPh₃)₂(HaaiMe)](OTf)₂, (1a), Found, C: 67.61, H: 4.9, N: 6.92, Calcd for [C₄₆H₄₀N₄PdP₂](OSO₂CF₃)₂: C: 67.64, H: 4.9, N: 6.93, IR (KBr disk) : v(C=C) 1610 cm⁻¹, v(N=N) 1300 cm⁻¹, v(C=N) 1560 cm⁻¹ v (PPh₃)₂, 1102,755,695 cm⁻¹; ESIMS: 816.5(M-OTf); ¹H NMR (CDCl₃): 7.1(d, 7 and 11H, J = 5Hz), 7.2(d, 8 and 10 H, J = 5 Hz), 7.19-7.28, 7.31-7.42 (Ph of (PPh₃)₂), 7.58(m, 4 and 5 H), ³¹P {¹H} NMR (CDCl₃) : 28.70 ppm; ¹⁹F {¹H} NMR (CDCl₃) : -78 ppm; Analysis of [Pd(PPh₃)₂(MeaaiMe)](OTf)₂, (1b), Found, C: 67.9, H: 5.1, N: 6.72, Calcd for [C₄₇H₄₂N₄PdP₂](OSO₂CF₃)₂: C: 67.94, H: 5.11, N: 6.73, IR (KBr disk) : v(C=C) 1614 cm⁻¹, v(N=N) 1302 cm⁻¹, v(C=N) 1560 cm⁻¹ v (PPh₃)₂, 1112,755,695 cm⁻¹; ESIMS: 830.5(M-OTf); ¹H NMR (CDCl₃): 7.1(d, 7 and 11H, J = 5Hz), 7.19(d, 8 and 10 H, J = 5 Hz), 7.13-7.27, 7.3-7.42 (Ph of (PPh₃)₂), 7.58(m, 4 and 5 H), ³¹P {¹H} NMR (CDCl₃) : 28.65 ppm; ¹⁹F {¹H} NMR (CDCl₃) : -78 ppm; Analysis of [Pd(PPh₃)₂(ClaiiMe)](OTf)₂, (1c), Found, C: 64.94, H: 4.61, N: 6.6, Calcd for [C₄₆H₃₉N₄PdClP₂](OSO₂CF₃)₂: C: 64.4, H: 4.61, N: 6.63, IR (KBr disk) : v(C=C) 1610 cm⁻¹, v(N=N) 1300 cm⁻¹,



Scheme 1.

$\nu(\text{C}=\text{N})$ 1560 cm^{-1} ν (PPh_3)₂, 1102,759,695 cm^{-1} ; ESIMS: 851 (M-OTf); ^1H NMR (CDCl_3): 7.5(d, 7 and 11H, J = 5Hz), 7.4(d, 8 and 10 H, J = 5 Hz), 7.19-7.270, 7.3-7.42 (Ph of (PPh_3)₂), 7.58(m, 4 and 5 H), ^{31}P { ^1H } NMR (CDCl_3): 28.66 ppm; ^{19}F { ^1H } NMR (CDCl_3): -78 ppm; Analysis of [$\text{Pd}(\text{PPh}_3)_2(\text{HaaiBz})$](OTf)₂, (3a), Found, C: 69.94, H: 4.91, N: 6.4, Calcd for [$\text{C}_{52}\text{H}_{44}\text{N}_4\text{PdP}_2$](OSO₂CF₃)₂: C: 69.94, H: 4.93, N: 6.3, IR (KBr disk): $\nu(\text{C}=\text{C})$ 1610 cm^{-1} , $\nu(\text{N}=\text{N})$ 1300 cm^{-1} , $\nu(\text{C}=\text{N})$ 1560 cm^{-1} ν (PPh_3)₂, 1112,759,695 cm^{-1} ; ESIMS: 892.5(M-OTf); ^1H NMR (CDCl_3): 7.5(d, 7 and 11H, J = 5Hz), 7.49(d, 8 and 10 H, J = 5 Hz), 7.133-7.27, 7.3-7.42 (Ph of (PPh_3)₂, Bz), 7.58(m, 4 and 5 H), 5.1(querter, J = 5 Hz), ^{31}P { ^1H } NMR (CDCl_3): 28.66 ppm; ^{19}F { ^1H } NMR (CDCl_3): -78 ppm; Analysis of [$\text{Pd}(\text{PPh}_3)_2(\text{MeaaiBz})$](OTf)₂, (3b), Found, C: 70.24, H: 5.15, N: 6.2, Calcd for [$\text{C}_{53}\text{H}_{46}\text{N}_4\text{PdP}_2$](OSO₂CF₃)₂: C: 70.28, H: 5.1, N: 6.3, IR (KBr disk): $\nu(\text{C}=\text{C})$ 1614 cm^{-1} , $\nu(\text{N}=\text{N})$ 1308 cm^{-1} , $\nu(\text{C}=\text{N})$ 1560 cm^{-1} ν (PPh_3)₂, 1102,755,695 cm^{-1} ; ESIMS: 906.5(M-OTf); ^1H NMR (CDCl_3): 7.5(d, 7 and 11H, J = 5Hz), 7.49(d, 8 and 10 H, J = 5 Hz), 7.143-7.27, 7.3-7.42 (Ph of (PPh_3)₂, Bz), 7.58(m, 4 and 5 H), 5.24(querter, J = 5 Hz), ^{31}P { ^1H } NMR (CDCl_3): 28.65 ppm; ^{19}F { ^1H } NMR (CDCl_3): -78 ppm; Analysis of [$\text{Pd}(\text{PPh}_3)_2(\text{ClaaiBz})$](OTf)₂, (3c), Found, C: 67.4, H: 4.65, N: 6.2, Calcd for [$\text{C}_{52}\text{H}_{43}\text{N}_4\text{PdClP}_2$](OSO₂CF₃)₂: C: 67.4, H: 4.65, N: 6.03, IR (KBr disk): $\nu(\text{C}=\text{C})$ 1615 cm^{-1} , $\nu(\text{N}=\text{N})$ 1300 cm^{-1} , $\nu(\text{C}=\text{N})$ 1560 cm^{-1} ν (PPh_3)₂, 1102,755,695 cm^{-1} ; ESIMS: 927(M-OTf); ^1H NMR (CDCl_3): 7.5(d, 7 and 11H, J = 5Hz), 7.19(d, 8 and 10 H, J = 5 Hz), 7.13-7.27, 7.3-7.42 (Ph of Bz, (PPh_3)₂), 7.58(m, 4 and 5 H), 5.24(querter, J = 5 Hz), ^{31}P { ^1H } NMR (CDCl_3): 28.66 ppm; ^{19}F { ^1H } NMR (CDCl_3): -78 ppm.

RESULTS AND DISCUSSION

Reaction of [$\text{Pd}(\text{PPh}_3)_2(\text{Cl})_2$] with AgOTf gives [$\text{Pd}(\text{PPh}_3)_2(\text{OTf})_2$] followed by arylazoimidazole in dichloromethane medium leads to [$\text{Pd}(\text{PPh}_3)_2(\text{RaaiR})$], (1-3), [$\text{RaaiR}/ = \text{p-R-C}_6\text{H}_4\text{-N}=\text{N-C}_3\text{H}_2\text{-NN-1-R'}$, abbreviated as N,N'-chelator, where N(imidazole) and N(azo) represent N and N', respectively; R = H (a), Me

(b), Cl (c) and R/ = Me (1), CH₂CH₃ (2), CH₂Ph (3), OSO₂CF₃ is the triflate anion]. All these complexes are obtained in a very good yield (Scheme 1, nearly 75%). All these nine phosphines are yellow to orange in color. All the structural assignments are supported by elemental analysis and the complexes were characterised by IR, multinuclear NMR (^1H , ^{13}C , ^{31}P , ^{19}F , ^1H ^1H COSY, ^1H ^{13}C HMQC) and ESI mass spectrophotometrically. I.r spectra of the complexes shown in a 1:1 correspondence to the spectra of the dichloro and dibromo analogue, except the appearance of intense stretching at 1605 - 1650 and 1290 - 1350 cm^{-1} with concomitant loss of $\nu(\text{Pd-Cl})$ or Ni-Br at 380 - 340 cm^{-1} .

Vibrations assigned to $\nu(\text{C}=\text{C})$ and $\nu(\text{N}=\text{N})$ appear near at 1600 and 1300 cm^{-1} , respectively. The ESI mass spectrum of a MeCN solution in the positive ion mode is structurally enlightening, since it displays a series of characteristic singly. The ^1H n.m.r. spectra of (1-3) complexes were assigned (measured in CDCl_3 , Figure 1) by comparison with parent palladium dichloro complex and the free ligand. The aromatic portion shows a broad peak, mostly from 7.22 - 7.66 region for the phenyl protons of the triphenylphosphine ligands. The complex shows a sharp peak near at 4 ppm due to the ethyl substitution on RaaiEt. The complexes 1c, 2c, 3c, show broad peak at 4.6 - 4.8 due to CH₂ of the benzyl ring, whereas 1b, 2b, 3b complexes show peaks near at 2.16 ppm due to methyl group of RaaiEt. The proton movement upon substitution (9-R) is corroborated with the electromeric effect of R. The aryl protons (7-H - 11-H) of the complexes are shifted downfield by 0.1-0.7 ppm as compared to those of the parent derivatives. They are affected by substitution; 8- and 10-H are severely perturbed due to changes in the electronic properties

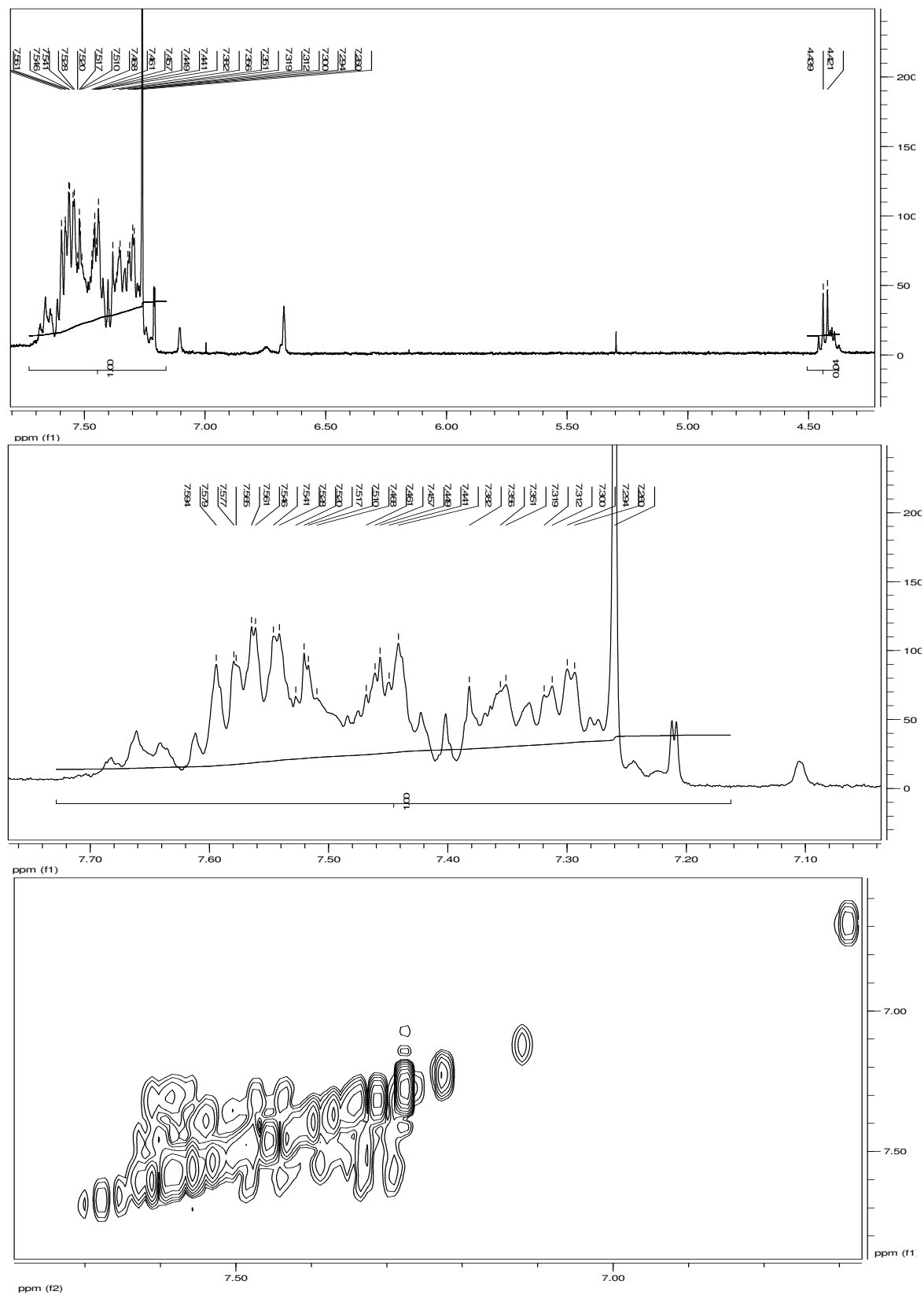
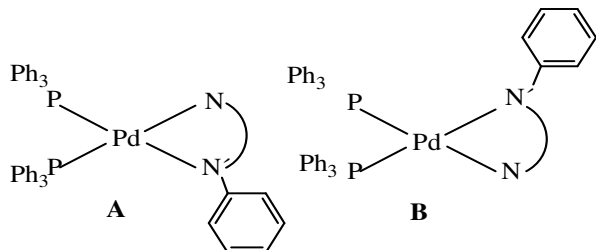


Figure 1. ^1H , ^1H and COSY NMR of complex 2a and ^{31}P (^1H), ^{13}C (^1H), and HMQC NMR of 2b.



Scheme 2.

of the substituents in the C(9)-position (isomer A and B). Phosphorous NMR (measured in CDCl_3) gives direct information about the complex formation and the complex nature. All the complexes of $(\text{PPh}_3)_2$ show one sharp singlet signal near 28.65 ppm. Fluorine NMR, $^{19}\text{F}\{^1\text{H}\}$ NMR, (measured in CDCl_3) show a sharp peak for the triflate ion at near -78 in case of all the complexes.

The COSY spectrum reveals (measured in CDCl_3) the ^1H - ^1H coupling interactions in the molecule. The cross peaks along both the sides of the diagonal identify the nuclei that are coupled to each other. On the contrary, the protons that are decoupled from the adjacent ones due to the lack of α -protons will show no correlation in the spectrum. Extending horizontal and vertical lines from $\delta = 7.32$ ppm and 7.68 ppm [$\text{C}(\text{PPh}_3)\text{H}$] encounter cross peaks at $\delta = 7.12$ ppm and 7.23 ppm, where the C(imidazole)H resonances are merged into multiplets along with the phenyl ring proton resonances. This also helps to accurately assign phenyl and arylazo moiety protons to their respective values, and these protons interact with $(\text{PPh}_3)_2$ moiety. The evidence for the presence of protons attached to the different types of carbon atoms in the spectrum is obtained from the ^1H - ^{13}C HMQC spectrum. The ^1H - ^{13}C heteronuclear multiple-quantum coherence (HMQC) spectrum provides information (measured in CDCl_3) regarding to the interaction between the protons and the carbon atoms to which they are directly attached. In the present complexes, the absence of any contours at higher frequency region assign them C-azoimine, C- $(\text{PPh}_3)_2$, carbon atoms respectively (Scheme 2). This is because they belong to the non-protonated carbon atoms on the dppe and azoimine rings. The peaks observed at $\delta = 134, 131, 135.6$ ppm and 137.6 ppm are assigned to the phenyl of arylazo carbon atoms respectively (C7,C11;C8,C10), due to their interaction with H resonance at $\delta = 7.42$ -7.5, 7.55, 7.82, 7.80 ppm and 7.38 ppm.

Conclusion

This work describes the isolation of a novel series of

palladium(II) arylazoimidazole complexes with a $(\text{PPh}_3)_2$ link and their spectral and elemental characterisation. ^1H NMR study suggests azoimine and $(\text{PPh}_3)_2$ linkage. ^{31}P $\{^1\text{H}\}$ NMR shows one sharp signals which is at lower field than that of the parent dichloro and dibromo complexes. ^{19}F $\{^1\text{H}\}$ NMR suggest the presence of triflate ion. ^{13}C . ^1H - ^1H COSY spectrum as well as the contour peaks in the ^1H - ^{13}C HMQC spectrum of the present complexes, confirm their assignment of accurate structure and in solution proton proton interaction, proton-carbon interaction, respectively.

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