



Synthesis and Characterization of Novel Cationic Phosphinoamine-Pd(II) Complexes of Imidazole

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Two new cationic Pd(II) complexes $[\text{PdCl}\{\eta^2\text{-(P,N)PPh}_2\text{py}\}\{\eta^1\text{-(N)DiphIm}\}](\text{PF}_6)$ (**1**) and $[\text{PdCl}\{\eta^2\text{-(P,N)PPh}_2\text{Etpy}\}\{\eta^1\text{-(N)DiphIm}\}](\text{PF}_6)$ (**2**), where PPh₂py is 2-(diphenylphosphino)pyridine and PPh₂Etpy is 2-{2-(diphenylphosphino)ethyl}pyridine, have been synthesized by reacting 4,5-diphenylimidazole (4,5-DiphIm) with the respective complexes $[\text{PdCl}_2\{\eta^2\text{-(P,N)PPh}_2\text{py}\}]$ and $[\text{PdCl}_2\{\eta^2\text{-(P,N)PPh}_2\text{Etpy}\}]$ in 1:1 molar ratio by stirring in dichloromethane in presence of NH₄PF₆ under N₂ at room temperature. The complexes were characterized by elemental analysis, ESI(+)-MS, UV-vis, FTIR, conductivity measurements, thermal analysis and ¹H and ³¹P{¹H} NMR studies.

Keywords: Coordination chemistry, Palladium(II), Cationic complex, Imidazole, Room temperature.

INTRODUCTION

The coordination chemistry of platinum group metals (PGMs) is pivotal in catalysis, particularly in various chemical transformations. The six PGMs—platinum, palladium, rhodium, ruthenium, iridium and osmium are known for their ability to form a wide range of coordination complexes with different ligands, which significantly enhances their catalytic properties [1-6]. In last few couples of years, numerous Pd(II) complexes featuring diverse ligand systems have been reported to enhance the efficiency of coupling reactions [6-14]. Among the many chemical processes, the Pd-catalyzed cross-coupling reaction has emerged as one of the key techniques for creating carbon-carbon and carbon-heteroatom bonds in the production of novel polymers, bioactive natural products, agrochemicals and pharmaceuticals (primarily herbicides, fungicides and insecticides [15-18]. The phosphinoamine-Pd(II)-imidazole complexes represent a category of palladium complexes featuring phosphinoamine and imidazole ligands. The inclusion of phosphinoamine and imidazole ligands in these complexes can give rise to intriguing structural characteristics and reactivity behaviours. The hemilability of these ligands, wherein one coordination bond can be reversibly disrupted while the other remains intact, is a significant attribute that can impact the catalytic efficacy of these complexes [9].

To the best of our knowledge, a few Pd(II) complex bearing both phosphinoamine and imidazole ligands are reported in the

literature [9]. Moreover, the presence of two bulky, electron-rich ligands within the same coordination sphere increases the steric congestion around the Pd metal, which speeds up the rate of both the steps of oxidative addition and reductive elimination of the reaction mechanism [6,19].

The imidazoles are very attractive N-donor ligands for organometallic chemistry due to their commercial availability, low cost and ability to stabilize metal centres through a combination of σ -donation and weak π -acceptance. This makes them useful for applications like catalysis [20-24]. Here, we reported the synthesis of two new cationic palladium(II) complexes **1** and **2** containing two sterically crowded ligands, specifically an P,N-donor and an N-donor imidazole. The identities of the complexes were confirmed by different physico-chemical and spectroscopic methods.

EXPERIMENTAL

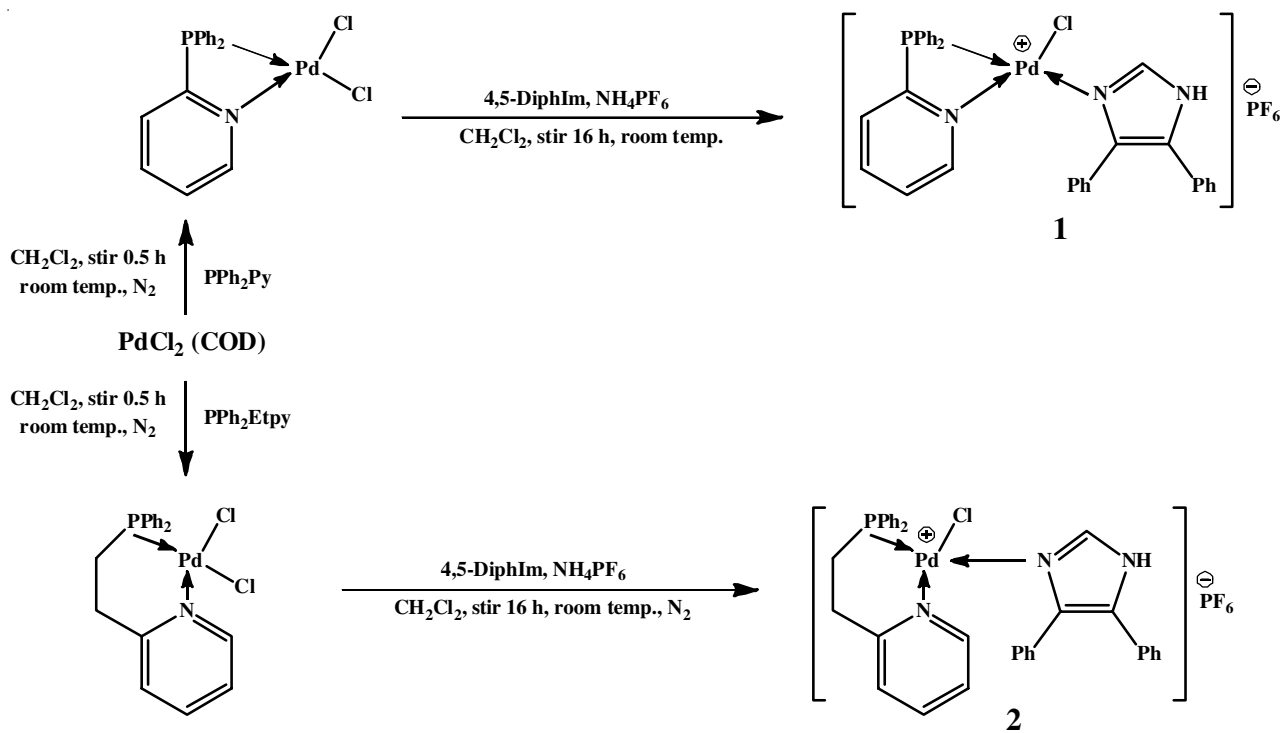
Palladium(II) chloride (PdCl₂), 1,5-cyclooctadiene (COD) and tetrabutylammonium perchlorate (TBAP) were purchased from Acros Chemicals. Ammonium hexafluorophosphate (NH₄PF₆) was procured from Fluka and used as received, whereas 4,5-diphenylimidazole (4,5-DiphIm) was procured from Aldrich, USA and was used without further purification. The precursor complexes $[\text{PdCl}_2(\text{COD})]$ [25] and $[\text{PdCl}_2\{\eta^2\text{-(P,N)PPh}_2\text{py}\}]$ [26] were synthesized as reported. Another reported precursor complex $[\text{PdCl}_2\{\eta^2\text{-(P,N)PPh}_2\text{Etpy}\}]$ was

synthesized by using $[\text{PdCl}_2(\text{COD})]$ [9] instead of $[\text{PdCl}_2(\text{PhCN})_2]$ [27] was also synthesized according to the literature. The solvents used were of AR grade were purchased from different Indian firms and distilled and dried over 4 Å molecular sieves prior to use. The reactions were performed in inert atmosphere of dry nitrogen.

Synthesis of $[\text{PdCl}\{\eta^2\text{-(P,N)PPh}_2\text{py}\}\{\eta^1\text{-(N)DiphIm}\}]\text{-}(\text{PF}_6)$ (1): To a suspension of $[\text{PdCl}_2\{\eta^2\text{-(P,N)PPh}_2\text{py}\}]$ (0.150 g, 0.341 mmol) in dichloromethane (20 mL), NH_4PF_6 (0.039 g, 0.239 mmol) was added and stirred for 2 h under N_2 at room temperature resulting a yellow mixture. To this mixture, 4,5-DiphIm (0.075 g, 0.341 mmol) solution in THF (10 mL) was added with constant stirring during which the colour sharply changed from yellow to wine red. The resulting mixture was stirred for 16 h at room temperature. The white precipitate of NH_4Cl was separated by filtration and the filtrate was evaporated *in vacuo*. The sticky residue was washed with ethyl ether and recrystallized from dichloromethane to yield the product as brown solid (**Scheme-I**). Yield: 82% (0.123 g); m.p.: 80 °C; $\Lambda = 88 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Elemental anal. of calcd. (found) % for $\text{C}_{32}\text{H}_{26}\text{N}_3\text{P}_2\text{ClF}_6\text{Pd}$: C, 49.87 (49.40); H, 3.40 (3.21); N, 5.45 (5.22). Selected IR frequencies (KBr, ν_{max} , cm^{-1}): 1575(m) $\nu_{\text{py}}(\text{C}=\text{N})$, 843(s) $\nu(\text{P}-\text{F})$, 563(m) $\delta(\text{PFP})$, 534(s), 509(m) $\nu_{\text{py}}(\text{Pd}-\text{N})$, 451(w) $\nu(\text{Pd}-\text{P})$, 365(s) $\nu(\text{Pd}-\text{Cl})$, 278(ms) $\nu_{\text{im}}(\text{Pd}-\text{N})$. ESI(+) MS, m/z (% intensity): 793 $[\text{M}+\text{Na}]^+$, 770 $[\text{M}]^+$, 625 $[\text{M}-\text{PF}_6]^+$ (base peak), 589 $[\text{M}-\text{Cl}^{35}-\text{PF}_6]^+$; UV-vis [λ nm, (CHCl_3): 349 ($n \rightarrow \pi^*$), 273 ($\pi \rightarrow \pi^*$), 228 ($\pi \rightarrow \pi^*$); ^1H NMR [δ , ppm]: (CDCl_3 , RT): 12.09 (s, 1H, H^1), 8.60 (d, $J_{\text{H-H}} = 4.2$ Hz, 1H, H^6), 8.59 (m, 1H, H^4), 8.39 (s, 1H, H^2), 7.29-7.38 (m, 10H, Ph), 7.44-7.74 (m, 2H, $\text{H}^{3,5}$), 6.97-7.38 (m, 20H, Ph); $^{31}\text{P}\{^1\text{H}\}$ NMR [δ , ppm]: (CDCl_3 , RT): -9.62(s, 1P, PPh_2), -161.01(spt, $J_{\text{P-F}} = 711\text{Hz}$, PF_6^-).

Synthesis of $[\text{PdCl}\{\eta^2\text{-(P,N)PPh}_2\text{Etpy}\}\{\eta^1\text{-(N)DiphIm}\}]\text{-}(\text{PF}_6)$ (2): A solution of 4,5-DiphIm (0.052 g, 0.236 mmol) in 8 mL THF was added dropwise to a well-stirred suspension of $[\text{PdCl}_2\{\eta^2\text{-(P,N)PPh}_2\text{Etpy}\}]$ (0.110 g, 0.235 mmol) and NH_4PF_6 (0.039 g, 0.239 mmol) in dichloromethane. The colour of the solution changed gradually from yellow to light yellow. This reaction mixture was stirred at room temperature for 16 h. The white precipitate of NH_4Cl was removed by filtration and the filtrate was evaporated under reduced pressure to get a solid mass. The sticky residue was washed with hexane and petroleum ether and recrystallized from dichloromethane to get the final product as pale yellow solid compound (**Scheme-I**). Yield: 72% (0.079 g); m.p. 99 °C; $\Lambda = 84 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Elemental anal. of calcd. (found) % for $\text{C}_{34}\text{H}_{29}\text{N}_3\text{P}_2\text{ClF}_6\text{Pd}$: C, 51.13 (50.97); H, 3.63 (3.25); N, 5.26 (5.11). Selected IR frequencies (KBr, ν_{max} , cm^{-1}): 3111(m), 3061(m) $\nu(\text{C}-\text{H})$, 1609(m) $\nu_{\text{py}}(\text{C}=\text{N})$, 845(s) $\nu(\text{P}-\text{F})$, 559(s) $\delta(\text{PFP})$, 532(m), 509(w) $\nu_{\text{py}}(\text{Pd}-\text{N})$, 446(m) $\nu(\text{Pd}-\text{P})$, 349(s) $\nu(\text{Pd}-\text{Cl})$, 291(ms) $\nu_{\text{im}}(\text{Pd}-\text{N})$. ESI(+)MS, m/z (% intensity): 654 $[\text{M}+1-\text{PF}_6]^+$, 653 $[\text{M}-\text{PF}_6]^+$ (base peak), 544 $[\text{M}+1\text{-DiphIm}-\text{Cl}^{35}]^+$, 434 $[\text{M}+\text{H}-\text{PF}_6\text{-DiphIm}]$; UV-vis [λ nm, (CHCl_3): 340 ($n \rightarrow \pi^*$), 266 ($\pi \rightarrow \pi^*$), 228 ($\pi \rightarrow \pi^*$); ^1H NMR [δ , ppm]: (CDCl_3 , RT): 12.10 (s, 1H, H^1), 9.02 (d, $J_{\text{H-H}} = 5.60$ Hz, 1H, H^6), 7.96 (s, 1H, Im, H^2), 7.82-7.86 (m, 1H, H^4), 7.52-7.62 (m, 10H, Ph), 7.29-7.38 (m, 10H, Ph), 7.29-7.39 (m, 10H, Ph, $\text{H}^{4,5}$), 6.89-6.94 (m, 2H, $\text{H}^{3,5}$), 3.99-4.11 (m, 2H, H^7), 2.87-3.02 (m, 2H, H^8); $^{31}\text{P}\{^1\text{H}\}$ NMR [δ , ppm]: (CDCl_3 , RT): 14.35 (s, 1P, PPh_2), -160.73 (spt, $J_{\text{P-F}} = 712$ Hz, PF_6^-).

Physical measurements: The melting points of the complexes were determined using a Buchi B450 (BÜCHI Labor-technik AG, Switzerland) melting point apparatus. Elemental analyses were carried out on Elementar Vario EL III Carlo Erba 1108 instrument. The FT-IR spectra (4000-240 cm^{-1}) of the



Scheme-I: Synthesis of complexes 1 and 2

complexes were recorded in KBr disk on a Shimadzu Prestige-21 FTIR spectrophotometer (Shimadzu Corp., Japan). The UV-visible spectra of the complexes (800-200 nm) were recorded in acetonitrile and dichloromethane on Shimadzu-Graphicord UV-1700 spectrometer using 1 cm³ quartz cell. The conductivity of the complexes was measured by using a digital conductivity bridge (type ELICO-CM-180) in dichloromethane and acetonitrile (10⁻² M) at 25 °C. The ¹H and ³¹P{¹H} NMR spectra were recorded on a Bruker Advance II 400 NMR spectrometer (Bruker India Scientific Pvt. Ltd, India) operating at 400.13, 100 and 161.98 MHz, respectively. All the spectra were recorded in deuterated solvents such as CD₃CN/CDCl₃ using TMS for ¹H spectra and 85% aqueous H₃PO₄ for ³¹P{¹H} NMR spectra as standard. The ¹H NMR assignments were performed with respect to the labelling chart and the ESI(+) mass spectra were recorded in CD₃CN/CDCl₃ on a Waters ZQ-4000 mass.

RESULTS AND DISCUSSION

The reaction of one molar equivalent of the neutral complexes [PdCl₂{η²-(P,N)PPh₂py}] and [PdCl₂{η²-(P,N)PPh₂Etpy}] with one molar equivalent of 4,5-DiphIm in presence of NH₄PF₆ by stirring in CH₂Cl₂ at room temperature for 14 h and 16 h under N₂ led to the formation of two cationic complexes **1** and **2**, respectively (**Scheme-I**). The complexes gave satisfactory elemental analysis (C, H, N) are in agreement with the proposed structures. The ESI(+) mass spectrum of complex **1** shows three molecular ion peaks at *m/z* 770 [M]⁺, 793 [M+Na]⁺ and 625 [M-PF₆]⁺ (base peak, 100%). The peak at *m/z* 589 corresponds to [M-Cl³⁵-PF₆]⁺ fragment. Similarly, complex **2** exhibits two molecular ion peaks at *m/z* 654 [M+I-PF₆]⁺ and 653 [M-PF₆]⁺. The position of the various peaks and overall fragmentation patterns in the mass spectra of the complexes conform well with their assigned formulation.

FTIR spectral studies: The IR spectrum of complex **1** exhibits a strong absorption band at 843 cm⁻¹ which is attributed to the ν(P-F) stretching bands of the PF₆⁻ anion. The δ(PFP) vibrational mode of PF₆⁻ anion was observed as medium strong band at 563 cm⁻¹ [28] (Fig. 1a). The IR spectrum of complex **1** exhibits the characteristic peaks for ν(Pd-P), ν(Pd-N), ν(Pd-Cl) and ν(Pd-N_{imidazole}) vibrations in the ranges 451, 515, 365 and 278 cm⁻¹, respectively with small shift compared to the precursor complex [PdCl₂{η²-(P,N)PPh₂py}] [29].

Similar to complex **1**, the IR spectrum of complex **2** shows the strong ν(P-F) stretching bands of the PF₆⁻ anion at 845 cm⁻¹. The δ(PFP) vibrational mode of PF₆⁻ anion of the complex appears as medium-strong band at 559 cm⁻¹ [28]. The complex displays the characteristic peaks for ν(Pd-P), ν(Pd-N) and ν(Pd-Cl) vibrations in the range 376-349 cm⁻¹ [29] with small shift as compared to the precursor complex [PdCl₂{η²-(P,N)PPh₂Etpy}]. In the far-IR region, a new medium-strong intensity band at 272-291 cm⁻¹ region may be assigned to ν(Pd-N_{imidazole}) stretching vibration for the complex [29] (Fig. 1b).

UV-vis spectral studies: The UV-vis spectrum of complex **1** in dichloromethane shows three bands in the regions 228-273 nm and 349 nm presumably due to intraligand π→π* and n→π* transitions [30-32], respectively (Fig. 2a). The complex may contain some contribution of Cl⁻→Pd²⁺ charge transfer transition. Compared to the starting compound [PdCl₂{η²-(P,N)PPh₂py}] (394 nm), the band for n→π* transition is blue shifted, indicating a change of ligand environment about the Pd²⁺ ion [33,34].

The UV-vis spectrum of complex **2** shows two intraligand π→π* transitions in the region 228 nm and 266 nm. The intraligand n→π* transition for these complexes appeared in the region 340 nm with some contribution of Cl⁻→Pd²⁺ charge transfer transition [35] (Fig. 2b). Compared to [PdCl₂{η²-(P,N)PPh₂Etpy}], (λ_{max}, n→π* = 346 nm), n→π* transition is shifted blue. This indicates the change of electronic environment of the ligand about the Pd²⁺ ion [33,34] due to complexation.

NMR spectral studies: The ³¹P{¹H} NMR spectrum of complex **1** displays one singlet at δ 9.62 ppm with a significant upfield shift of 0.47 ppm, as compared to their neutral parent compound [PdCl₂{η²-(P,N)PPh₂py}] (δ 9.15 ppm), indicates the formation of new complexes. The upfield resonances in complex **1** is known to be diagnostic of four membered chelate complex [36-38]. The coordination of imidazole ligands might increase the electron density on the Pd ion due to their good electron donating ability. This increases the degree of back-donation from Pd ion to pyridylphosphine ligand (dπ-pπ) in comparison to their precursor complex [39]. The ³¹P resonance of PF₆⁻ counter ion for the complex is observed at δ = 161.01 ppm (*J_{P-F}* = 711 Hz) [28].

The ¹H NMR spectra of complex **1** exhibits a singlet at δ 8.39 ppm due to H^{2'} (Fig. 3a) proton of 4,5-DiphIm, with

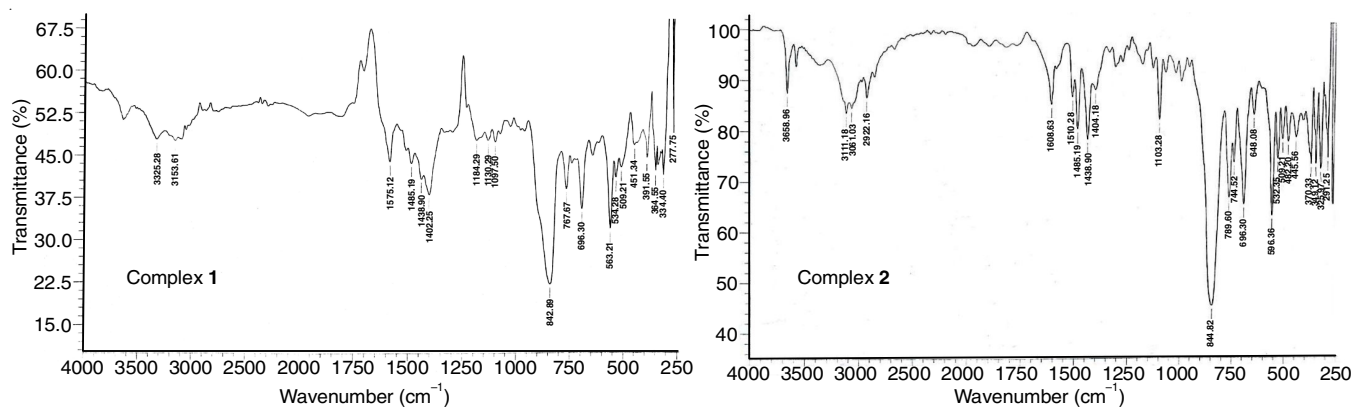


Fig. 1. FTIR spectra of the complexes **1** and **2**

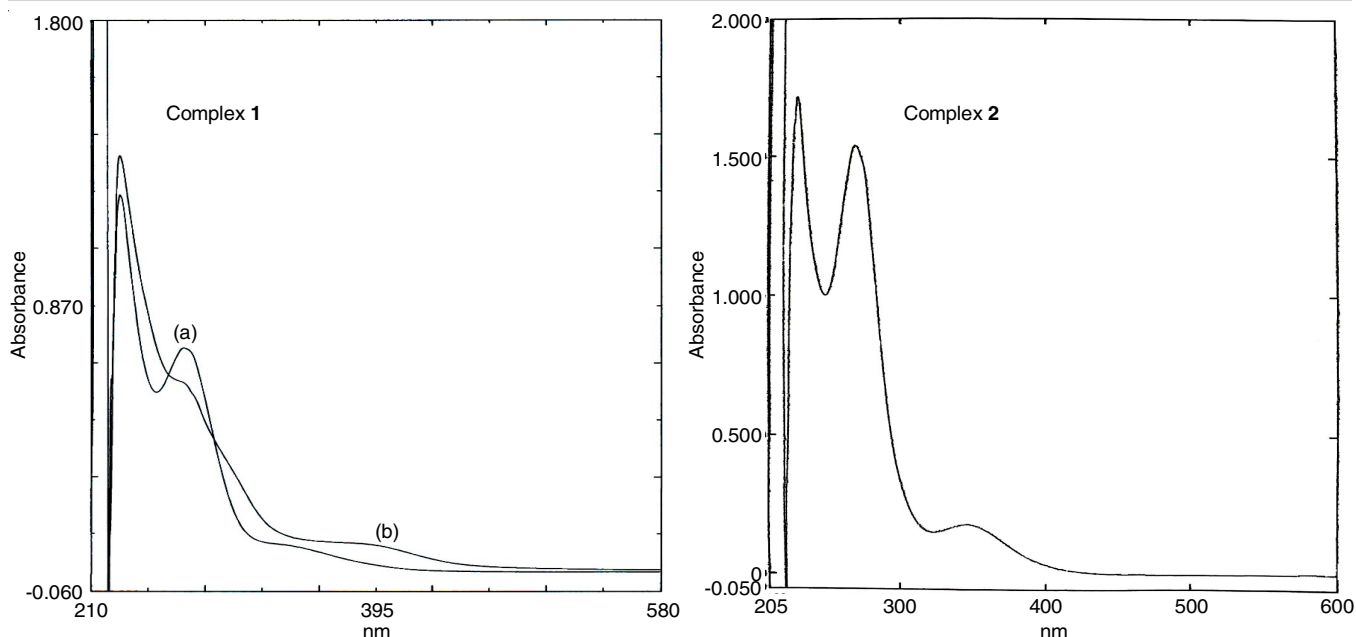


Fig. 2. UV-vis spectra of complex 1 (a), precursor complex $[\text{PdCl}_2\{\eta^2\text{-(P,N)PPh}_2\text{py}\}]$ (b) and complex 2

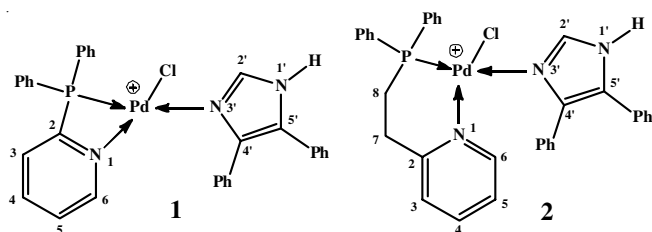


Fig. 3. Numbering of H-atom positions in pyridyl, imidazole and alkyl groups of complexes 1 and 2

significant downfield shift compared to the free imidazole, clearly indicates coordination of the imidazole through the N(3') atom. In addition, multiplets at δ 6.97-7.38 ppm can be assigned to phenyl protons. The singlets at δ 12.09 ppm in complex 1 can be attributed to the N(1')-H proton. Moreover, the presence of characteristic peaks for the protons of phenyl and pyridine rings further support the formation of the complex.

In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex 2, a singlet is observed at δ 14.35 ppm, assignable to ^{31}P nucleus of PPh_2Etpy ligand (Fig. 3b). The signal associated with ^{31}P nucleus of

PPh_2Etpy exhibited a significant downfield shift in the complex in comparison to the starting complex $[\text{PdCl}_2\{\eta^2\text{-(P,N)PPh}_2\text{-Etpy}\}]$ (δ 6.85 ppm) [35,40]. The signal for ^{31}P nucleus of PF_6^- ion of complex 2 is detected as septet at δ 160.73 ppm ($J_{\text{P,F}} = 712$ Hz) [28]. The ^1H NMR spectrum of complex 2 shows the multiplets in the range δ 7.29-7.52 ppm are characteristic of aromatic ring protons. The signals for H^2 protons of complex 2 are observed at δ 7.96 ppm. The downfield shift of resonance for H^2 proton compared to free imidazole supports coordination of imidazole through the N(3') atom. The N(1')-H proton of 4,5-DiphIm in complex 2 resonates at δ 12.10 ppm.

TGA-DTG studies: The TGA data are also in agreement with the proposed molecular formulation of the complexes. In the TGA analysis, complex 1 exhibit major weight loss of 77.5% (calcd. 78.2%) in the temperature range 185.9-358.9 °C assigned to the loss of PPh_2py , 4,5-DiphIm and PF_6^- ions (Fig. 4a). The thermogravimetry analysis of complex 2 remains thermally stable up to 124 °C and displays major weight of 78.3% (calcd. 79.4%) in the temperature range 125-379 °C due to loss of PPh_2Etpy , 4,5-DiphIm and PF_6^- ions (Fig. 4b).

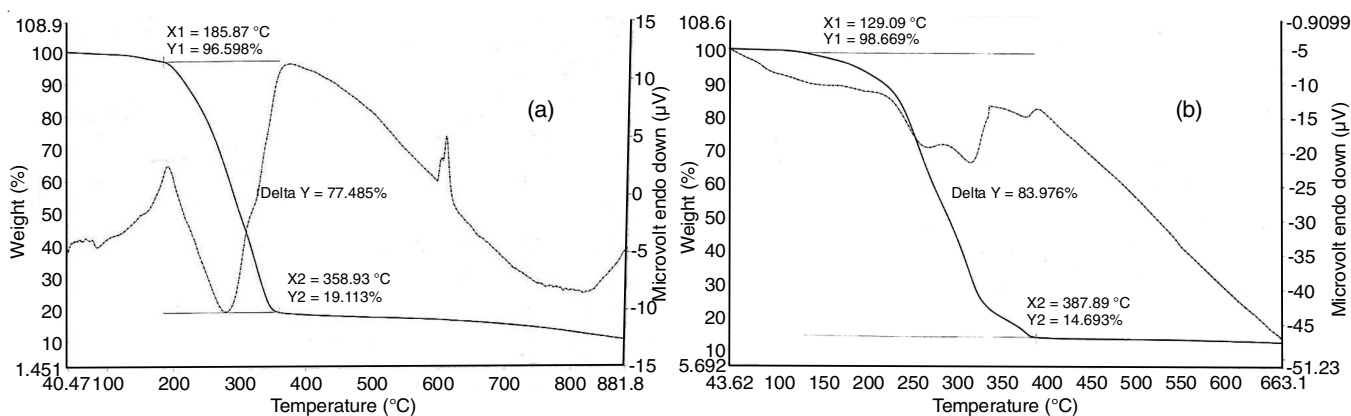


Fig. 4. TGA-DTA of complexes 1 (a) and 2 (b)

Conclusion

Two new cationic Pd(II) complexes containing two sterically crowded ligands, specifically an P,N-donor and an N-donor imidazole have been synthesized. The identity of the complexes were established using FT-IR, ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR and ESI(+) mass spectroscopies.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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