



Original Article

Palladium(II) Complex with Tridentate Ligand Containing Pyrenyl Core

Nguyen Minh Hai^{1,*}, Tran Thi Tam Thu¹, Dinh Thi Thao²

¹Faculty of Chemistry, VNU University of Science, 19 Le Thanh Tong, Hanoi, Vietnam

²Department of Chemistry, Faculty of Science, Army Academy 1, Co Dong, Son Tay, Hanoi, Vietnam

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Abstract: A series of ligands containing pyrenyl core which are **PyEt1**, **PyEt2**, and **PyEt3** have been successfully synthesized. **PyEt2**, a bidentate ligand and **PyEt3**, a tridentate ligand were used to prepared Pd(II) complexes by reactions with PdCl₂(CH₃CN)₂. The titled compounds displayed intriguing geometries around the central palladium atoms. ¹H-NMR results showed that palladium in **Pd-PyEt3** adopts a five-coordinate configuration.

Keywords: Pyrene, palladium, five coordination.

1. Introduction

Polycyclic aromatic hydrocarbons (PAH) are a class of compounds that possess extended π conjugated systems. This unique structural property renders PAHs strong absorption and emission in visible region. However, PAH-based research is often limited by their low solubility in common organic solvents. Functionalization of pyrene by appending solubilizing groups that contain donor atoms like nitrogen proved to be an effective strategy to overcome its poor solubility and open up its coordination chemistry [1-4].

Palladium(II) complexes are well-known for its stable d⁸ square-planar geometries. Large crystal field stabilization is attributed to this preferential structure. Other coordination modes rather than square-planar would be of unusually fundamental importance [5]. The ligands with multiple donor atoms are expected to give rise such structures.

In the present work, we describe the syntheses and NMR structural determination of a series of ligands which contain pyrenyl moiety and their interactions with palladium(II) ion. Our

* Corresponding author.

Email address: minhhai.nguyen@hus.edu.vn

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results show that **PyEt3** can bind to the Pd(II) ion to form an unusual five-coordinate complex.

2. Experimental

2.1. Materials and instruments

All the chemical reagents used in the experiments were obtained from commercial sources as guaranteed-grade reagents and used without further purification.

The FT-IR spectra of the complexes were measured on a FT-IR 8700 infrared spectrophotometer ($4000\text{--}400\text{ cm}^{-1}$) in KBr pellets. The $^1\text{H-NMR}$ spectra were recorded on a Bruker-500 MHz spectrometer in CDCl_3 solution at 300K.

2.2. Synthesis of PyEt1

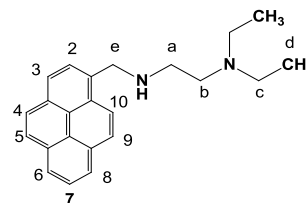
To a 10 ml ethanolic solution of pyrene-1-carbaldehyde (0.100 g, 0.435 mmol) was added N,N-diethylethylenediamine (0.166 g, 1.426 mmol). The resulting mixture was stirred and refluxed for 5 h. The solvent was reduced to dryness and then a large amount of water was used for washing to produce a yellow semi-solid. Yield: 0.12 g (85%).

Data for PyEt1: IR: $\nu_{\text{max}}/\text{cm}^{-1} = 3606$ (w), 2964 (w), 1624 (s), 1597 (m), 1449 (m), 1201 (s), 1176 (s), 1060 (s), 1143 (s), 844 (s), 713 (m); $^1\text{H NMR}$ (CDCl_3 , δ ppm): 9.33 (s, 1H, H_e, imine), 8.91 (d, $J = 9$ Hz, 1H, H₁₀, pyrenyl), 8.52 (d, $J = 8.0$ Hz, 1H, H₂, pyrenyl), 8.23-8.02 (m, 7H, H_{3,4,5,6,7,8,9}, pyrenyl), 3.95 (t, $J = 7.0$ Hz, 2H, H_a, CH₂), 2.94 (t, $J = 7.0$ Hz, 2H, H_b, CH₂), 2.69 (q, $J = 7.0$ Hz, 4H, H_c, CH₂), 1.11 (t, $J = 7.0$ Hz, 6H, H_d, CH₃).

2.3. Synthesis of PyEt2

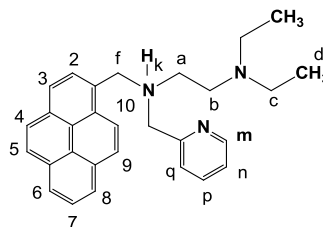
To a yellow solution of **PyEt1** (0.115 g, 0.360 mmol) in CH_2Cl_2 /methanol (10/5 mL) was added NaBH_4 (0.760 g, 2.000 mmol). The mixture was stirred overnight, then dried and washed with water to give a pale yellow product. Yield: 0.10 g (83%).

Data for PyEt2: IR: $\nu_{\text{max}}/\text{cm}^{-1} = 3294$ (w), 1600 (s), 1587 (s), 1454 (s), 1382 (m), 1066 (m), 846 (s), 756 (s); $^1\text{H NMR}$ (CDCl_3 , δ ppm): 8.37 (d, $J = 9$ Hz, 1H, H₁₀, pyrenyl), 8.18-7.97 (m, 8H, H_{2,3,4,5,6,7,8,9}, pyrenyl), 4.50 (s, 2H, H_f, CH₂), 2.85 (t, $J = 6.0$ Hz, 2H, H_a, CH₂), 2.62 (t, $J = 6.0$ Hz, 2H, H_b, CH₂), 2.49 (q, $J = 7.0$ Hz, 4H, H_c, CH₂), 0.99 (t, $J = 7.0$ Hz, 6H, H_d, CH₃).



2.4. Synthesis of PyEt3

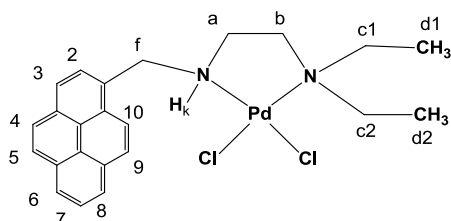
0.100 g (0.304 mmol) of **PyEt2** was dissolved in 10 mL of CH_3CN in a 100 mL round bottom flask. To the resulting solution was added 0.050 g (0.304 mmol) of 2-(chloromethyl)pyridine hydrochloride and 1.000 g of $\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$. The mixture was refluxed for 72 h in the absence of light. The solvent was then removed by rotary evaporation. Extraction with CH_2Cl_2 yielded a brownish solid. Yield: 0.090 g (71%).



Data for PyEt3: IR: $\nu_{\text{max}}/\text{cm}^{-1} = 3039$ (w), 1649 (s), 1587 (s), 1431 (s), 1373 (m), 1066 (m), 844 (s), 756 (s). $^1\text{H NMR}$ (CDCl_3 , δ ppm): 8.59 (d, $J = 9$ Hz, 1H, H₁₀, pyrenyl), 8.47 (dd, $J = 6$ Hz, 1H, H_m, pyridine), 8.19-7.98 (m, 8H, H_{2,3,4,5,6,7,8,9}, pyrenyl), 7.55 (dt, $J = 6$ Hz, 1H, H_n, pyridine), 7.43 (d, $J = 6$ Hz, 1H, H_p, pyridine), 7.07 (dt, $J = 6$ Hz, 1H, H_q, pyridine), 4.39 (s, 2H, H_f, CH₂), 3.87 (s, 2H, H_g, CH₂), 2.78 (t, $J = 6.0$ Hz, 2H, H_a, CH₂), 2.72 (t, $J = 6.0$ Hz, 2H, H_b, CH₂), 2.46 (q, $J = 7.0$ Hz, 4H, H_c, CH₂), 0.93 (t, $J = 7.0$ Hz, 6H, H_d, CH₃).

2.5. Synthesis of Pd-PyEt2

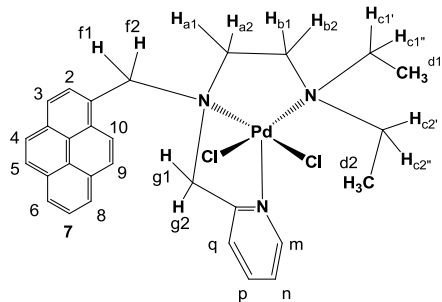
To a CH_2Cl_2 solution of **PyEt2** (0.010 g, 0.030 mmol) was added $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ (0.008 g, 0.031 mmol). A clear yellowish solution was obtained after 4 h of stirring at room temperature. The solvent was reduced and excess hexane was added to afford the titled product. Yield: 0.011 g (72%).



Data for Pd-PyEt2: IR: $\nu_{\text{max}}/\text{cm}^{-1} = 3041$ (w), 1641 (s), 1597 (s), 1434 (s), 1383 (m), 1069 (m), 843 (s), 759 (s). $^1\text{H NMR}$ (CDCl_3 , δ ppm): 8.67 (d, 1H, H_{10} , pyrenyl), 8.38-8.11 (m, 8H, $\text{H}_{2,3,4,5,6,7,8,9}$, pyrenyl), 6.07 (m, 2H, H_f , CH_2), 5.34 (d, 2H, H_a , CH_2), 4.50 (t, 2H, H_b , CH_2), 2.81 (q, 2H, H_{c1} , CH_2), 2.61 (q, 2H, H_{c2} , CH_2), 1.49 (t, 3H, H_{d1} , CH_3), 1.49 (t, 3H, H_{d2} , CH_3).

2.6. Synthesis of Pd-PyEt3

The compounds were prepared following the procedures for **Pd-PyEt2**, except that **PyEt3** was used instead of **PyEt2**. Yield: 77%.



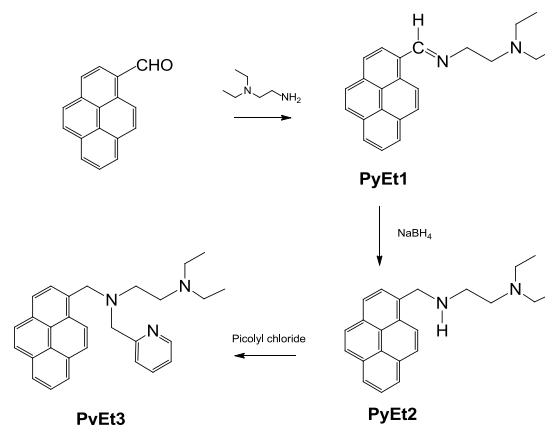
Data for Pd-PyEt3: IR: $\nu_{\text{max}}/\text{cm}^{-1} = 3032$ (w), 1651 (s), 1590 (s), 1434 (s), 1376 (m), 1069 (m), 847 (s), 756 (s). $^1\text{H NMR}$ (CDCl_3 , δ ppm): 9.29 (d, 1H, H_{10} , pyrenyl), 8.88-7.83 (m, 8H, $\text{H}_{2,3,4,5,6,7,8,9}$, pyrenyl), 7.60 (d, 1H, H_m , pyridine), 6.49 (d, 1H, H_q , pyridine), 6.46 (t, 1H, H_p , pyridine), 5.94 (t, 1H, H_n , pyridine), 5.42 (m, 2H, $\text{H}_{f1, f2}$, CH_2), 5.12 (m, 2H, $\text{H}_{g1, g2}$, CH_2), 4.55 (d,

1H, H_{a1} , CH_2), 4.43 (t, 1H, H_{a2} , CH_2), 3.91 (m, 1H, $\text{H}_{c1'}$, CH_2), 3.70 (t, 1H, H_{b1} , CH_2), 3.44 (m, 1H, $\text{H}_{c1''}$, CH_2), 3.10 (d, 1H, H_{b2} , CH_2), 3.02 (m, 1H, $\text{H}_{c2'}$, CH_2), 2.56 (m, 1H, $\text{H}_{c2''}$, CH_2), 1.66 (t, 3H, H_{d1} , CH_3), 1.48 (t, 3H, H_{d1} , CH_3).

3. Results and Discussion

3.1. Syntheses

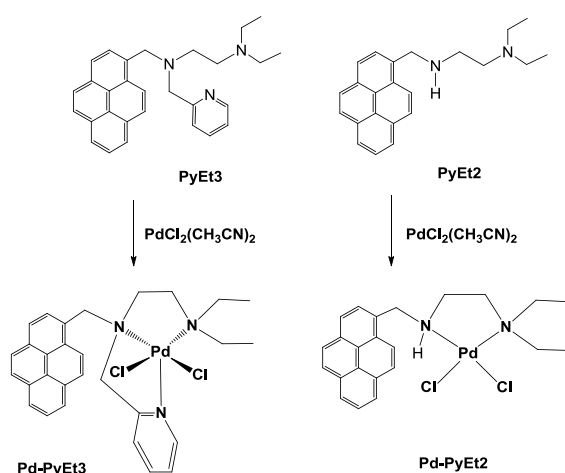
The ligand **PyEt1** was synthesized by a condensation reaction between pyrene-1-carbaldehyde and N,N-diethylethylenediamine in good yields. Reduction of imine fragment in **PyEt1** by sodium borohydride produced **PyEt2** with robust C-N single bonds. A picolyl part was introduced by the reflux of **PyEt2** in acetonitrile over 72 h. The three ligands are pale yellow semi-solids and very well-soluble in common organic solvents like CH_2Cl_2 , CHCl_3 , acetone, THF...



Scheme 1. Synthetic scheme of the ligands.

The palladium complexes of **PyEt2** and **PyEt3** were prepared by simple mixing of $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ with the two ligands, respectively. The weakly coordinating ligand, CH_3CN , was easily displaced to yield the complexes in high yields. The complexes are well-soluble in CHCl_3 but sparingly soluble in hexane. Numerous attempts to obtain the crystalline solids of **Pd-PyEt2** and **Pd-PyEt3** suitable for X-ray single crystal diffraction failed.

The ligands and the complexes were characterized by infrared spectroscopy. As the results indicated, the strong band at 1624 cm^{-1} confirmed the formation of **PyEt1**. The disappearance of the band in **PyEt2** implied that the C=N bond was completely reduced. The infrared spectra of **PyEt3** and the two complexes **Pd-PyEt2** and **Pd-PyEt3** showed characteristic bands of the aromatic moieties.



Scheme 2. Synthetic scheme of the complexes.

3.2. Characterization of complexes by $^1\text{H-NMR}$

The distinct differences between the $^1\text{H-NMR}$ spectrum of **PyEt2** and that of **Pd-PyEt2** (Figure 2) are noted. The signals responsible for methylene groups of pyrenyl rings (6.07 ppm) and ethylenediamine fragments (5.34 ppm and 4.50 ppm) in the complex are down field shifted, compared to those of the free ligand. This evidence confirms the presence of metal atom in connection with two nitrogen donor atoms. The patterns of these signals also change significantly due to the rigidity of the chelate ring formed upon the complexation. The pyrenyl methylene protons give no longer a singlet but a complex multiplet due to spin coupling with its surrounding N-H and N-CH₂ protons. More interestingly, the signals for ethylenediamine protons which are assigned for the two triplets in **PyEt2**, are a doublet and a triplet in **Pd-PyEt2**. This is reasonable in light of the fact that the four

protons are now fixed and forms different dihedral angles with carbon atoms which in turn give rise to different coupling constant values. Due to effective inversion of substituents around nitrogen atom, the two ethyl groups in **PyEt2** gave a set of signals including a triplet and a quartet. However, because of the coordination of palladium atom in **Pd-PyEt2**, the inversion is now firmly locked, making two ethyl groups chemically inequivalent. This is evidenced by the appearance of two sets of triplet and quartet in the up field region.

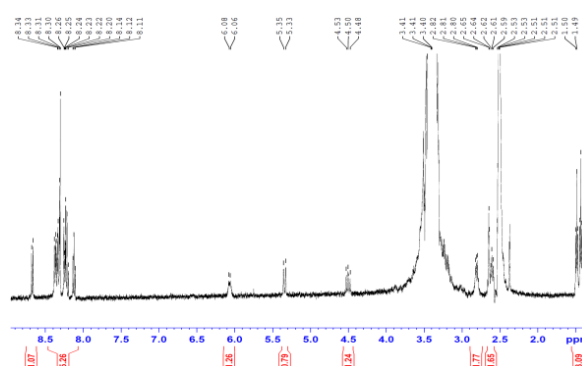


Figure 2. $^1\text{H-NMR}$ spectrum of **Pd-PyEt2** in CDCl_3 .

The $^1\text{H-NMR}$ spectrum of palladium complex of **PyEt3** (Figure 3) is much more complicated than that of **PyEt3**. Upon complexation, the H₁₀ signal of pyrenyl ring is downfield shifted (9.29 ppm) while the pyridyl signals are upfield shifted (7.60 – 5.94 ppm). This result implies the engagement of pyridyl nitrogen atom in coordination sphere of palladium. The two protons of methylene group attached to pyrenyl and pyridyl rings are no longer equivalent, giving rise to doublet signals (5.42 ppm and 5.12 ppm) due to spin coupling between them. Similar to the pattern observed in **Pd-PyEt2**, the four protons of ethylenediamine moiety are manifested in the spectrum as two doublets (4.55 ppm and 3.10 ppm) and two triplets (4.43 ppm and 3.70 ppm). This reveals a very crowded coordination sphere, making further signal splitting to each separate proton. Another piece of evidence confirms that the connection of pyridyl nitrogen to palladium is

the four multiplets corresponding to four methylene protons of ethyl groups. This may suggest a square pyramidal configuration of the complex as pyridyl ring could be in closer approach to ethyl groups.

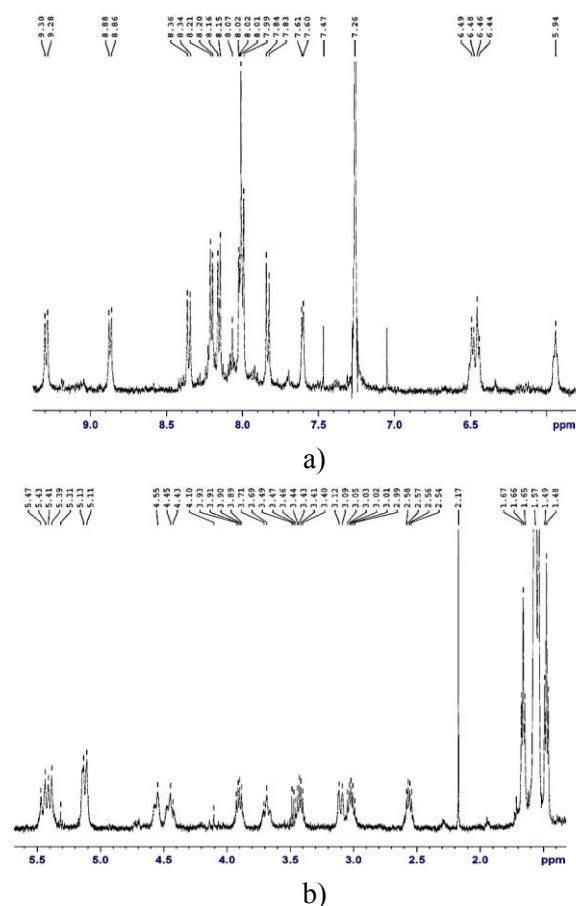


Figure 3. ^1H NMR spectrum of **Pd-PyEt3** in CDCl_3 .

4. Conclusion

In summary, a series of ligand **PyEt1**, **PyEt2**, and **PyEt3** which contain pyrenyl core have been synthesized and characterized. The pre-organized three nitrogen donor atoms in **PyEt3** took part in unusual five-coordinate mode

with palladium(II) which was revealed by ^1H -NMR spectroscopic results. Ongoing studies about luminescent properties of this complex are presently underway in our laboratories.

Acknowledgments

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