Original Article

Palladium(II) Complex with Tridentate Ligand Containing Pyrenyl Core

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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

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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 (4000-400 cm⁻¹) in KBr pellets. The ¹H-NMR spectra were recorded on a Bruker-500 MHz spectrometer in CDCl₃ 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:** νₘₐₓ/cm⁻¹ = 3606 (w), 2964 (w), 2915 (w), 1624 (s), 1597 (m), 1201 (s); ¹H NMR (CDCl₃, δ ppm): 9.33 (s, 1H, Hₘ, imine), 8.91 (d, J = 9 Hz, 1H, Hₙ, pyrenyl), 8.52 (d, J = 8.0 Hz, 1H, H₂, pyrenyl), 8.20-8.02 (m, 7H, H₃,4,5,6,7,8,9, pyrenyl), 3.95 (t, J = 7.0 Hz, 2H, Hₗ, CH₂), 2.94 (t, J = 7.0 Hz, 2H, Hₗ, CH₂), 2.69 (q, J = 6.0 Hz, 2H, Hₗ, CH₂), 1.11 (t, J = 7.0 Hz, 6H, Hₗ, CH₃).

2.3. Synthesis of PyEt2

To a yellow solution of PyEt1 (0.115 g, 0.360 mmol) in CH₂Cl₂/methanol (10/5 mL) was added NaBH₄ (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:** νₘₐₓ/cm⁻¹ = 3294 (w), 1600 (s), 1587 (s), 1454 (s), 1382 (m), 1066 (m), 846 (s), 756 (s); ¹H NMR (CDCl₃, δ ppm): 8.37 (d, J = 9 Hz, 1H, H₁₀, pyrenyl), 8.18-7.97 (m, 8H, H₃,4,5,6,7,8,9, pyrenyl), 4.50 (s, 2H, Hₗ, CH₂), 2.85 (t, J = 6.0 Hz, 2H, Hₗ, CH₂), 2.62 (t, J = 6.0 Hz, 2H, Hₗ, CH₂), 2.49 (q, J = 7.0 Hz, 4H, Hₗ, CH₂), 0.99 (t, J = 7.0 Hz, 6H, Hₗ, CH₃).

2.4. Synthesis of PyEt3

0.100 g (0.304 mmol) of PyEt2 was dissolved in 10 mL of CH₃CN 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 K₂CO₃.1.5H₂O. The mixture was refluxed for 72 h in the absence of light. The solvent was then removed by rotary evaporation. Extraction with CH₂Cl₂ yielded a brownish solid. Yield: 0.090 g (71%).

**Data for PyEt3: IR:** νₘₐₓ/cm⁻¹ = 3039 (w), 1649 (s), 1587 (s), 1431 (s), 1373 (m), 1066 (m), 844 (s), 756 (s); ¹H NMR (CDCl₃, δ ppm): 8.59 (d, J = 9 Hz, 1H, H₁₀, pyrenyl), 8.47 (dd, J = 6 Hz, 1H, Hₘ, pyridine), 8.47 (dd, J = 6 Hz, 1H, Hₘ, pyridine), 7.43 (d, J = 6 Hz, 1H, Hₗ, pyridine), 7.07 (dt, J = 6 Hz, 1H, Hₗ, pyridine), 4.39 (s, 2H, Hₗ, CH₂), 3.87 (s, 2H, Hₗ, CH₂), 2.78 (t, J = 6.0 Hz, 2H, Hₗ, CH₂), 2.72 (t, J = 6.0 Hz, 2H, Hₗ, CH₂), 2.46 (q, J = 7.0 Hz, 4H, Hₗ, CH₂), 0.93 (t, J = 7.0 Hz, 6H, Hₗ, CH₃).
2.5. Synthesis of Pd-PyEt2

To a CH2Cl2 solution of PyEt2 (0.010 g, 0.030 mmol) was added PdCl2(CH3CN)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: νmax/cm⁻¹ = 3041 (w), 1641 (s), 1597 (s), 1434 (s), 1383 (m), 1069 (m), 843 (s), 759 (s).

1H NMR (CDCl3, δ ppm): 8.67 (d, 1H, H10, pyrenyl), 8.38-8.11 (m, 8H, H2,3,4,5,6,7,8,9, pyrenyl), 6.07 (m, 2H, Hf, CH2), 5.34 (d, 2H, Ha, CH2), 4.50 (t, 2H, Hb, CH2), 2.81 (q, 2H, Hc1, CH2), 2.61 (q, 2H, Hc2, CH2), 1.49 (t, 3H, Hd1, CH3), 1.49 (t, 3H, Hd2, CH3).

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: νmax/cm⁻¹ = 3032 (w), 1651 (s), 1590 (s), 1434 (s), 1376 (m), 1069 (m), 847 (s), 756 (s).

1H NMR (CDCl3, δ ppm): 9.29 (d, 1H, H10, pyrenyl), 8.88-7.83 (m, 8H, H2,3,4,5,6,7,8,9, pyrenyl), 7.60 (d, 1H, Hm, pyridine), 6.49 (d, 1H, Hq, pyridine), 6.46 (t, 1H, Hp, pyridine), 5.94 (t, 1H, Hn, pyridine), 5.42 (m, 2H, Hl2, CH2), 5.12 (m, 2H, Hl1, CH2), 4.55 (d, 1H, Hf1, CH2), 4.43 (t, 1H, Hg2, CH2), 3.91 (m, 1H, Hc1, CH2), 3.70 (t, 1H, Hg1, CH2), 3.44 (m, 1H, Hc1', CH2), 3.10 (d, 1H, Hg2, CH2), 3.02 (m, 1H, Hc2', CH2), 2.56 (m, 1H, Hc2', CH2), 1.66 (t, 3H, Hd1, CH3), 1.48 (t, 3H, Hdi, CH3).

3. Results and Discussion

3.1. Syntheses

The ligand PyEt1 was synthesized by a condensation reaction between pyrene-1-carbaldehyde and N,N-diethylethelenediamine 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 CH2Cl2, CHCl3, acetone, THF...
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.

3.2. Characterization of complexes by \(^1\)H-NMR

The distinct differences between the \(^1\)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 downfield 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-CH\(_2\) 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.

The \(^1\)H-NMR spectrum of palladium complex of PyEt3 (Figure 3) is much more complicated than that of PyEt3. Upon complexation, the H\(_{10}\) 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.

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.

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References


