Synthesis of Asymmetric Dibenzoylated Tetraazacyclo[14]annulenepalladium(II) Complexes: Structure of 3,10-Di(*p*-methylbenzoyl)-2,4,9,11-tetramethyl-1,5,8,12-monobenzotetraazacyclo[14]annulenepalladium(II)

Sang Hee Shin, Dong Il Kim, Yu Kyung Lee, Young Hoon Lee, Zun Ung Bae, Hun Gil Na,† Tapashi Ghosh Roy,‡ and Yu Chul Park*

*Department of Chemistry, Kyungpook National University, Daegu 702-701, Korea. *E-mail: ychpark@knu.ac.kr*
†Department of Chemistry, Daejin University, Pochon 487-800, Korea
‡Department of Chemistry, University of Chittagong, Chittagong 4331, Bangladesh
Received July 28, 2007

Key Words : Di(*p*-*X*benzoyl)monobenzotetraazacyclo[14]annulenepalladium(II), Spectral and electrochemical properties, X-ray structure

Several tetraazaannulenenickel(II) complexes have been synthesized by a one-step template method in a high yield. The replacement of the central metal atom, by other transition metals, is possible only by demetallating nickel complexes. These complexes have been known to possess different chemical and thermal stabilities and electrocatalytic activities by substituents at the methine sites such as *p*-substituted benzoyl chloride, nicotinyl chloride and acetyl chloride, etc.[1-5] These tetraazaannulene complexes were mostly symmetric nickel(II) complexes with substituents at methine sites, while the examples of asymmetric complexes were rarely reported.[3,5-9] In previous papers we have reported on the reaction, spectral and electrochemical properties and crystal structures of the asymmetric monobenzotetraaza-[14]annulenenickel(II) complexes with five types of *p*-substituted benzoyl or thiophenecarbonyl groups at the methine sites.[10-12] Also, we have studied the crystal structures of asymmetric monobenzotetraaza[14]annulenepalladium(II) and -copper(II) complexes.[13,14] On the other hand, no one has investigated on the reaction, property and crystal structure of the asymmetric palladium(II) complex with *para* substituted benzoyl groups at the methine sites, as π-conjugated electron system.

In the present work, we report that the synthesis and characterization of new asymmetric 3,10-dibenzoylmonobenzotetraaza[14]annulenepalladium(II) complexes, also the electronic effects of the substituents of the *p*-*X*benzoyl group (X = CH_3, H, Cl and NO_2) on the infrared, electronic absorption and NMR spectra and cyclovoltammograms for the complexes. The structure of complex **2** is identified by X-ray diffraction analysis.

Experimental Section

Materials and measurements. The solvents such as methanol, ethanol, acetonitrile and dichloromethane were refluxed over calcium hydride or sodium metal under nitrogen, and checked for purities by GC just before use. Tetraethylammonium perchlorate (TEAP) used as a supporting electrolyte, was prepared and purified by the method described by Kolthoff and Coetzee.[15]

Elemental analyses (C, H, N) of the prepared complexes were carried out on a Carlo-Ebra, EA 1108 instrument. Infrared spectra were recorded on a Matteson Instruments, Inc. Galaxy 7020 A using KBr disc. ^{1}H- and ^{13}C-NMR spectra (300 MHz) were obtained in $CDCl_3$ by a 300NB Varian instrument. Electronic absorption spectra were obtained on a Shimadzu UV-265 spectrophotometer.

Cyclic voltammetry was performed using a Bioanalytical System (BAS) CV-50W electrochemical analyzer and a C2 cell stand at room temperature. The three-electrode system for the electrochemical measurements composed of the glassy carbon electrode as a working electrode, Ag/Ag^+ (0.01 M $AgNO_3$ in 0.1 M TEAP-DMSO solution) as a reference electrode and a platinum wire as an auxiliary electrode was used.

Synthesis of ligand (L) and complex (1). The free ligand **L** and complex **1**, asymmetric tetraaza[14]annulenepalladium(II) as a starting compound, were prepared by the method previously conducted in this laboratory.[13,16,17]

3,10-Di(*p*-*X*benzoyl)-2,4,9,11-tetramethyl-1,5,8,12-monobenzotetraazacyclo[14]annulenepalladium(II): X = CH_3 (**2**), H (**3**), Cl (**4**), NO_2 (**5**). These complexes were prepared by modifying the method reported in literature.[10,18] The complex **1** (0.1123 g, 0.5 mmol) was dissolved in benzene (50 cm^3) containing triethylamine (0.101 g, 1.0 mmol) and added the corresponding *p*-*X*benzoyl chloride (1.0 mmol) in benzene (30 cm^3) using dropping funnel. The mixture was heated under reflux for 6 h with stirring and bubbling nitrogen gas into solution for protecting from moisture. The reaction mixture was left to stand for 24 h at room temperature and filtered. The filtrate was evaporated to dryness under a reduced pressure and the resulting solid was recrystallized from a mixture 1:2 of dichloromethane and *n*-hexane and dark brown crystals were obtained. For $C_{34}H_{34}N_4O_2Pd$ (**2**): Yield 25%. Anal. Calcd. (%): C, 64.10; H, 5.38; N, 8.79; Found: C, 64.27; H, 5.22; N, 8.72. IR (KBr disc, cm^{-1}): ν (C=C), 1549; ν (C=N), 1604; ν (C=O), 1648; ν (aromatic), 734 and 841. UV-vis: λ_{max} (nm) and ε_{max} (M^{-1} cm^{-1}) in chloroform 374 and 17000, and 453 and 12200. ^{1}H-

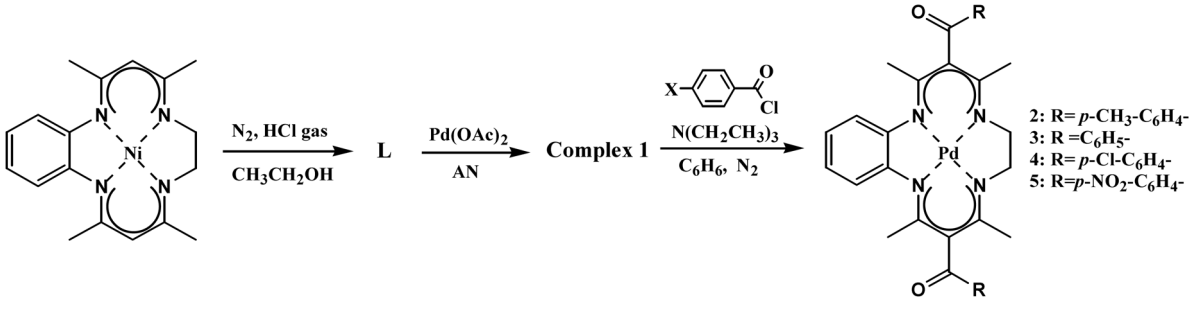
NMR ($CDCl_3$, δ): 2.027, 2.371, 2.438 (s) (methyl, 18H), 3.900 (s) (ethylene, 4H), 6.826-7.326 (m) (benzene of macrocycle, 4H), 7.209 (d, J = 8.3), 7.906 (d, J = 8.3) (benzene of benzoyl, 8H). ^{13}C-NMR ($CDCl_3$, δ): 19.437, 21.501, 23.950 (methyl), 55.610 (ethylene), 115.095 (methine), 153.406, 156.722 (diiminate), 120.815, 121.842, 144.684 (benzene of macrocycle), 129.505, 129.885, 137.865, 143.812 (benzene of benzoyl group), 200.496 (C=O). For $C_{32}H_{30}N_4O_2Pd$ (**3**): Yield 28%. Anal. Calcd. (%): C, 63.11; H, 4.97; N, 9.20; Found: C, 62.92; H, 5.11; N, 9.09. IR (KBr disc, cm^{-1}): ν (C=C), 1552; ν (C=N), 1595; ν (C=O), 1657; ν (aromatic), 722 and 807. UV-vis: λ_{max} (nm) and ε_{max} (M^{-1} cm^{-1}) in chloroform 374 and 22900, and 453 and 17950. ^{1}H-NMR ($CDCl_3$, δ): 2.026, 2.374 (s) (methyl, 12H), 3.907 (s) (ethylene, 4H), 6.849-7.558 (m) (benzene of macrocycle, 4H), 7.480-8.004 (m) (benzene of benzoyl, 10H). ^{13}C-NMR ($CDCl_3$, δ): 19.556, 24.064 (methyl), 55.624 (ethylene), 115.011 (methine), 153.690, 156.944 (diiminate), 120.941, 121.905, 144.656 (benzene of macrocycle), 128.785, 129.673, 132.919, 140.425 (benzene of benzoyl group), 200.759 (C=O). For $C_{32}H_{28}N_4O_2Cl_2Pd$ (**4**): Yield 32%. Anal. Calcd. (%): C, 56.70; H, 4.16; N, 8.26; Found: C, 56.88; H, 4.06; N, 8.37. IR (KBr disc, cm^{-1}): ν (C=C), 1547; ν (C=N), 1584; ν (C=O), 1648; ν (aromatic), 746 and 845. UV-vis: λ_{max} (nm) and ε_{max} (M^{-1} cm^{-1}) in chloroform 372 and 23500, and 451 and 18550. ^{1}H-NMR ($CDCl_3$, δ): 2.014, 2.359 (s) (methyl, 12H), 3.898 (s) (ethylene, 4H), 6.880-7.309 (m) (benzene of macrocycle, 4H), 7.436 (d, J = 8.3), 7.937 (d, J = 8.3) (benzene of benzoyl, 8H). ^{13}C-NMR ($CDCl_3$, δ): 19.611, 24.129 (methyl), 55.640 (ethylene), 114.632 (methine), 153.823, 156.951 (diiminate), 121.181, 121.976, 144.584 (benzene of macrocycle), 129.113, 131.030, 138.870, 139.374 (benzene of benzoyl group), 199.383 (C=O). For $C_{32}H_{28}N_6O_6Pd$ (**5**): Yield 18%. Anal. Calcd. (%): C, 54.98; H, 4.04; N, 8.02; Found: C, 54.83; H, 4.13; N, 7.91. IR (KBr disc, cm^{-1}): ν (C=C), 1548; ν (C=N), 1601; ν (C=O), 1649; ν (NO_2), 1342; ν (aromatic), 726 and 849. UV-vis: λ_{max} (nm) and ε_{max} (M^{-1} cm^{-1}) in chloroform 370 and 22650, and 441 and 15500. ^{1}H-NMR ($CDCl_3$, δ): 2.018, 2.366 (s) (methyl, 12H), 3.920 (s) (ethylene, 4H), 6.885-7.294 (m) (benzene of macrocycle, 4H), 8.135 (d, J = 8.7), 8.317 (d, J = 8.7) (benzene of benzoyl, 8H). ^{13}C-NMR ($CDCl_3$, δ): 21.887, 24.973 (methyl), 56.177 (ethylene), 115.163 (methine), 155.245, 158.105 (diiminate), 122.122, 122.656, 144.961 (benzene of macrocycle), 124.482, 130.778, 146.053, 150.521 (benzene of benzoyl group), 198.819 (C=O).

X-ray crystallographic analysis. The crystallographic data for the complex **2**; $C_{35}H_{36}Cl_2N_4O_2Pd$ F_W = 721.98, monoclinic, space group $P2_1/c$, a = 11.666(1) Å, b = 28.599(3) Å, c = 9.949(1) Å, β = 105.230(2)°, V = 3203.0(6) $Å^3$, Z = 4, D_c = 1.497 Mg/m^3, F(000)=1480, 9751 reflections collected, 5645 independent reflections, $R_1[I > 2\sigma(I)]$ = 0.0352, $wR_2[I > 2\sigma(I)]$ = 0.0849. Diffraction studies were performed using Mo-Kα radiation (λ = 0.71073 Å) on an Enraf-Nonius CAD4 computer controlled k-axis diffractometer equipped with a graphite crystal, incident-beam monochromator. Cell constants and orientation matrices for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections. The data were collected for Lorentz-polarization and absorption correction was applied to the data. The structure was solved by direct methods using SHELXS-86 and refined by full-matrix least-squares calculations with SHELX-97.[19,20]

Results and Discussion

The free ligand (**L**) and the palladium(II) complexes **1-5** were prepared by a synthetic procedure as illustrated in Scheme 1. The reaction of complex **1** with *p-X*benzoyl chloride in a 1:2 molar ratio was carried out in refluxing benzene in the presence of triethylamine. The reaction was led to the corresponding 3,10-di(*p-X*)benzoylated palladium(II) complexes (**2-5**) in 18-32% yields.

IR and UV-visible spectra. As shown in Experimental section, the IR spectra of all the dibenzoyolated palladium(II) complexes showed a very strong band in the range 1648-1657 cm^{-1}, which are attributable to the stretching modes of C=O. They were similar to those of the asymmetric tetraaza[14]annulenenickel(II) complexes dibenzoylated.[12] The aromatic bands for the complexes **2-5** had two characteristic modes around 750 (macrocycle) and 850 cm^{-1} (benzoyl groups), respectively. The NO_2 of the complex **5** exhibited another strong band at 1342 cm^{-1}. The stretching modes of the C=C and C=N bonds of complex **1** appeared at 1514 and 1569 cm^{-1}, respectively,[13] while those of new complexes **2-5** were at around 1547-1552 and 1584-1604 cm^{-1}, respectively. The C=C and C=N stretching modes after benzoylation at the methine sites moved to higher frequencies around 30-40 and 20-30 cm^{-1}, respectively,



Scheme 1

depending on the substituents of the benzoyl groups.

The electronic absorption spectra of complexes **2-5** exhibited two bands at around 370 and 450 nm, as shown in the Experimental section. The bands of the near UV region (370-374 nm), with molar absorptivities of 27000 to 24000 M^{-1} cm^{-1}, might be attributed to π–π^* transitions. The spectra in the visible region showed bands between 440 and 460 nm (ε_{max} = 12000-19000 M^{-1} cm^{-1}), which are attributed to LMCT from the highest occupied ligand molecular orbital to the lowest empty *d*-orbital of palladium(II). These bands of complexes **2-5** appeared at lower energy region around 1-5 nm for π–π^* transitions and 10-20 nm for LMCT than those of complex **1** as a starting compound.

^{1}H- and ^{13}C-NMR spectra. Chemical shift assignments were accomplished on the basis of comparisons with complex **1**. The methine proton signals of the complexes **2-5** disappeared due to benzoylation. The methyl proton signals exhibited upfield shifts to about 0.15-0.20 ppm, which might be due to the magnetic anisotropy of benzoyl groups. The ethylene proton resonance of the complexes exhibited downfield shifts to around 0.10-0.15 ppm relative to those of complex **1**. The substituent effects on the phenyl proton signals of benzoyl groups were similar to that on the ethylene proton ones. The proton resonances were typically somehow affected by the shielding and deshielding effects of the benzoyl groups. The carbon resonance of the complexes were singlet and shifted to upfield and downfield shifts resulting from the shielding and deshielding effect by benzoylation as in the proton NMR. The carbon signals for the carbonyl and phenyl groups, on the basis of benzoylation, were observed at 198-201 ppm and 128-150 ppm, respectively. The methine carbon peaks for complexes **2-5** moved downfield to about 10 ppm, as compared to that of complex **1**.

Electrochemical behavior and Hammett plots. The redox potentials of the complexes, before and after dibenzoylation, were measured in 0.1 M TEAP-DMSO solutions *vs.* Ag/Ag^+ (0.01 M) at 25°C and sweep rates of 100 mV s^{-1} under nitrogen atmosphere. The results were listed in Table 1. Typical voltammograms, in the range of +1.1 to –3.0 V *vs.* Ag/Ag^+ of the complexes, were shown in Figure 1. The voltammograms of the complexes **2-5** show two irreversible oxidation waves ($Mc/Mc^{\bullet+}$ and $Mc^{\bullet+}/Mc^{2+}$) by ligand (Mc) in the ranges of +0.40 to +0.66 V and a quasi-reversible reduction one by metal ($Pd^{2+} \rightarrow Pd^+$) in the range of –2.66 to –2.85 V. The other reduction peaks might be associated with benzoyl groups and their substituents were compared with voltammograms for ligand **L** and complex **1**.[16] The oxidations of tetrazaannulene parts and the reduction of palladium(II) of complexes shifted to more positive and negative values according to the electron-withdrawal of the substituents on the benzoyl groups, respectively. The substituent effects on the oxidation (E_{op}) and reduction (E_{rp}) potentials could be examined by means of Hammett equation. The relationships between reduction potentials and $2\sigma_p$[21] for complexes **2-5** were positively linear with slopes of +0.051 and +0.054 for the 1st and 2nd oxidation potentials ($E_{op(1)}$ and $E_{op(2)}$) by ligand, respectively, while negative slope of –0.082 for the reduction potential ($E_{rp(m)}$) by palladium(II). These results imply that the electron densities of the oxidation and reduction sites were considerably affected by the substituents on the benzoyl groups, in the order of NO_2 > Cl > H > CH_3.

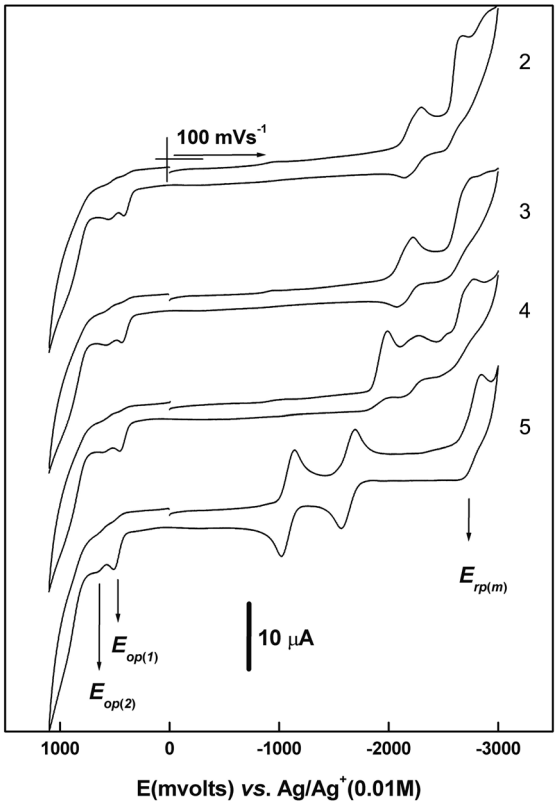


Figure 1. Cyclic voltammograms of the complexes **2-5** (0.001 M) in a 0.1 M TEAP-DMSO solution *vs.* Ag/Ag^+ (0.01 M) at 25 °C and scan rate of 100 mV s^{-1}.

Table 1. Redox potential (E_{op} and E_{rp}) data for complexes **1-5**[a]

Comp.	$E_{op(1)}$, mV $0 \rightarrow +1$	$E_{op(2)}$, mV $+1 \rightarrow +2$	$E_{rp(1)}$, mV $0 \rightarrow -1$	$E_{rp(2)}$, mV $-1 \rightarrow -2$	$E_{rp(m)}$, mV $Pd^{2+} \rightarrow Pd^+$
1[b]	+90	+700			–2710
2	+414	+549	–2303		–2669
3	+434	+578	–2212		–2758
4	+454	+607	–1994	–2265	–2776
5	+512	+655	–1143	–1694	–2845

[a]All data were measured in 0.1 M TEAP-DMSO solutions *vs.* Ag/Ag^+ (0.01 M $AgNO_3$ in DMSO) at 25 °C. [b]ref. [16]

X-ray structure of complex 2. The structure of 3,10-di(*p*-methylbenzoyl)-2,4,9,11-tetramethyl-1,5,8,12-monobenzotetraazacyclo[14]annulenepalladium(II) was illustrated in Figure 2. The average of four Pd-N distances 1.963 Å, which is a little longer than the corresponding M-N distances observed for Ni(II)-tetraazaannulene (1.865 Å) and Cu(II)-tetraazaannulene (1.916 Å).[14,23] This increase might be due to the larger palladium ionic radius. The bond distances of N(3)-C(18) (1.316 Å) and N(4)-C(22) (1.323 Å) were

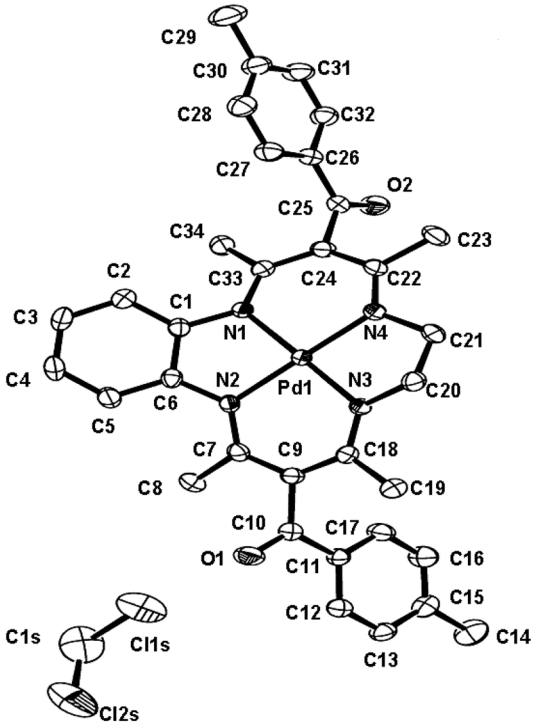


Figure 2. The molecular structure of complex **2**. Selected bond lengths (Å) and angles (°) (standard uncertainties in parentheses); Pd(1)-N(1) 1.971(3), Pd(1)-N(4) 1.957(3), N(1)-C(1) 1.416(4), N(4)-C(21) 1.474(5), N(4)-C(22) 1.323(4), N(1)-C(33) 1.349(4), C(10)-O(1) 1.219(4), N(1)-Pd(1)-N(4) 95.57(1), N(2)-Pd(1)-N(1) 84.32(1), N(4)-Pd(1)-N(2) 179.08(1), N(4)-Pd(1)-N(3) 85.18(1), N(2)-Pd(1)-N(3) 94.96(1), N(3)-Pd(1)-N(1) 178.08(1).

shorter than those of N(1)-C(33) (1.343 Å) and N(2)-C(7) (1.349 Å). Such an observation might be attributable to the difference of basicities between phenylenediamine and ethylenediamine.[22] The average distance of C-C in the six-membered chelate rings was 1.420 Å similar to those of benzene (1.40 Å), reflecting some it's aromaticity. On the other hand, the bond length of C(20)-C(21) (1.524 Å) was similar to that of sp^3 hybrid. The average angles of N-Pd-N of five and six member rings were 84.75 and 95.265°, respectively. The angles of N(1)-Pd-N(3) and N(2)-Pd-N(4) were 178.08 and 179.08°, respectively, which is close to a square planar.

Supplementary material. Crystallographic data for the structural analysis have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number CCDC (245074). Copies of this information can be obtained free of charge *via* E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk; Tel: +44-1233-336031; Fax: +44-1223-336033.

Acknowledgements. This work was supported by Korea Research Foundation Grant (KRF-2007-005-C00009). Also Kim and Park wish to acknowledge the support of BK21 PROGRAM.

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