Synthesis, Molecular Structure and Mesomorphic Phase Behavior of η^1-Benzylideneaniline Palladium(II) Complexes

Yong-Sik Yoo, Jun-Hwan Im, Bong-Hwan Han, Myongsoo Lee,* and Moon-Gun Choi*

Department of Chemistry, Yonsei University, Shinchon 134, Seoul 120-749, Korea

Received May 16, 2001

The synthesis and characterization of very stable Pd(II) η^1-imine complexes of bis(3,4-dialkyloxybenzylidene-3′,4′-dialkyloxyaniline)dichloropalladium(II) with alkyl chain of hexyl (**8**), octyl (**9**), decyl (**10**) and dodecyl (**11**) groups, and of bis(4-ethyloxybenzylidene-4′-ethyloxyaniline)dichloropalladium(II) as a model complex are described. The molecular structure with twisted board-like geometry of the complex resulting from the coordination of Pd(II) with η^1-imine bonding was confirmed by X-ray crystallographic analysis of the model complex. In contrast to the imine ligands, all the complexes with an exception of **11** display a thermally stable monotropic smectic A mesophase without any decomposition of the complex. These results, characterized by a combination of differential scanning calorimetry, optical polarized microscopy, and powder X-ray scattering experiments, are discussed.

Keywords : Pd(II)-metallomesogen, η^1-Imine bonding, Thermotropic LC.

Introduction

The most common structural principle in the design of a liquid crystal has been to choose molecules or associations of molecules which display a high aspect ratio. Thus, most liquid crystals exhibit anisotropic rodlike or disclike shapes which facilitate attractive dipolar interactions in liquid crystalline phase. Metallomesogenic molecules containing transition metals which share certain general characteristics of both organic molecules and the metals provide typical examples for liquid crystals with high intermolecular interactions.[1] Linear[2] and square planar[3] coordinations of metal atom into conventional organic mesogens have been used to increase the aspect ratio of aromatic core and therefore enhance the thermal stability of both crystal and liquid crystal phases.

A large and predominant class of metallomesogens is that organometallic complexes derived from orthocyclopalladated imines[4] and azines,[5] as well as azobenzenes.[6] This class of mesogens is represented by palladium derivatives mainly, due to the formation of stable complexes and the ease of the orthocyclopalladation reaction which produces aromatic core with planar structure, thus leading to the formation of liquid crystalline phase. As a chemical diversity, these complexes offer many opportunities for the formation of novel palladium metal based materials.

The coordination reaction of azobenzene with K_2PdCl_4 in ethanol is illustrated to affords the dinuclear orthocyclometallated complex with chloro bridges.[7] Dinuclear orthocyclopalladated complexes with halo bridges can also be prepared from the acetato bridged complex resulting from orthocyclopalladated reaction with $Pd(OAc)_2$.[4] The chloro bridges can yield coplanar geometry of the two square planar palladium centers and therefore enhance the thermal stability of both crystal and liquid crystal phases.[4b,8] The dinuclear orthopalladated imine complexes exhibit various liquid crystalline phases depending on the number of peripheral chains. The complexes with tetrasubstituted aliphatic chains are reported to show calamitic smectic phases.[4a,9] On the other hand, the presence of four additional chains in the aromatic core of dinuclear orthopalladated complexes produces a more disc-like molecular shape, thus leading to the formation of the columnar mesophase.[10]

In spite of this intense interest, the current status of liquid crystallinity in cyclopalladated metallomesogens is limited by high melting points due to increase of rigidity of aromatic core caused by cyclometallation. A possible approach to overcome this limitation is the introduction of asymmetric molecular shape[11] or non-coplanarity.[5,11b] The central nonplanar structure of the complexes is expected to reduce intermolecular interactions due to perturbing the crystal packing of the molecules and thus, leading to the lower melting transition temperatures.

We have made an attempt for design and synthesis of mononuclear Pd(II) complexes with η^1-benzylideneaniline derivatives as novel metallomesogenic materials. In contrast to the Pd(II) orthometallated complexes derived from benzylideneaniline ligand,[4-6] the η^1-benzylideneaniline complexes would provide an acyclic core structure which gives rise to noncoplanar aromatic core caused by free rotation of the ligand about Pd-N bond. Consequently, η^1-bonding of the complexes will give rise to the decrease of intermolecular interactions and thus, leading to the lower transition temperatures.

It is well documented that Pd(II) complexes with η^1-ligands can be easily produced by a ligand exchange reaction of $[PdCl_2(PhCN)_2]$ with nitrile ligand.[12] The introduction of the metal atom into calamitic mesogenic ligands increases the phase transition temperatures. The ligand exchange reaction of non-mesogenic nitrile ligands with half disc-like shape can even give rise to discotic liquid crystalline properties as a result of dimeric association of two half disc-like ligands through palladium complexation.[13] However, almost no attempts have been made for the ligand exchange reaction with imine ligands in order to create novel liquid crystalline materials.[13,14]

We have synthesized octaalkoxy-substituted mononuclear Pd(II) metallomesogens with η^1-benzylideneaniline derivatives by a ligand exchange reaction used for the synthesis of Pd(II)-nitrile complexes.[12] The resulting complexes exhibit an liquid crystalline phase behavior, in spite of their aromatic core with semi-flexible non-coplanar structure. The goal of this article is to describe the synthesis and detailed chemical characterization of bis(η^1(*N*)-3,4-dialkyloxybenzylidene-3′,4′-dialkyloxyaniline)dichloropalladium(II) with hexyl (**8**), octyl (**9**), decyl (**10**) and dodecyl (**11**) alkyl groups and the molecular structure of a model complex characterized by X-ray single crystallographic experiments. We also describe the mesomorphic phase behavior of the resulting complexes, characterized by a combination of DSC, optical polarized microscopy and powder X-ray scattering experiments.

Experimental Section

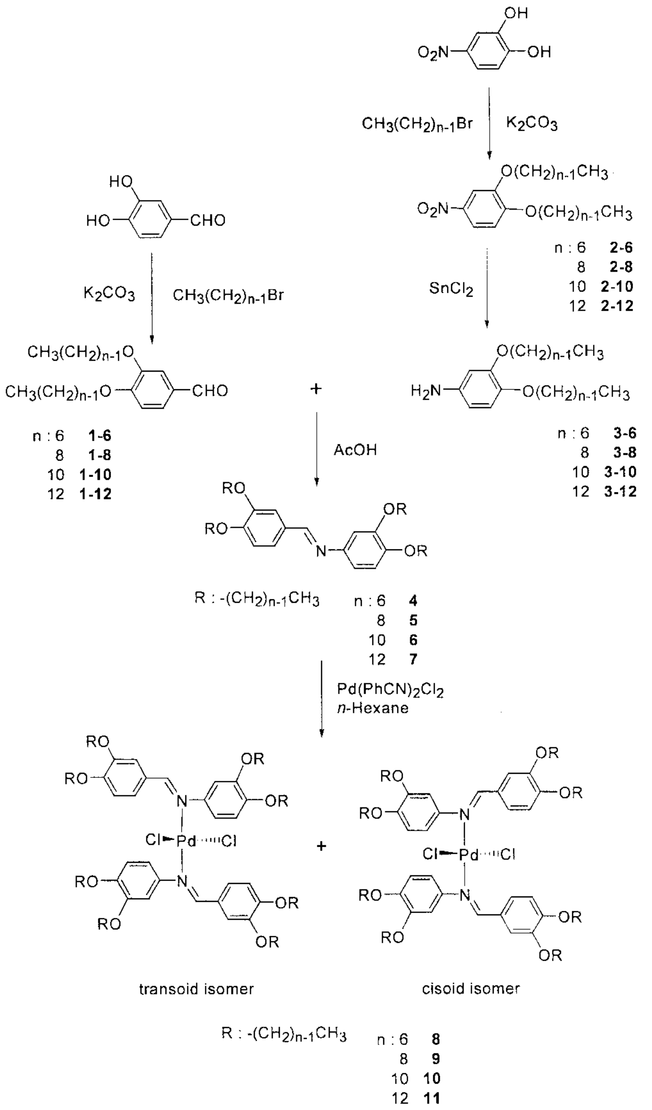
Materials. Bromoethane (98%), 1-bromohexane (98%), 1-bromooctane (99%), 1-bromodecane (98%), 1-bromododecane (97%), 4-nitrophenol (98%), 4-hydroxybenzaldehyde (98%), 4-nitrocatechol (97%), 3,4-dihydroxybenzaldehyde (97%), tin chloride (98%), dichloropalladium(II) (99%) (all from Aldrich) and the other conventional reagents were used as received. Bis(benzonitrile)dichloropalladium(II) was prepared according to the procedure described previously.[13]

Techniques. ^{1}H-NMR spectra were recorded from chloroform-*d* solution or toluene-d_8 solution for high temperature ^{1}H-NMR spectra on a Bruker DPX 250 spectrometer operating at 250 MHz proton frequency. TMS was used as internal standard. Infrared (IR) spectra were recorded on a Nicolet Impact 400 FT IR spectrophotometer using KBr pellet. A Perkin Elmer DSC-7 differential scanning calorimeter, equipped with a 1020 thermal analysis controller was used to determine the thermal transitions which were reported as the maxima and minima of their endothermic or exothermic peaks, respectively. In all cases, heating and cooling rates were 10 ^{o}C/min unless otherwise specified. A Nikon Optiphot 2-pol optical polarized microscope (magnification: 100 ×) equipped with a Mettler FP 82 hot stage and a Mettler FP 90 central processor was used to observe the thermal transitions and to analyze the anisotropic textures.[15] X-ray scattering measurements were performed in transmission mode with nickel-filtered Cu Kα radiation supplied by a Rigaku Denki generator operating at 40 kv, 40 mA. In order to investigate structural changes on heating, the samples were held in an aluminum sample holder which was sealed with the window of 8 μm thick Kapton films on both sides. The samples were heated with two catridge heaters and the temperature of the samples was monitered by a thermocouple placed close to the sample. Background scattering correction was made by subtracting the scatterings from the Kapton. The small-angle X-ray scattering measurements were performed with a Kratky camera fitted with an M. Broun linear position sensitive detector. The correction for the slit length smearing was applied by means of Strobl's algorithm. Microanalyses were performed with a Perkin Elmer 240 elemental anlayser at Korea Research Institute of Chemical Technology. Thermogravimetric analysis was performed with a TGA analysis Dupant 2100. The Pd(II)-imine complexes were purified by chromatography (silica gel, methylene chloride eluent).

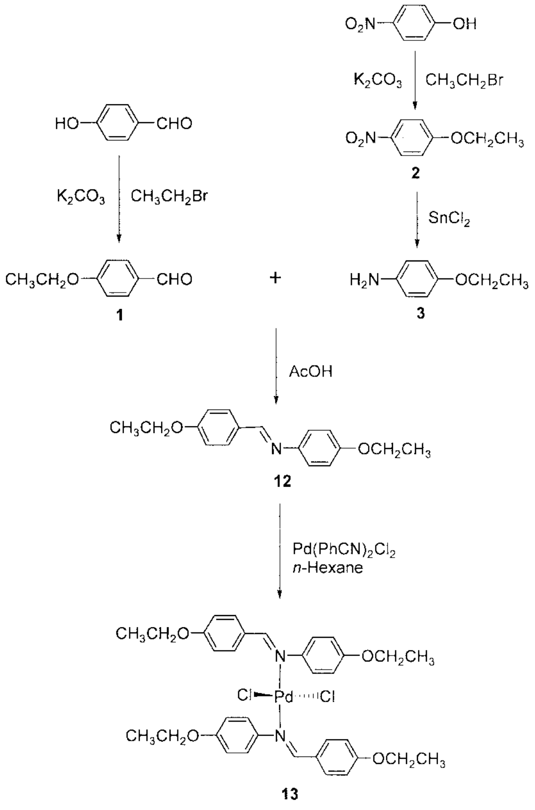
Crystal structure determination of the model complex. Crystals suitable for X-ray diffraction studies were grown from vapor diffusion method (CH_2Cl_2/Ether). A crystal was mounted on a glass fiber, transferred to a Siemens SMART diffractometer/CCD area detector,[16a] and centered in the beam. Preliminary orientation matrix and cell constants were determined by collection of 20 20-second and frames, followed by spot intergration and least-squares refinement. A hemisphere of data was collected using 0.3^o ω scans at 20-seconds per frame. The raw data were intergrated (XY spot spread = 1.60^o, Z spot spread = 0.6^o) and the unit cell parameters refined (8122 reflection with $I > 3\sigma$) using SAINT.[16b] Data analysis and absorption correction were performed using Siemens XPREP.[16c] The unit-cell parameters indicated a primitive monoclinic cell and systematic absences indicated space group P2(1)/c (no. 14). The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. The 7923 reflections measured were averged ($R_{int} = 0.0974$) yielding 2818 unique reflections. The structure was solved and refined with the SHELX-97 program using direct methods[16d] and expanded using Fourier techniques.[17] All non-hydrogen atoms were refined anisotropically. The final resuduals for the 198 variables refined aganist the 2179 data for which $F^2 > 2\sigma(F^2)$ were R = 0.0342, R′ = 0.0856 and the R vaule for all 2818 data was 0.0542.

Synthesis. The synthesis of imine ligands and their corresponding Pd complexes is outlined in Scheme I. The synthesis of a model compound was outlined in Scheme II. The complexation reactions were carried out under an atmosphere of prepurified N_2 at refluxing *n*-hexane by using standard Schlenk techniques.[18]

Synthesis of 3,4-dialkyloxybenzaldehyde (1-6, 1-8, 1-10, 1-12): 3,4-Dialkyloxybenzaldehydes were all synthesized using the same procedure. A representative example is described for 3,4-didecyloxybenzaldehyde. A mixture of 1-bromodecane (3.1 g, 14.5 mmol), 3,4-dihydroxybenzaldehyde (0.5 g, 3.6 mmol) and K_2CO_3 (2 g, 14.5 mmol) in 50 mL of ethanol was refluxed for 24 h. After cooled to room temperature, the solution was acidified with dilute aqueous formic acid solution. The solution was extracted with CH_2Cl_2 and then CH_2Cl_2 solution was dried over anhydrous $MgSO_4$. The solvent was removed in a rotary evaporator. The obtained solid was purified by recrystallization from ethanol to yield 1.05 g (69%) of white crystals: mp 64-65 ^{o}C; ^{1}H-NMR (250 MHz, $CDCl_3$, δ) 0.89 (t, 6H, $C\underline{H}_3CH_2$, *J* = 6.4 Hz), 1.31-1.60 (m, 28H, $CH_3(C\underline{H}_2)_7$), 1.79-1.92 (m, 4H, $OCH_2C\underline{H}_2$), 4.03-



Scheme I. Synthesis of the Pd-complexes **8**, **9**, **10** and **11**.



Scheme II. Synthesis of the model complex.

4.11 (m, 4H, $OC\underline{H}_2$), 6.97 (d, 1H, *m* to CHO, *J* = 7.9 Hz), 7.40-7.44 (m, 2H, *o* to CHO), 9.82 (s, 1H, $C\underline{H}O$).

3,4-Dihexyloxybenzaldehyde (1-6): Yield 78%; mp 40-42 °C; ^{1}H-NMR (250 MHz, $CDCl_3$, δ) 0.88 (t, 6H, $C\underline{H}_3CH_2$, *J* = 6.7 Hz), 1.28-1.61 (m, 12H, $CH_3(C\underline{H}_2)_3$), 1.78-1.93 (m, 4H, $OCH_2C\underline{H}_2$), 4.00-4.13 (m, 4H, $OC\underline{H}_2$), 6.98 (d, 1H, *m* to CHO, *J* = 7.9 Hz), 7.40-7.44 (m, 2H, *o* to CHO), 9.82 (s, 1H, $C\underline{H}O$).

3,4-Dioctyloxybenzaldehyde (1-8): Yield 81%; mp 54-55 °C; ^{1}H-NMR (250 MHz, $CDCl_3$, δ) 0.88 (t, 6H, $C\underline{H}_3CH_2$, *J* = 6.4 Hz), 1.29-1.61 (m, 20H, $CH_3(C\underline{H}_2)_5$), 1.78-1.94 (m, 4H, $OCH_2C\underline{H}_2$), 4.02-4.13 (m, 4H, $OC\underline{H}_2$), 6.96 (d, 1H, *m* to CHO, *J* = 7.8 Hz), 7.40-7.44 (m, 2H, *o* to CHO), 9.83 (s, 1H, $C\underline{H}O$).

3,4-Didodecyloxybenzaldehyde (1-12): Yield 64%; mp 70-72 °C; ^{1}H-NMR (250 MHz, $CDCl_3$, δ) 0.89 (t, 6H, $C\underline{H}_3CH_2$, *J* = 6.7 Hz), 1.30-1.55 (m, 36H, $CH_3(C\underline{H}_2)_9$), 1.80-1.94 (m, 4H, $OCH_2C\underline{H}_2$), 4.05-4.13 (m, 4H, $OC\underline{H}_2$), 6.98 (d, 1H, *m* to CHO, *J* = 7.6 Hz), 7.41-7.44 (m, 2H, *o* to CHO), 9.81 (s, 1H, $C\underline{H}O$).

Synthesis of 3,4-dialkyloxynitrobenzene (2-6, 2-8, 2-10, 2-12): 3,4-Dialkyloxynitrobenzenes were all synthesized using the same procedure. A representative example is described for 3,4-didecyloxynitrobenzene. A mixture of 1-bromodecane (2.85 g, 12.8 mmol), 4-nitrocatechol (0.5 g, 3.2 mmol) and K_2CO_3 (1.78 g, 12.8 mmol) in 50 mL of ethanol was refluxed for 24 h. After cooled to room temperature, the solution was acidified with dilute aqueous formic acid solution. The solution was extracted with CH_2Cl_2 and then CH_2Cl_2 solution was dried over anhydrous $MgSO_4$. The solvent was removed in a rotary evaporator. The obtained solid was purified by recrystallization from ethanol to yield 1.3 g (93%) of white crystals: mp 68-69 °C; ^{1}H-NMR (250 MHz, $CDCl_3$, δ) 0.89 (t, 6H, $C\underline{H}_3CH_2$, *J* = 6.4 Hz), 1.30-1.51 (m, 28H, $CH_3(C\underline{H}_2)_7$), 1.80-1.93 (m, 4H, $OCH_2C\underline{H}_2$), 4.05-4.13 (m, 4H, $OC\underline{H}_2$), 6.92 (d, 1H, *m* to NO_2, *J* = 8.9 Hz), 7.75 (d, 1H, *o* to 3-decyloxy, *J* = 2.6 Hz), 7.90 (dd, 1H, *p* to 3-decyloxy, *J* = 8.9, 2.6 Hz).

3,4-Dihexyloxynitrobenzene (2-6): Yield 71%; mp 53-54 °C; ^{1}H-NMR (250 MHz, $CDCl_3$, δ) 0.89 (t, 6H, $C\underline{H}_3CH_2$, *J* = 6.4 Hz), 1.31-1.56 (m, 12H, $CH_3(C\underline{H}_2)_3$), 1.80-1.93 (m, 4H, $OCH_2C\underline{H}_2$), 4.01-4.13 (m, 4H, $OC\underline{H}_2$), 6.90 (d, 1H, *m* to NO_2, *J* = 8.9 Hz), 7.75 (d, 1H, *o* to 3-hexyloxy, *J* = 2.6 Hz), 7.90 (dd, 1H, *p* to 3-hexyloxy, *J* = 8.9, 2.6 Hz).

3,4-Dioctyloxynitrobenzene (2-8): Yield 63%; mp 62-63 °C; ^{1}H-NMR (250 MHz, $CDCl_3$, δ) 0.88 (t, 6H, $C\underline{H}_3CH_2$, *J* = 6.7 Hz), 1.28-1.48 (m, 20H, $CH_3(C\underline{H}_2)_5$), 1.78-1.93 (m, 4H, $OCH_2C\underline{H}_2$), 4.05-4.13 (m, 4H, $OC\underline{H}_2$), 6.90 (d, 1H, *m* to

NO_2, J = 8.9 Hz), 7.75 (d, 1H, *o* to 3-octyloxy, J = 2.6 Hz), 7.90 (dd, 1H, *p* to 3-octyloxy, J = 8.9, 2.6 Hz).

3,4-Didodecyloxynitrobenzene (2-12): Yield 65%; mp 72-73 °C; ^{1}H-NMR (250 MHz, $CDCl_3$, δ) 0.88 (t, 6H, $C\underline{H}_3CH_2$, J = 5.9 Hz), 1.31-1.49 (m, 36H, $CH_3(C\underline{H}_2)_7$), 1.79-1.92 (m, 4H, $OCH_2C\underline{H}_2$), 4.02-4.12 (m, 4H, $OC\underline{H}_2$), 6.90 (d, 1H, *m* to NO_2, J = 8.9 Hz), 7.75 (d, 1H, *o* to 3-dodecyloxy, J = 2.7 Hz), 7.90 (dd, 1H, *p* to 3-dodecyloxy, J = 8.9, 2.7 Hz).

Synthesis of 3,4-dialkyloxyaniline (3-6, 3-8, 3-10, 3-12): 3,4-Dialkyloxyanilines were all synthesized using the same procedure. A representative example is described for 3,4-didecyloxyaniline. A mixture of 3,4-didecyloxynitrobenzene (1.0 g, 2.3 mmol) and $SnCl_2$ (2.3 g, 11.5 mmol) in 20 mL of absolute ethanol was refluxed under nitrogen for 2 h. After cooled to room temperature, the reaction mixture was poured into water. The solution was slightly basicified with dilute aqueous $NaHCO_3$ solution. The solution was extracted with ethyl acetate, washed with a saturated NaCl solution, treated with charcoal and then ethyl acetate solution was dried over anhydrous Na_2SO_4. The solvent was then removed in a rotary evaporator to yield 0.8 g (86%). The obtained aniline derivative was used without further purification: ^{1}H-NMR (250 MHz, $CDCl_3$, δ) 0.89 (t, 6H, $C\underline{H}_3CH_2$, J = 6.7 Hz), 1.29-1.47 (m, 28H, $CH_3(C\underline{H}_2)_7$), 1.75-1.83 (m, 4H, $OCH_2C\underline{H}_2$), 3.45 (br s, 2H, $N\underline{H}_2$), 3.90-4.02 (m, 4H, $OC\underline{H}_2$), 6.22 (dd, 1H, *p* to 3-decyloxy, J = 8.3, 2.6 Hz), 6.31 (d, 1H, *o* to 3-decyloxy, J = 2.6 Hz), 6.75 (d, 1H, *m* to NH_2, J = 8.3 Hz).

3,4-Dihexyloxyaniline (3-6): Yield 88%; ^{1}H-NMR (250 MHz, $CDCl_3$, δ) 0.88 (t, 6H, $C\underline{H}_3CH_2$, J = 6.5 Hz), 1.30-1.47 (m, 12H, $CH_3(C\underline{H}_2)_3$), 1.75-1.83 (m, 4H, $OCH_2C\underline{H}_2$), 3.45 (br s, 2H, $N\underline{H}_2$), 3.89-4.03 (m, 4H, $OC\underline{H}_2$), 6.22 (dd, 1H, *p* to 3-hexyloxy, J = 8.4, 2.6 Hz), 6.31 (d, 1H, *o* to 3-hexyloxy, J = 2.6 Hz), 6.75 (d, 1H, *m* to NH_2, J = 8.4 Hz).

3,4-Dioctyloxyaniline (3-8): Yield 90%; ^{1}H-NMR (250 MHz, $CDCl_3$, δ) 0.89 (t, 6H, $C\underline{H}_3CH_2$, J = 5.8 Hz), 1.29-1.51 (m, 20H, $CH_3(C\underline{H}_2)_5$), 1.77-1.83 (m, 4H, $OCH_2C\underline{H}_2$), 3.45 (br s, 2H, $N\underline{H}_2$), 3.90-4.05 (m, 4H, $OC\underline{H}_2$), 6.22 (dd, 1H, *p* to 3-octyloxy, J = 8.4, 2.6 Hz), 6.31 (d, 1H, *o* to 3-octyloxy, J = 2.6 Hz), 6.75 (d, 1H, *m* to NH_2, J = 8.4 Hz).

3,4-Didodecyloxyaniline (3-12): Yield 93%; ^{1}H-NMR (250 MHz, $CDCl_3$, δ) 0.88 (t, 6H, $C\underline{H}_3CH_2$, J = 6.7 Hz), 1.30-1.47 (m, 36H, $CH_3(C\underline{H}_2)_9$), 1.75-1.83 (m, 4H, $OCH_2C\underline{H}_2$), 3.45 (br s, 2H, $N\underline{H}_2$), 3.90-4.02 (m, 4H, $OC\underline{H}_2$), 6.23 (dd, 1H, *p* to 3-dodecyloxy, J = 8.4, 2.5 Hz), 6.31 (d, 1H, *o* to 3-dodecyloxy, J = 2.5 Hz), 6.75 (d, 1H, *m* to NH_2, J = 8.4 Hz).

Synthesis of 3,4-dialkyloxybenzylidene-3′,4′-dialkyloxyaniline (4, 5, 6, 7): 3,4-Dialkyloxybenzylidene-3′,4′-dialkyloxyanilines were all synthesized using the same procedure. A representative example is described for 3,4-didecyloxybenzylidene-3′,4′-didecyloxyanilines (**6**). A mixture of 3,4-didecyloxybenzaldehyde (1.0 g, 2.4 mmol) and 3,4-didecyloxyaniline (1.0 g, 2.5 mmol) in acetic acid catalyzed 20 mL of absolute ethanol was refluxed for 4h. After cooled to room temperature, the reaction mixture was filtered. The obtained solid was purified by recrystallization form ethyl acetate to yield 1.7 g (86%) of brown crystals: mp 95.5 °C (DSC); ^{1}H-NMR (250 MHz, $CDCl_3$, δ) 0.89 (t, 12H, $C\underline{H}_3CH_2$, J = 6.2 Hz), 1.27-1.48 (m, 56H, $CH_3(C\underline{H}_2)_7$), 1.78-1.90 (m, 8H, $OCH_2C\underline{H}_2$), 3.97-4.12 (m, 8H, $OC\underline{H}_2$), 6.76 (dd, 1H, *m* to N=CH-Ph, J = 8.4, 2.3 Hz), 6.84-6.93 (m, 1H, *o* to N=CH-Ph and *o* to 3′-decyloxy, 1H, *m* to CH=N-Ph, 1H, *m* to N=CH-Ph), 7.26 (dd, 1H, *o* to CH=N-Ph and *m* to 4-decyloxy, overlapped with $CHCl_3$ signal), 7.56 (d, 1H, *o* to CH=N-Ph and *o* to 3-decyloxy, J = 1.8 Hz), 8.36 (s, 1H, $C\underline{H}$=N)); IR (KBr) 1631 ($\nu_{C=N}$) cm^{-1}. Anal. Calcd for $C_{53}H_{91}N_1O_4$: C, 78.95; H, 11.38; N, 1.74. Found C, 78.67; H, 11.48; N, 1.54.

Ligand **4**. Yield 60%; mp 84.2 °C (DSC); ^{1}H-NMR (250 MHz, $CDCl_3$, δ) 0.91 (t, 12H, $C\underline{H}_3CH_2$, J = 6.8 Hz), 1.34-1.51 (m, 24H, $CH_3(C\underline{H}_2)_3$), 1.79-1.88 (m, 8H, $OCH_2C\underline{H}_2$), 4.00-4.12 (m, 8H, $OC\underline{H}_2$), 6.76 (dd, 1H, *m* to N=CH-Ph, J = 8.4, 2.4 Hz), 6.84-6.92 (m, 1H, *o* to N=CH-Ph and *o* to 3′-hexyloxy, 1H, *m* to CH=N-Ph, 1H, *m* to N=CH-Ph), 7.26 (dd, 1H, *o* to CH=N-Ph and *m* to 4-hexyloxy, overlapped with $CHCl_3$ signal), 7.55 (d, 1H, *o* to CH=N-Ph and *o* to 3-hexyloxy, J = 1.8 Hz), 8.36 (s, 1H, $C\underline{H}$=N)); IR (KBr) 1630 ($\nu_{C=N}$) cm^{-1}. Anal. Calcd for $C_{37}H_{59}N_1O_4$: C, 76.37; H, 10.22; N, 2.41. Found C, 76.56; H, 10.36; N, 1.97.

Ligand **5**. Yield 60%; mp 87.5 °C (DSC); ^{1}H-NMR (250 MHz, $CDCl_3$, δ) 0.89 (t, 12H, $C\underline{H}_3CH_2$, J = 6.5 Hz), 1.27-1.48 (m, 40H, $CH_3(C\underline{H}_2)_5$), 1.79-1.88 (m, 8H, $OCH_2C\underline{H}_2$), 4.00-4.12 (m, 8H, $OC\underline{H}_2$), 6.76 (dd, 1H, *m* to N=CH-Ph, J = 8.4, 2.4 Hz), 6.85-6.93 (m, 1H, *o* to N=CH-Ph and *o* to 3′-octyloxy, 1H, *m* to CH=N-Ph, 1H, *m* to N=CH-Ph), 7.26 (dd, 1H, *o* to CH=N-Ph and *m* to 4-octyloxy, overlapped with $CHCl_3$ signal), 7.55 (d, 1H, *o* to CH=N-Ph and *o* to 3-octyloxy, J = 1.8 Hz), 8.36 (s, 1H, $C\underline{H}$=N)); IR (KBr) 1630 ($\nu_{C=N}$) cm^{-1}. Anal. Calcd for $C_{45}H_{75}N_1O_4$: C, 77.86; H, 10.90; N, 2.02. Found C, 77.63; H, 11.14; N, 2.28.

Ligand **7**. Yield 85%; mp 97.8 °C (DSC); ^{1}H-NMR (250 MHz, $CDCl_3$, δ) 0.88 (t, 12H, $C\underline{H}_3CH_2$, J = 6.4 Hz), 1.27-1.48 (m, 72H, $CH_3(C\underline{H}_2)_9$), 1.76-1.88 (m, 8H, $OCH_2C\underline{H}_2$), 3.98-4.12 (m, 8H, $OC\underline{H}_2$), 6.77 (dd, 1H, *m* to N=CH-Ph, J = 8.4, 2.3 Hz), 6.84-6.93 (m, 1H, *o* to N=CH-Ph and *o* to 3'-dodecyloxy, 1H, *m* to CH=N-Ph, 1H, *m* to N=CH-Ph), 7.26 (dd, 1H, *o* to CH=N-Ph and *m* to 4-dodecyloxy, overlapped with $CHCl_3$ signal), 7.55 (d, 1H, *o* to CH=N-Ph and *o* to 3-dodecyloxy, J = 1.8 Hz), 8.36 (s, 1H, $C\underline{H}$=N)); IR (KBr) 1630 ($\nu_{C=N}$) cm^{-1}. Anal. Calcd for $C_{61}H_{107}N_1O_4$: C, 79.77; H, 11.74; N, 1.52. Found C, 79.58; H, 11.68; N, 1.30.

Synthesis of Bis(3,4-dialkyloxybenzylidene-3′,4′-dialkyloxyaniline)dichloropalladium(II) (8, 9, 10, 11): Complexes were all synthesized using the same procedure. A representative example is described for **10**. A mixture of compound **6** (42 mg, 52 mmol) and bis(benzonitrile)dichloropalladium (II) (10 mg, 26 mmol) in 10 mL of *n*-hexane was refluxed under nitrogen for 6 h. The solvent was removed under vacuum. The resulting yellow residue was then purified by column chromatography (silica gel, CH_2Cl_2) to yield 24 mg (53%, transoid : cisoid = 85 : 15) of yellow crystals: T_m 79.7 °C (DSC); ^{1}H-NMR (250 MHz, $CDCl_3$, δ) 0.88 (t, 24H, $C\underline{H}_3CH_2$, J = 5.8 Hz), 1.26-1.54 (m, 112H, $CH_3(C\underline{H}_2)_7$), 1.68-1.86 (m, 16H, $OCH_2C\underline{H}_2$), 3.71-3.76 (m, 4H, $OC\underline{H}_2$, *m* to CH=N-Ph), 3.86-3.91 (m, 4H, $OC\underline{H}_2$, *m* to N=CH-Ph), 4.02-

4.11 (m, 4H, OC$\underline{H}_2$, *p* to CH=N-Ph, 4H, OC$\underline{H}_2$, *p* to N=CH-Ph), 6.80-6.87 (m, 2H, *m* to N=CH-Ph, 2H, *m* to CH=N-Ph: cisoid, overlapped with transoid), 7.09 (dd, 2H, *o* to N=CH-Ph and *m* to 4′-decyloxy, *J* = 8.4, 2.4 Hz: cisoid, overlapped with transoid), 7.53 (d, 2H, *o* to N=CH-Ph and *o* to 3'-decyloxy, *J* = 2.4 Hz: cisoid, 7.69), 7.83 (s, 2H, C$\underline{H}$=N: cisoid, 7.93), 8.20 (d, 2H, *o* to CH=N-Ph and *m* to 3-decyloxy, *J* = 1.7 Hz: cisoid, 8.28), 9.04 (dd, 2H, *o* to CH=N-Ph and *m* to 4-decyloxy, *J* = 8.4, 1.7 Hz: 8.43); IR (KBr) 1615 ($\nu_{C=N}$) cm^{-1}. Anal. Calcd for $C_{106}H_{182}N_2O_8Cl_2Pd$: C, 71.13; H, 10.25; N, 1.57; Cl, 3.96. Found C, 71.17; H, 10.39; N, 1.42; Cl, 4.58.

Pd-Complex **8**. Yield 44% (transoid:cisoid = 85:15); T_m 91.8 °C (DSC); ^{1}H-NMR (250 MHz, $CDCl_3$, δ) 0.90 (t, 24H, C$\underline{H}_3$CH$_2$, *J* = 6.0 Hz), 1.29-1.51 (m, 48H, CH$_3$(C$\underline{H}_2$)$_3$), 1.65-1.86 (m, 16H, OCH$_2$C$\underline{H}_2$), 3.70-3.75 (m, 4H, OC$\underline{H}_2$, *m* to CH=N-Ph), 3.86-3.90 (m, 4H, OC$\underline{H}_2$, *m* to N=CH-Ph), 4.02-4.14 (m, 4H, OC$\underline{H}_2$, *p* to CH=N-Ph, 4H, OC$\underline{H}_2$, *p* to N=CH-Ph), 6.77-6.93 (m, 2H, *m* to N=CH-Ph, 2H, *m* to CH=N-Ph: cisoid, overlapped with transoid), 7.09 (dd, 2H, *o* to N=CH-Ph and *m* to 4′-hexyloxy, *J* = 8.4, 2.4 Hz: cisoid, overlapped with transoid), 7.53 (d, 2H, *o* to N=CH-Ph and *o* to 3′-hexyloxy, *J* = 2.4 Hz: cisoid, 7.66), 7.83 (s, 2H, C$\underline{H}$=N: cisoid, 7.91), 8.20 (d, 2H, *o* to CH=N-Ph and *m* to 3-hexyloxy, *J* = 1.9 Hz: cisoid, 8.28), 9.03 (dd, 2H, *o* to CH=N-Ph and *m* to 4-hexyloxy, *J* = 8.4, 1.9 Hz: cisoid, 8.39); IR (KBr) 1615 ($\nu_{C=N}$) cm^{-1}. Anal. Calcd for $C_{74}H_{118}N_2O_8Cl_2Pd$: C, 66.28; H, 8.87; N, 2.09. Found C, 66.24; H, 8.90; N, 1.78.

Pd-Complex **9**. Yield 60% (transoid:cisoid = 85:15); T_m 90.7 °C (DSC); ^{1}H-NMR (250 MHz, $CDCl_3$, δ) 0.88 (t, 24H, C$\underline{H}_3$CH$_2$, *J* = 6.9 Hz), 1.27-1.56 (m, 80H, CH$_3$(C$\underline{H}_2$)$_5$), 1.67-1.89 (m, 16H, OCH$_2$C$\underline{H}_2$), 3.70-3.76 (m, 4H, OC$\underline{H}_2$, *m* to CH=N-Ph), 3.86-3.90 (m, 4H, OC$\underline{H}_2$, *m* to N=CH-Ph), 4.02-4.11 (m, 4H, OC$\underline{H}_2$, *p* to CH=N-Ph, 4H, OC$\underline{H}_2$, *p* to N=CH-Ph), 6.76-6.92 (m, 2H, *m* to N=CH-Ph, 2H, *m* to CH=N-Ph: cisoid, overlapped with transoid), 7.10 (dd, 2H, *o* to N=CH-Ph and *m* to 4′-octyloxy, *J* = 8.4, 2.4 Hz: cisoid, overlapped with transoid), 7.53 (d, 2H, *o* to N=CH-Ph and *o* to 3′-octyloxy, *J* = 2.4 Hz: cisoid, 7.67), 7.83 (s, 2H, C$\underline{H}$=N: cisoid, 7.91), 8.20 (d, 2H, *o* to CH=N-Ph and *m* to 3-octyloxy, *J* = 1.7 Hz: cisoid, 8.28), 9.05 (dd, 2H, *o* to CH=N-Ph and *m* to 4-octyloxy, *J* = 8.4, 1.7 Hz: cisoid, 8.40); IR (KBr) 1615 ($\nu_{C=N}$) cm^{-1}. Anal. Calcd for $C_{90}H_{150}N_2O_8Cl_2Pd$: C, 69.10; H, 9.67; N, 1.79. Found C, 69.17; H, 9.90; N, 1.98.

Pd-Complex **11**. Yield 45% (transoid : cisoid = 85 : 15); mp 73.4 °C (DSC); ^{1}H-NMR (250 MHz, $CDCl_3$, δ) 0.88 (t, 24H, C$\underline{H}_3$CH$_2$, *J* = 5.6 Hz), 1.25-1.54 (m, 144H, CH$_3$(C$\underline{H}_2$)$_9$), 1.67-1.86 (m, 16H, OCH$_2$C$\underline{H}_2$), 3.70-3.75 (m, 4H, OC$\underline{H}_2$, *m* to CH=N-Ph), 3.86-3.91 (m, 4H, OC$\underline{H}_2$, *m* to N=CH-Ph), 4.02-4.12 (m, 4H, OC$\underline{H}_2$, *p* to CH=N-Ph, 4H, OC$\underline{H}_2$, *p* to N=CH-Ph), 6.76-6.94 (m, 2H, *m* to N=CH-Ph, 2H, *m* to CH=N-Ph: cisoid, overlapped with transoid), 7.10 (dd, 2H, *o* to N=CH-Ph and *m* to 4′-dodecyloxy, *J* = 8.4, 2.3 Hz: cisoid, overlapped with transoid), 7.53 (d, 2H, *o* to N=CH-Ph and *o* to 3′-dodecyloxy, *J* = 2.3 Hz: cisoid, 7.69), 7.83 (s, 2H, C$\underline{H}$=N: cisoid, 7.91), 8.20 (d, 2H, *o* to CH=N-Ph and *m* to 3-dodecyloxy, *J* = 1.7 Hz: cisoid, 8.28), 9.03 (dd, 2H, *o* to CH=N-Ph and *m* to 4-dodecyloxy, *J* = 8.4, 1.7 Hz: cisoid, 8.41); IR (KBr) 1631 ($\nu_{C=N}$) cm^{-1}. Anal. Calcd for $C_{122}H_{214}N_2O_8Cl_2Pd$: C, 72.74; H, 10.71; N, 1.39. Found C, 73.32; H, 10.92; N, 1.15.

Synthesis of a model complex: The ligand and the model compound were synthesized according to the procedure described for the complex **10**. The model complex with only transoid isomer was purified by column chromatography (silica gel) using methylene chloride eluent and was then further purified by several careful recrystallizations from CH_2Cl_2.

4-Ethyloxybenzaldehyde (1): Yield 75%; ^{1}H-NMR (250 MHz, $CDCl_3$, δ) 1.37-1.44 (m, 6H, C$\underline{H}_3$), 3.93-4.05 (m, 4H, OC$\underline{H}_2$), 6.98 (d, 2H, *m* to CHO, *J* = 8.7 Hz), 7.81 (d, 2H, *o* to CHO, *J* = 8.7 Hz), 9.88 (s, 1H, C$\underline{H}$O).

4-Ethyloxynitrobenzene (2): Yield 80%; ^{1}H-NMR (250 MHz, $CDCl_3$, δ) 1.35-1.42 (m, 6H, C$\underline{H}_3$), 3.95-4.04 (m, 4H, OC$\underline{H}_2$), 6.93 (d, 2H, *m* to NO$_2$, *J* = 9.0 Hz), 8.18 (d, 2H, *o* to NO$_2$, *J* = 9.0 Hz).

4-Ethyloxyaniline (3): Yield 76%; ^{1}H-NMR (250 MHz, $CDCl_3$, δ) 1.34-1.40 (m, 6H, C$\underline{H}_3$CH$_2$), 3.91-4.00 (m, 4H, OC$\underline{H}_2$), 6.65 (m, 2H, *o* to NH$_2$), 6.75 (m, 2H, *m* to NH$_2$).

4-Ethyloxybenzylidene-4′-ethyloxyaniline (12): Yield 70%; mp 147-149 °C; ^{1}H-NMR (250 MHz, $CDCl_3$, δ) 1.40-1.47 (m, 12H, C$\underline{H}_3$), 4.01-4.14 (m, 8H, OC$\underline{H}_2$), 6.89-6.98 (m, 2H, *m* to N=CH-Ph, 2H, *m* to CH=N-Ph), 7.19 (d, 2H, *o* to N=CH-Ph, *J* = 8.7 Hz), 7.82 (d, 2H, *o* to CH=N-Ph, *J* = 8.7 Hz), 8.40 (s, 1H, C$\underline{H}$=N).

Bis(4-ethyloxybenzylidene-4′-ethyloxyaniline)dichloropalladium(II) (13): Yield 50%; mp >250 °C (dec); ^{1}H-NMR (250 MHz, $CDCl_3$, δ) 1.46-1.55 (m, 12H, C$\underline{H}_3$), 4.08-4.17 (m, 8H, OC$\underline{H}_2$), 6.88-7.03 (m, 2H, *m* to N=CH-Ph, 2H, *m* to CH=N-Ph), 7.69 (d, 2H, *o* to N=CH-Ph, *J* = 8.8 Hz), 7.84 (s, 1H, C$\underline{H}$=N) 9.16 (d, 2H, *o* to CH=N-Ph, *J* = 8.8 Hz).

Results and Discussion

Synthesis of the palladium(II) complexes. The tetraalkoxy substituted benzylideneaniline ligands were prepared from the corresponding 3,4-dialkoxybenzaldehyde and 3,4-dialkoxyaniline in ethanol in the presence of small amounts of glacial acetic acid as outlined in Scheme I. The palladium (II) complexes with η^1-benzylideneaniline were prepared from the corresponding free ligands by a ligand exchange reaction as shown in Scheme I. The reactions of the benzylideneanilines with [PdCl$_2$(PhCN)$_2$] in *n*-hexane afford light yellow complexes [PdCl$_2$(ligand)$_2$]. The resulting complexes were purified by column chromatography (silica gel) using methylene chloride as eluent and were obtained in reasonable yields. The elemental analyses for the complexes given in the Experimental section are agreed well with the expected chemical structures. The IR spectra show that stretching frequency of the C=N bond was shifted to a lower wavenumber (*ca*. 15 cm^{-1}) than for the free ligand after complexation. This shift is due to the reduction of double bond character of the C=N bond caused by the coordination of the nitrogen atom into the metal atom and consistent with the

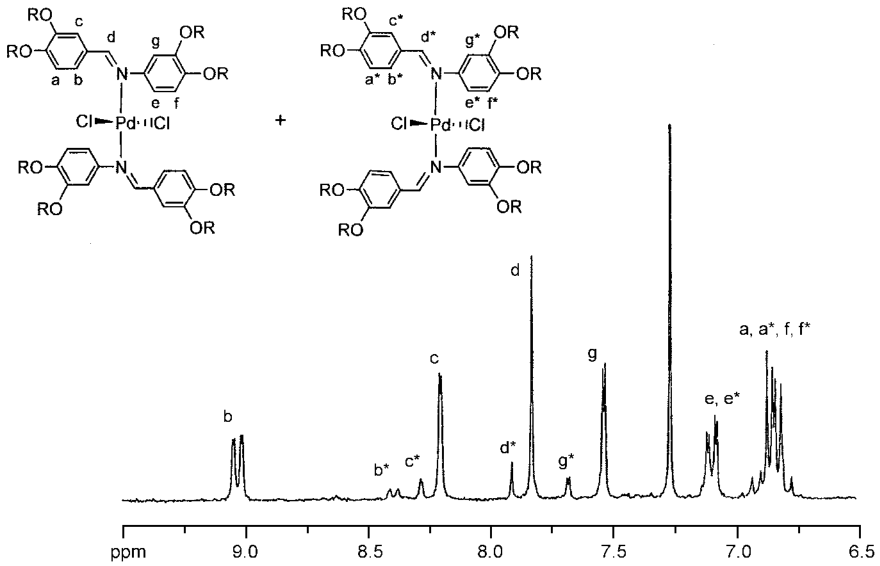


Figure 1. 250 MHz ^{1}H-NMR spectrum corresponding to imine and aromatic protons of the complex **10**.

results obtained from the orthocyclopalladated complexes described previously.[19]

The ^{1}H-NMR spectra of the complexes are all very similar. Figure 1 presents the aromatic region of a typical 250 MHz ^{1}H-NMR spectrum of the complex **10** together with its proton assignments. As shown in Figure 1, all aromatic protons including imine proton give rise to a pair of each signal which means that the existence of the two possible isomers, transoid and cisoid which are different dispositions of the ligand orientation. The ratio of transoid and cisoid is appeared to be 85 : 15, calculated from the intensity of two types of proton resonances. The spectrum exhibits a pair of imine proton resonances at 7.83 ppm for transoid and 7.93 ppm for cisoid, respectively which represent an upfield shift for this proton upon complexation. This shift would result from the expected decrease in bond order due to the nitrogen coordination, and agrees well with the shifts reported for the orthocyclopalladated imine.[4,20]

On the basis of the splitting patterns and the positions of the chemical shifts, the proton resonances corresponding to aromatic protons can be readily assigned. The aromatic proton resonances apparently arise from a proposed structure of η^1-imine Pd(II) complex. If the coordination reaction undergoes to yield the orthocyclopalladated complex, the protons b, c in the *ortho*-positions of a phenyl ring should disappear after complexation.[4,19,20] In contrast, the proton resonances b, c with ortho-position of a phenyl ring can be clearly observed at 9.0, 8.2 ppm for transoid isomer and 8.4, 8.3 ppm for cisoid isomer, respectively. These results support that the ligand exchange reaction of the benzylideneanilines with [$PdCl_2(PhCN)_2$] in *n*-hexane yields the Pd(II) complex with η^1-benzylideneaniline.

In order to investigate thermal stability of the η^1-Pd(II) complexes, thermogravimetric analysis (TGA) and high temperature ^{1}H-NMR spectroscopic measurements were performed with the complex **10**. As shown in Figure 2, TGA result of the complex **10** indicates that the η^1-Pd(II) complex appears to be themally stable up to about 200 °C without the appearance of any sign for decomposition. Furthermore, the high temperature ^{1}H-NMR investigations with the complex **10** did not show any spectral changes. These results indicate that the η^1-Pd(II) complex appears to be a lack of interconversion of the transoid and cisoid isomers, and maintaining η^1 structure even on extensive heating the complex.

In order to make the resonance assignment clearer and confirm the molecular structure by a single X-ray crystallographic analysis, a model compound was synthesized as shown in Scheme II. The pure trans isomer could be isolated

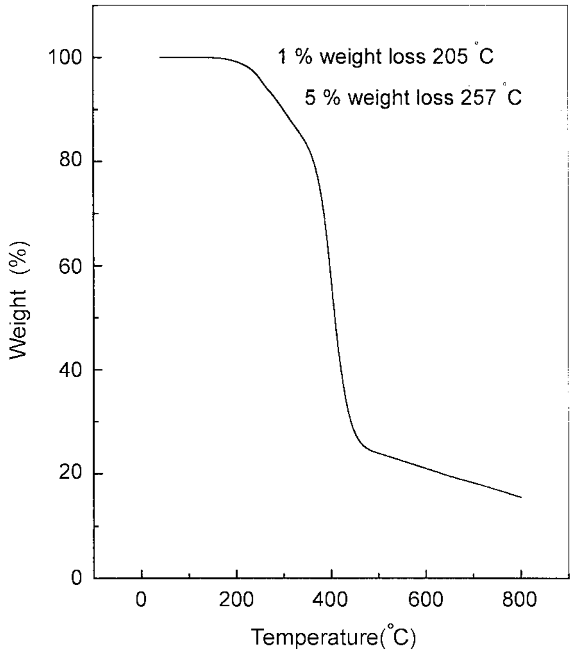


Figure 2. TGA curve of the complex **10**.

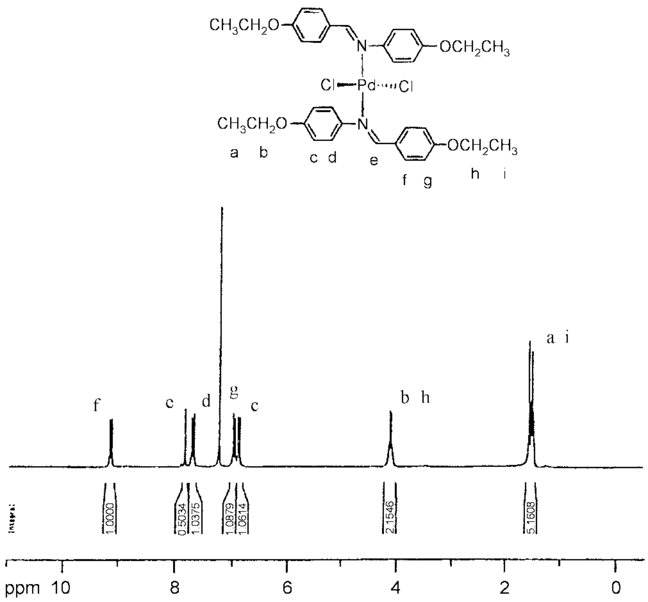


Figure 3. ^{1}H-NMR spectrum of the model complex.

from a mixture of two isomers in the ratio of 85 : 15 (transoid : cisoid) by several careful recrystallizations from methylene chloride, unlike the octaalkoxy substituted complexes. The model compound was characterized by ^{1}H-NMR spectrum as shown in Figure 3. The resonance positions of both imine and aromatic protons in the range of 7.0-9.0 ppm are agreed well with those of transoid isomer for the complex **10**.

Molecular structure of η^1-benzylideneaniline Pd(II) complex. A single X-ray crystallographic analysis has been performed with the model complex in order to confirmed the molecular structure of η^1-benzylidenaniline Pd(II) complex. The molecular structure together with the atom numbering scheme is illustrated in Figure 4. The ORTEP drawing of a model complex shows η^1-coordination of benzylideneaniline through nitrogen atom. The mononuclear complex consists of a Pd(II) center coordinated nitrogen atoms of the ligands and chlorine atoms in a square planar geometry with transoid disposition of the ligand orientation. The Pd-N bond distance 2.024(3) Å and the Pd-Cl distance 2.308(1) Å are similar to the corresponding bond distances in the ortho-cyclopalldated complex.[21,22] The molecular arrangement of the model complex in its crystalline phase is shown in the packing diagram in Figure 5. The two rotational free phenyl rings are noncoplanar with the dihedral angle of 70°, probably due to steric repulsion for the closest packing of the molecule. On the whole, the aromatic core in the complex takes a twisted board like geometry. In contrast to cyclopalladated complexes which show a weak Pd-Pd non-bonded intermolecular interaction (Pd-Pd intermolecular distance, 3.668(2) Å),[22] there is no Pd-Pd intermolecular interaction because the shortest Pd-Pd intermolecular distance is 8.39 Å. This is probably due to the existence of chlorine atoms out of the aromatic core.

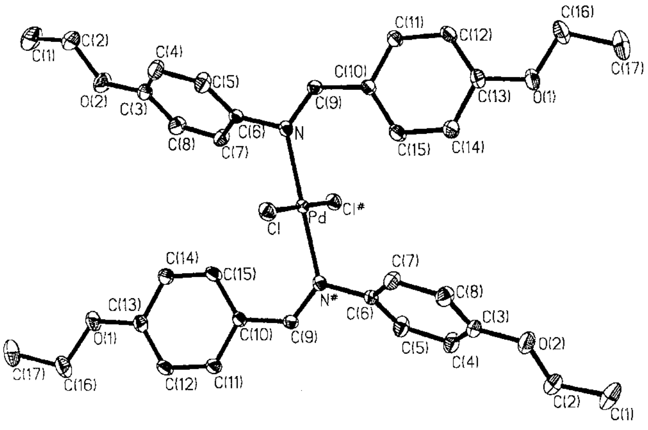


Figure 4. ORTEP drawing of the model complex. Hydrogen atoms were omitted for clarity.

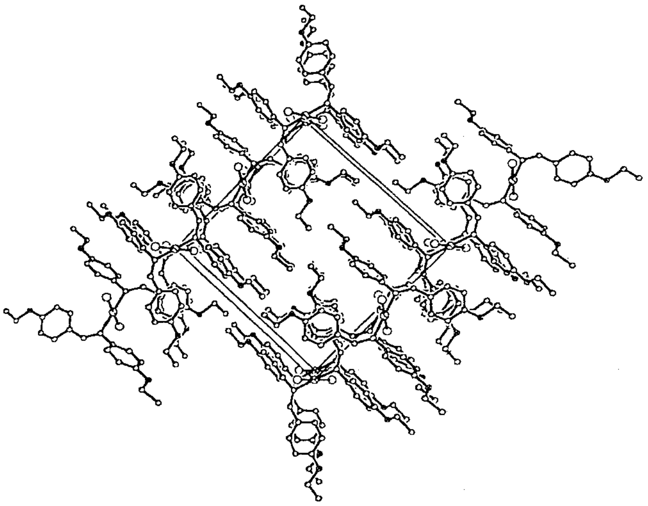


Figure 5. Crystal packing projection down the c axis.

The crystallographic data and positional coordinates are summarized in Tables 1 and 2, and selected bond distances and angles in Table 3, respectively.

Mesomorphic phase behavior. The phase behaviors of the complexes with octaalkoxy peripheral chains were characterized by a combination of techniques consisting of differential scanning calorimetry (DSC), thermal optical polarized microscopy and powder X-ray scattering experiments. The phase transition temperatures and the associated thermal parameters obtained from DSC experiments for both the ligands and the complexes are summarized in Table 4. Figure 6 shows DSC traces obtained from the first cooling scans of the complexes. As shown in Table 4, all imine ligands exhibit only a crystalline melting and do not show liquid crystalline phase behavior.

In contrast to the thermal behavior of the free ligands, the palladium complexes with the exception of the complex **11** exihibit a liquid crystalline phase. The complex **8** with hexyloxy peripheral chains melts into an isotropic liquid at 91.8 °C on heating scan. On cooling from the isotropic liquid, first batonnet-like growth of texture can be observed with a final development of focal conic domains which are

Table 1. Crystal data and structure refinement for the model complex

Empirical formula	$C_{34}H_{38}Cl_2O_4Pd_1$
Formula weight	715.96
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 14.2436(3) Å alpha = 90 deg. b= 13.85950(10) Å beta = 90.5900(10) deg. c= 8.3909(2) Å gamma = 90 deg.
Volume	1656.35(5) $Å^3$
Z, Calculated density	2, 1.436 mg/m^3
Absorption coefficient	0.761 mm^{-1}
F(000)	736
Crystal size	0.3 × 0.3 × 0.3 mm
Theta range for data collection	1.43 to 24.73 deg.
Index ranges	$-16 \leq h \leq 11$, $-16 \leq k \leq 13$, $-9 \leq l \leq 9$
Reflections collected/unique	923/2818 [R(int) = 0.0974]
Completeness to 2 theta = 24.73	95.4%
Refinement method	Full-matrix least-squares on F^2
Data/restrainst/parameters	2818/0/198
Goodness-of-fit on F^2	0.967
Final R indices [I > 2sigma(I)]	R1 = 0.0342, wR^2 = 0.0856
R indices (all data)	R1 = 0.0542, wR^2 = 0.0911
Largest diff. Peak and hole	0.428 and -0.926 e.A^{-3}

Table 2. Atomic coordinates ($\times 10^{-4}$) and equivalent isotropic displacement parameters ($A^2 \times 10^{-3}$) for the model complex. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
Pd	0	0	0	33(1)
Cl	-724(1)	529(1)	2287(1)	48(1)
N	377(2)	-1228(2)	1144(3)	36(1)
O(1)	-3300(2)	-3185(2)	-2129(4)	61(1)
O(2)	3819(2)	-1143(2)	4372(4)	69(1)
C(1)	4992(3)	-1552(4)	6263(7)	102(2)
C(2)	3968(3)	-1628(3)	5836(6)	79(2)
C(3)	2948(3)	-1170(3)	3665(5)	49(1)
C(4)	2898(3)	-885(3)	2107(5)	54(1)
C(5)	2060(3)	-899(3)	1277(5)	47(1)
C(6)	1246(2)	-1185(2)	2029(4)	38(1)
C(7)	1294(3)	-1433(3)	3599(5)	55(1)
C(8)	2146(3)	-1443(3)	4433(5)	60(1)
C(9)	-83(2)	-2030(2)	1193(4)	38(1)
C(10)	-952(2)	-2281(2)	392(4)	37(1)
C(11)	-1567(3)	-1643(2)	-362(5)	47(1)
C(12)	-2341(3)	-1963(3)	-1162(5)	48(1)
C(13)	-2533(3)	-2942(3)	-1255(5)	45(1)
C(14)	-1951(3)	-3584(3)	-493(5)	51(1)
C(15)	-1173(3)	-3257(2)	324(5)	45(1)
C(16)	-3451(3)	-4189(3)	-2445(6)	72(1)
C(17)	-4252(4)	-4263(4)	-3607(7)	95(2)

Table 3. Selected bond lengths [Å] and angles [deg] for the model complex

Pd-N	2.024(3)
Pd-Cl	2.3077(9)
N-C(9)	1.293(4)
N-C(6)	1.438(4)
O(1)-C(13)	1.353(4)
O(1)-C(16)	1.433(5)
O(2)-C(3)	1.371(4)
O-C(2)	1.414(5)
N-Pd-N$^\#$	180.0
N-Pd-Cl$^\#$	90.50(8)
N$^\#$-Pd-Cl$^\#$	89.50(8)
N-Pd-Cl	89.50(8)
N$^\#$-Pd-Cl	90.50(8)
Cl$^\#$-Pd-Cl	180.0
C(9)-N-C(6)	117.0(3)
C(9)-N-Pd	127.3(2)
C(6)-N-Pd	115.7(2)
C(13)-O(1)-C(16)	117.4(3)
C(3)-O(2)-C(2)	119.4(3)
O(2)-C(2)-C(1)	108.1(4)
C(4)-C(3)-O(2)	116.4(4)
C(5)-C(6)-N	121.5(3)
N-C(9)-C(10)	128.7(3)
C(11)-C(10)-C(9)	126.2(3)
O(1)-C(16)-C(17)	107.4(4)

Symmetry transformations used to generate equivalent atoms: $^\#$-x, -y, -z.

Table 4. Thermal transitions of the imine ligands and the Pd-imine complexes. (k: crystalline phase, s_A: smectic A phase, i: isotropic phase)

Compound	Phase transitions (°C) and corresponding enthalpy changes (kJ/mol)	
	Heating	Cooling
Ligand **4**	k 84.2 (45.2) i	i 71.0 (44.6) k
Ligand **5**	k 87.5 (50.5) i	i 60.9 (53.6) k
Ligand **6**	k 95.5 (90.1) i	i 74.4 (90.7) k
Ligand **7**	k 97.8 (97.0) i	i 77.9 (99.2) k
Pd-Complex **8**	k 91.8 (24.5) i	i 61.2 (1.5) s_A 50.3 (0.9) k
Pd-Complex **9**	k 90.7 (31.3) i	i 64.2 (4.2) s_A 46.2 (9.7) k
Pd-Complex **10**	k 79.7 (19.3) i	i 64.5 (4.3) s_A 55.0 (13.2) k
Pd-Complex **11**	k 73.4 (69.7) i	i 54.0 (65.5) k

characteristic of a smectic A mesophase exhibited by conventional calamitic mesogens.[15] A representative texture exhibited by the smectic A liquid crystalline phase of **8** is presented in Figure 7. As expected for a kinetically controlled first order transiton, crystallization occurs at substantial supercooling (Table 1). This is an expected behavior for metallomesogens with high melt viscosity which gives rise to a severe restriction of the molecular mobility.[23]

The complex **9** with octyloxy peripheral chains shows similar thermal behavior to the complex **8** which exhibits a monotropic smectic A mesophase. On heating, **9** melts into an isotropic liquid at 90.7 °C which is similar melting transition temperature to that of the corresponding ligand. The transition from the isotropic liquid on cooling can be seen by the formation of a focal conic fan-like texture

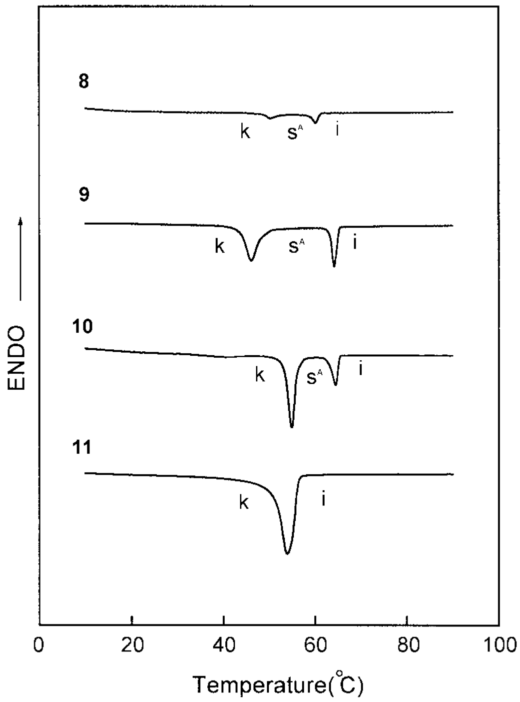


Figure 6. DSC traces (10 °C/min) recorded during the cooling scan of the complexes **8**, **9**, **10** and **11**.

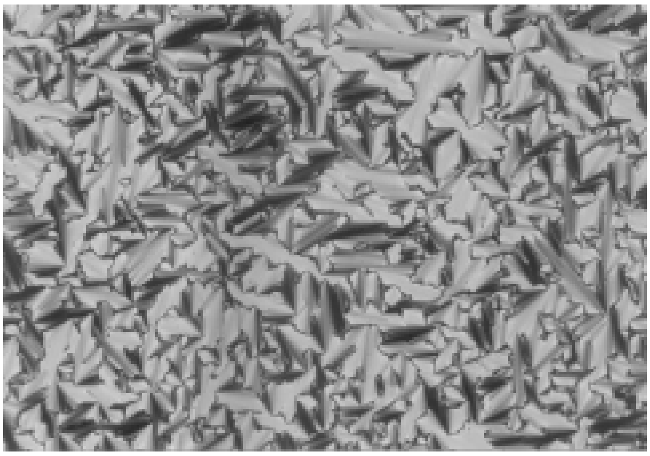


Figure 7. Representative optical polarized micrograph (100 ×) of the texture exhibited by the smectic A mesophase of complex **8** at 60 °C on the cooling scan.

indicating a smectic A mesophase. The complex **10** with decyloxy peripheral chains melts into an isotropic liquid at 79.7 °C which is even a lower melting transition temperature than the corresponding ligand. On cooling, the complex displays a smectic A mesophase followed by crystallization at 55 °C. On the contrary, the complex **11** with dodecyloxy peripheral chains exhibit only a crystalline phase and does not show mesomorphic phase behavior. This is most probably due to the high conformational disorder of the melted dodecyl alkyl chains which radiate towards the periphery of the aromatic core.[24]

In spite that coordination of Pd(II) with η^1-benzylideneaniline gives rise to the non-coplanar aromatic core structure

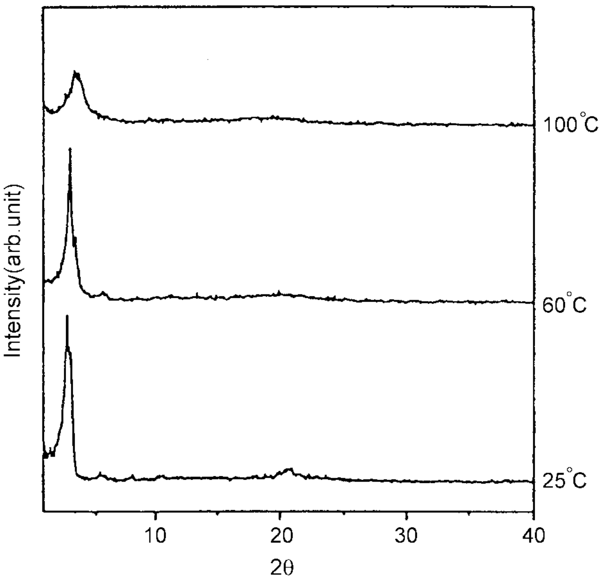


Figure 8. Powder X-ray diffraction patterns of the complex **10**. The curves show the data obtained at 25 °C, 60 °C and 100 °C.

of the complexes, the appearance of a mesomorphic phase for the complexes is notable. In addition, induction of comparable or even lower melting transition temperatures in the complexes compared to those of the ligands is very rare in calamitic metallomesogenic systems with symmetric molecular shape[11,25,26] and is rewarding in terms of their potential processability without decomposition. This interesting thermal behavior can be attributed to the semi-flexible non-coplanar core structure resulting from η^1-ligand coordination and the presence of flexible octaalkyl peripheral chains, leading to less efficient packing of the molecules.

In order to investigate the mesophase structure, powder X-ray diffraction experiments have been performed with the complex **10** at different temperatures as shown in Figure 8. The X-ray diffraction pattern of **10** in the crystalline state at 25 °C displays four reflections with reciprocal spacing ratio of 1 : 2 : 3 : 4 at the small angle region, while the sharps reflections are observed in the wide angle region. This indicates that the crystalline phase of **10** is a lamellar structure with 3.39 nm periodicity. Comparison with the calculated length of a fully extended molecular unit of *ca*. 3.44 nm suggests that the 3.39 nm periodicity arises from monolayers.

In the liquid crystalline phase at 60 °C, a sharp strong reflection and a weak reflection are observed with reciprocal spacing ratio of 1 : 2 in the small angle region, suggesting a lamellar phase with 3.13 nm periodicity, while the sharp reflections observed at crystalline phase in the wide angle region disappear and only a diffuse halo centered at $2\theta = 20^\circ$ is observed, indicating liquid like arrangements of the molecules within the layer. This result together with optical microscopic observations suggests that the mesophase exhibited by the complex is a smectic A mesophase with interlayer spacing of 3.13 nm. The decrease of interlayer spacing from 3.39 nm to 3.13 nm upon melting is most probably due to the

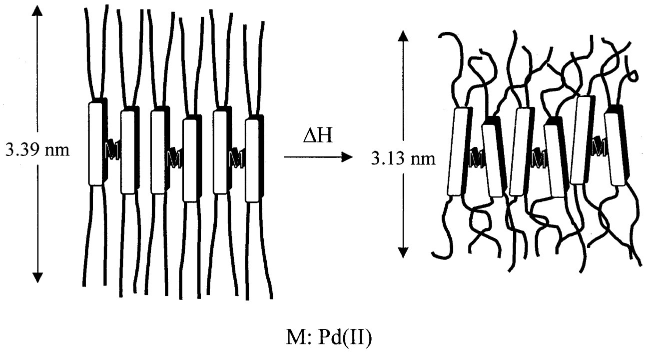


Figure 9. Schematic representation of the formation of a layer responsible for the generation of the smectic A mesophase of the complex **10**.

increase of interfacial surface area and coiling of flexible aliphatic chains as shown schematically in Figure 9. As a result, the layer thickness decreases in order to maintain a uniform density, which is similiar behavior to that reported previously in a rod-like molecule.[27]

X-ray measurements have also been performed in an isotropic liquid at 100 °C. The complex exhibits a small broad peak in the small angle region even on the isotropic liquid phase. This is a high temperature feature for conventional liquid crystal system[28] and is most probably due to the presence of dynamic density inhomogeneity in the liquid state.[29]

On the basis of the powder X-ray experimental results, the most probable mechanism responsible for the generation of the layered smectic phase is presented in Figure 9. The existence of a layered smectic phase is in contrast with the normal phase behavior of octaalkyl substituted metallomesogens which show a columnar type of supramolecular structures.[10,30] The lamellar crystalline structure observed in the complex **10** is the most efficient packing of individual molecules. Upon melting of the complex, the aromatic moeities of the imine ligands attached to a central metal will be twisted out of coplanar geometry to reduce steric repulsion. This distortion may provide a larger interfacial surface area and thus the peripheral chains are still not able to fill the space around the core efficiently. Consequently, the flexible chains tend to align in a preferred direction, leading to the lamellar self-organization. This is supported by the reduction of the layer periodicity observed for **10** from 3.39 nm in the crystalline phase to 3.13 nm in the mesophase.

Conclusion

We have been able to synthesize unusually stable η^1-benzylindeneaniline palladium(II) complexes with octaalkoxy peripheral chains by a ligand exchange reaction of the benzylideneanilines with $[PdCl_2(PhCN)_2]$. The novel chemical structure with η^1-benzylindeneaniline palladium(II) complex was identified by elemental analyses, IR and ^{1}H-NMR spectroscopic techniques, and X-ray single crystallographic determination. The resulting complexes show the low melting transition temperatures, comparable to those of the corresponding imine ligands. In contrast to the imine ligands which do not exhibit liquid crystalline phase behavior, the complexes with hexyloxy (**8**), octyloxy (**9**) and decyloxy (**10**) peripheral chains exhibit a thermally stable monotropic smectic A mesophase without any decomposition of the complexes, in spite of their semi-flexible non-coplanar core structure resulting from η^1-ligand coordination. These results suggest that novel Pd(II)-metallomesogenic materials with non coplanar geometry can be created by η^1-imine ligand coordination.

Acknowledgment. We thank Prof. W. -C. Zin for the powder X-ray measerments. This work was supported by the Korea Research Foundation (KRF-99-015-DP0189).

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