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A Novel Series of Heteropolynuclear Metallomesogens: Organopalladium Complexes with Ferrocenophane-Containing Ligands

Oleg N. Kadkin,*[a] Jaein An,[a] Haksoo Han,[a] and Yuri G. Galyametdinov[b]

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Ferrocenophane-containing (Fcph) Schiff's bases *p*-$C_{12}H_{25}O$-$(C_6H_4)CH{=}N(C_6H_4)$Fcph (**L^AH**) and *p*-$C_{12}H_{25}O(C_6H_4)COO$-$(C_6H_4)CH{=}N(C_6H_4)$Fcph (**L^BH**) react with palladium(II) acetate to form μ-acetato- and chloro-bridged dimeric organopalladium complexes. By exchanging acetato-groups with the chloride anions, μ-chloro-bridged heteropolynuclear dimers are obtained that show thermotropic smectic A phases over a temperature range of 198 to 260 °C. The complexes **$[PdClL^A]_2$** and **$[PdClL^B]_2$** can be transformed into a variety of mixed-ligand Pd^{II} complexes by treatment with salicylaldimine *p*-$C_{12}H_{25}O(C_6H_4)COO(C_6H_3)(OH)CH{=}N(C_6H_4)$-Fcph (**$L^CH$**) and β-aminovinyl ketone *p*-$C_{12}H_{25}O(C_6H_4)$-$COCH{=}CHNH(C_6H_4)$Fcph (**L^DH**). The obtained mixed-ligand heterometallic complexes **$[PdL^AL^C]$**, **$[PdL^BL^C]$**, **$[PdL^AL^D]$** and **$[PdL^BL^D]$** exhibit enantiotropic, thermotropic nematic phases over a broad temperature range from 71 to 205 °C. The structures of the synthesized compounds were characterized by means of ^1H NMR, IR and UV spectroscopy, as well as elemental analysis. The liquid crystalline properties were studied by polarising optical microscopy and DSC.

Introduction

Extensive research on metal-containing liquid crystals or metallomesogens has led to the discovery of many interesting kinds of liquid crystalline organometallic and coordination compounds.[1] The introduction of metal centres can bring valuable physical properties to liquid crystalline materials (colour, polarisability, magnetism, nonlinear optical behaviour, electric properties, etc.) and can potentially expand technological applications of liquid crystals. Metallomesogens with multiple metal centres are of special interest because of the potential advantageous physicochemical properties arising from a combination of dissimilar metals in one molecule and interactions between the metal centres. This consideration inspired us to pursue our research efforts on the syntheses and investigation of heterometallic liquid crystalline complexes.[2] Recently, heterometallic liquid crystalline complexes with rare earth elements and transition metals have been synthesized by Binnemans et al.[3] Interesting examples of ferrocenyl liquid crystals containing a thiourea coordination core, which is suitable for obtaining heterometallic mesogenic systems, were reported by Seshadri et al.[4]

[a] Department of Chemistry, Yonsei University,
134 Shinchon-Dong, Seodaemoon-Gu, Seoul 120-749, South Korea
Fax: +82-2-364-7050
E-mail: onk@yonsei.ac.kr
okadkin@hotmail.com
[b] Department of Physical and Colloid Chemistry, Kazan State Technological University,
68 K. Marx St, 420015 Kazan, Russia
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With regard to heterometallic liquid crystalline systems based on ferrocene-containing ligands the organopalladium complexes showed rather low transition temperatures and broad mesophases.[2d] Generally, cyclopalladated compounds are one of the most fruitful and widely explored areas of metallomesogens. Several research groups have successfully employed azines,[5] azomethines[6] and pyrimidines[7] in the preparation of liquid crystalline palladium(II) complexes. The most remarkable examples of the compounds discovered in this range are miscellaneous orthopalladated mesogens with ferroelectric properties,[8] which were pioneered by Espinet et al.[8a]

High transition temperatures and, frequently, instability of the majority of the known metallomesogens interfere with the demands of liquid crystalline technological applications. Organopalladium mesogens possess some unambiguous benefits from this point of view. Structural diversity and the possibility of symmetry perturbations in organopalladium complexes provide an additional powerful instrument for the controlled adjustments in their mesomorphic behaviour. The various mixed-bridged dinuclear and mixed-ligand mononuclear palladium(II) coordination compounds have exhibited the broad and relatively low-temperature mesophases.[2d,5d,5f,6e,6g,6i,6j,8b,8d]

The first liquid crystalline ferrocenophane derivatives by Friedrichsen et al. exhibited broader mesophases as compared with their unbridged counterparts.[9] Hence, we decided to use ferrocenophane-containing ligand systems for the syntheses of liquid crystalline heteropolynuclear organopalladates. Earlier we described the syntheses and phase behaviour of some liquid crystalline [3]ferroceno-

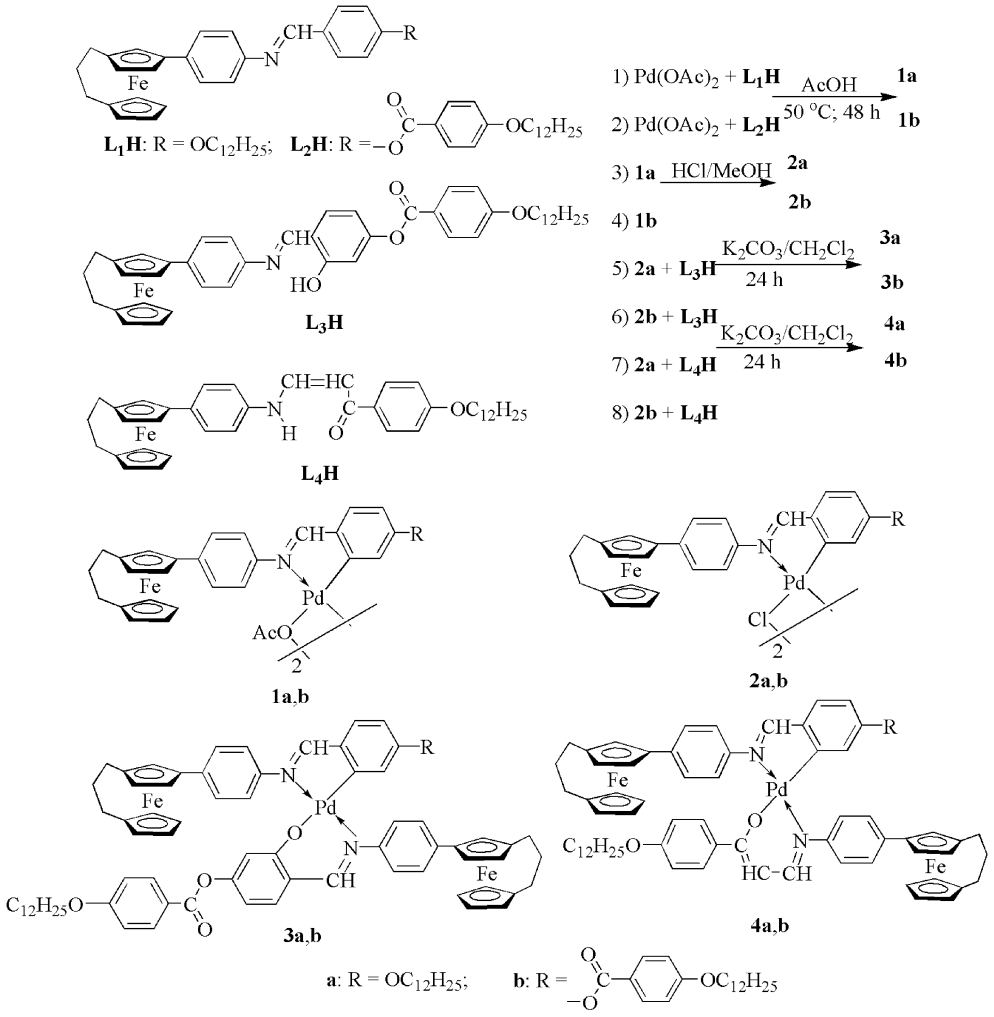
phane-containing Schiff's bases and β-enamino ketone, which represent superior organometallic ligands for obtaining heteropolynuclear liquid crystalline systems.[10] Further utilization of the prepared ferrocenomesogens in cyclopalladation and ligand exchange reactions gave rise to a novel series of heteropolynuclear metallomesogens: syntheses, spectroscopic data and liquid crystalline properties of some acetato- and chloro-bridged cyclopalladated dimers, as well as several mixed-ligand palladium(II) complexes, which contain a ferrocenophane unit, are reported in this article.

Results and Discussion

Syntheses and Spectral Properties

The chemical structures of ferrocenophane-containing ligands used in this work and the synthetic paths to the Pd^{II} complexes created with these ligands are illustrated in Scheme 1. The syntheses of ligands $\mathbf{L_1H}$, $\mathbf{L_2H}$, $\mathbf{L_3H}$ and $\mathbf{L_4H}$ have been reported recently.[10] The cyclopalladation reaction with ligands $\mathbf{L_1H}$ and $\mathbf{L_2H}$, which is carried out using $Pd(OAc)_2$ in glacial acetic acid as described earlier for some other azomethine ligands,[6a,6g,8d] afforded μ-acetato-bridged dimers **1a** and **1b**. The acetato bridges were substituted with chloride anions by an exchange reaction, with a solution of HCl in methanol, yielding μ-chloro-bridged dimeric complexes **2a** and **2b**. The treatment of the latter compounds with ligands $\mathbf{L_3H}$ and $\mathbf{L_4H}$ in dichloromethane in the presence of anhydrous potassium carbonate led to the range of mixed-ligand complexes **3a**, **3b**, **4a** and **4b**.

UV spectra of all the synthesized compounds **1**–**4** are represented by two absorption bands with maximums in the regions 320–330 and 390–400 nm, which are related to metal-to-ligand charge-transfer n–π* electronic transitions (see Table 1). The μ-acetato-bridged complexes **1a** and **1b** show an additional absorption with a maximum at 342 nm, which most likely arises from the n–π* charge-transfer transitions between the palladium(II) ion and the ligands. Intensive absorption in the region 260–280 nm, which is seen in all of the complexes **1**–**4**, has been ascribed to spin-allowed π–π* electronic transitions in the surrounding ligands. In the UV spectra the ferrocene group in compounds **1**–**4** shows characteristic nonintensive absorption bands at 430–450 nm attributed to d–d transitions of the iron atom.[11]



Scheme 1. Chemical structures of ferrocenophane-containing ligands and synthetic paths to the palladium(II) complexes.

Table 1. UV/Vis spectra of organopalladium complexes **1**–**4**.

	λ_{max} [nm] (log ε [L cm^{-1} м$^{-1}$])				
1a	276 (4.688)	–[b]	342 (4.497)	400 (4.321)	460[a] (4.054)
1b	269 (5.071)	330 (4.714)	342 (4.680)	400 (4.367)	474[a] (4.173)
2a	272 (4.779)	334 (4.605)	–	382 (4.359)	466 (4.018)
2b	263 (4.872)	327 (4.486)	–	382[a] (4.076)	475 (3.775)
3a	267 (5.024)	321 (4.619)	–	401 (4.453)	–[b]
3b	267 (5.057)	320 (4.600)	–	400 (4.358)	–[b]
4a	281 (4.654)	321 (4.407)	–	396 (4.475)	–[b]
4b	279 (4.845)	–[b]	–	391 (4.493)	–[b]

[a] Shoulder. [b] The band is evidently not revealed.

Characteristic absorptions in the IR spectra of complexes **1**–**4** are represented by stretching vibrations of the CH=N group of the ligands in the region of about 1605 cm^{-1}. The low frequency shift of the CH=N stretch, in comparison with the free ligands,[10] is consistent with *N*-coordination of palladium(II) ions to the azomethine ligand. Furthemore, additional absorption peaks from the stretching vibrations of the Pd–O, Pd–C and Pd–N bonds appear in the region 510–760 cm^{-1} in all of the complexes **1**–**4**.

The roof-shaped structure of the μ-acetato-bridged complex **1a** can be concluded from its ^{1}H NMR spectrum, since the two distinct multiplets at δ = 3.52 and 3.72 ppm for two diastereotopic CH_2O protons of the alkoxy chains were observed (see Figure 1). The stereochemistry of the μ-acetato-bridged *ortho*-palladated azomethine complexes, in terms of their folded structure, has already been described earlier in detail and with convincing proofs.[6c] In contrast to the latter compounds, Pd^{II} complexes **1a** and **1b** have additional elements of asymmetry connected with the planar chirality of their ferrocenophane fragments. Nevertheless, the possible diastereomeric pairs caused by the presence of several stereogenic units are not exposed in the ^{1}H NMR spectrum of **1a**.

Dramatic changes occurred in the^{1}H NMR spectrum of **1b** as compared with a spectrum of **1a** (see the details in the Supporting Information). For complex **1b** there are four

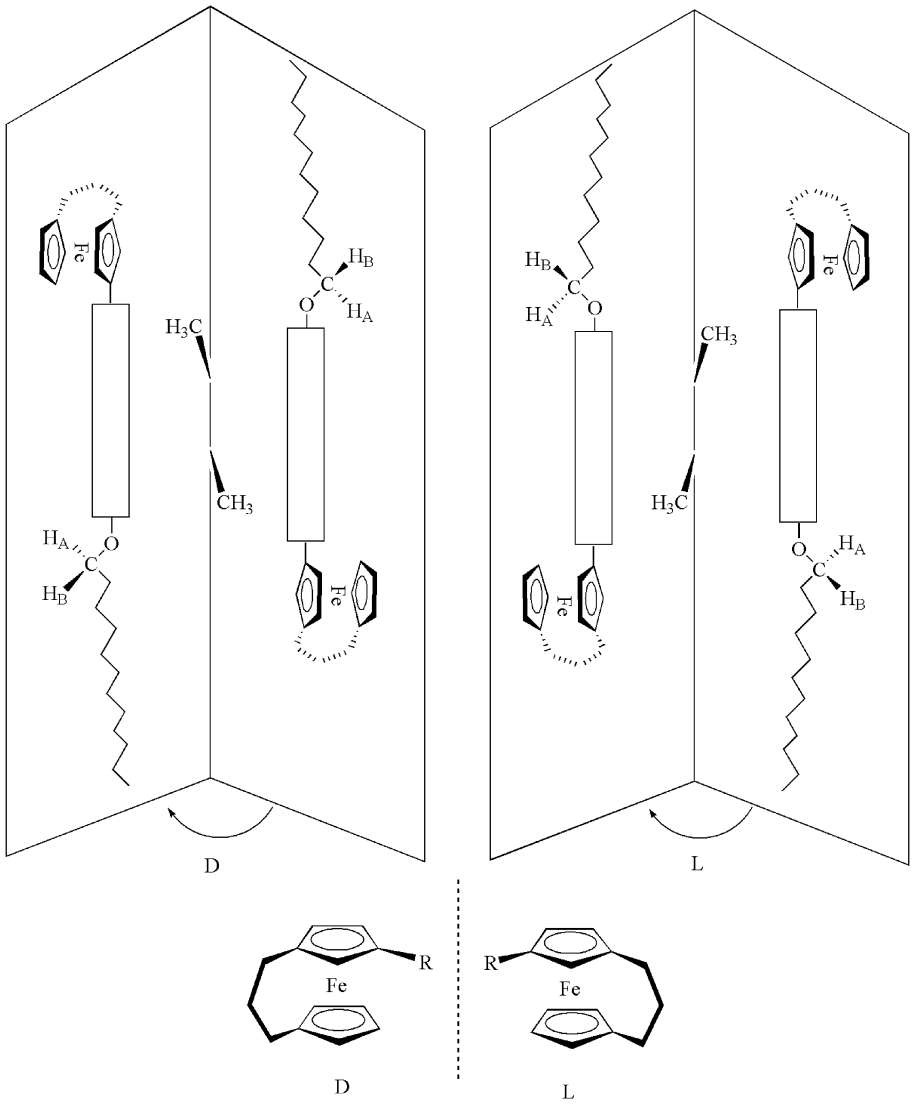


Figure 1. One of the possible enanthiomeric pairs in a roof-shaped structure of μ-acetato-bridged complexes **1a** and **1b**, which are conditionally designated here as LDL | DLD.

distinct NMR signals of the methyl groups in the acetato bridges, four distinct signals of the azomethine groups and four pairs of doublets for the aromatic AB system of a terminal 4-(dodecyloxy)benzoyl substituent. The appearance of the ^{1}H NMR signals described above is in accordance with four possible diastereomeric pairs ($2^n/2$, where n = the number of elements of chirality in a molecule) in **1b**. Contrary to **1a**, the influence of planar chirality of ferrocenophane substituents comes into effect in addition to the assymetry of a roof-shaped structure in the ^{1}H NMR spectrum of **1b**. Adding a bulky and polar phenyl carboxylic group significantly increases the overall asymmetry of a roof-shaped molecule, since the ferrocenophane-containing azomethine ligands obtain a more elongated structure. At the same time diastereotopic protons of the alkoxy chains (Ha and Hb, see Figure 1) become more distant from the elements of asymmetry so no splitting of the NMR signals for these protons was observed in **1b**.

According to their ^{1}H NMR spectra the μ-chloro-bridged palladium(II) complexes **2a** and **2b** have a planar structure with increased symmetry. There are no signal splittings for the methylene protons in the alkoxy chains of compound **2a** as compared with **1a**, and no such complex ^{1}H NMR patterns in **2b** as we observed in **1b**.

Two different chelates in mixed-ligand complexes from series **3** and **4** show a separate set of ^{1}H NMR signals for each ligand, which is in full agreement with the proposed structures. It is remarkable that in the case of complex **3b** the two ligands have only minimal differences. The palladium atom in one of the ligands is attached to an aromatic ring by a direct covalent bond with a carbon atom, and there is an oxygen atom between the palladium atom and a benzene ring in another ligand. Despite this distinction being rather small, two separate ligands are revealed in the ^{1}H NMR spectrum of compound **3b**.

Liquid Crystalline Properties

Complexes **1a** and **1b** did not exhibit mesomorphism, which is in agreement with the fact that liquid crystalline μ-acetato-bridged cyclopalladated complexes with azomethine ligands are thus far unknown. However, azine ligands do form mesogenic μ-acetato-bridged organopalladium dimers.[5c,5d] When the acetate anions were replaced by chloride ions the smectic A phase was observed in both compounds **2a** and **2b**. The mesophase was identified by characteristic focal-conic optical textures observed under a microscope between crossed polarisers. The phase transition temperatures were rather high in both compounds (see Table 2), especially in the case of the μ-chloro-bridged dimer **2b** with three benzene rings in a ligand rigid core, which is additionally extended by a cyclopentadienyl ring of a ferrocenophane fragment. In the latter case the mesophase was observed by placing a sample of the compound on a heating plate right before the mesophase transition to avoid longer exposure to high temperatures. The transition to the isotropic liquid state was accompanied by the decomposition of compounds **2a** and **2b**. The observed transition temperatures for the μ-chloro-bridged dimer **2a**, with two benzene rings in a ferrocenophane-containing ligand rigid core, are comparable with those for analogous μ-chloro-bridged organopalladium complexes with convenient organic azomethines.[6d,6e,6g] The thermal behaviour of the μ-chloro-bridged complexes **2a** and **2b** is consistent with their planar structure, when effective low-energy molecular packing can be realized in the solid state. In addition the presence of chloride ions contributes to further stabilization of the solid state by orthogonal interactions with palladium atoms of neighbouring molecules. Presumably the latter interactions also play a significant role in the packing of the μ-chloro-bridged dimer into smectic layers causing their smectic A mesomorphism. The ferrocenophane fragment undoubtedly has the effect of lowering the phase transition temperatures as could be seen for compounds **1a** and **1b**, which were compared with the analogous complexes containing the unbridged ferrocene.[2d]

Table 2. Thermooptical and thermodynamic data of phase transitions in palladium(II) complexes **1**–**4**. The dots symbolize temperature areas which are beyond phase-transition points.

	Crystal	T (ΔH) [°C] ([kJ/mol])	Mesophase type	T (ΔH) [°C] ([kJ/mol])	Isotropic liquid
1a	•	–	–	174 (40.0)	•
1b	•	–	–	205 (25.9)	•
2a	•	198 (47.5)	• SmA[a]	230 (–423.0[b])	•
2b	•	255[c]	• SmA	239[d] (–1395)	•
3a	•	71 (9.6)	• N[e]	148 (2.2)	•
3b	•	74 (11.1)	• N	205 (0.9)	•
4a	•	140 (32.0)	• N	148[f]	•
4b	•	148 (16.0)	• N	201 (2.1)	•

[a] Liquid crystalline phase of a smectic A type. [b] An exothermic peak revealed on the DSC curve from the decomposition of the compound. [c] Smectic A mesophase was observed with a polarisation optical microscope on the background of a decomposition process. [d] A complex exothermic peak on the DSC curve between 235 and 260 °C with a maximum at 239 °C. [e] Liquid crystalline phase of a nematic type. [f] The DSC peak of the isotropic transition is masked by the crystal–nematic transition peak.

All the compounds in both series **3** and **4** of the mixed-ligand palladium(II) complexes showed an enantiotropic nematic phase. Marbled and nematic schlieren optical textures were observed under a microscope between crossed polarizers. It is remarkable, that mesophase transition temperatures in this case were relatively low whereas most of the other known heteronuclear systems with ferrocene-containing ligands show high temperatures of the phase transitions.[2] Two factors undoubtedly play a significant role in lowering mesophase transition temperatures in the palladium(II) complexes **3** and **4**: (1) the presence of an alkylene bridge at the end of the ferrocenophane fragment of ligands; (2) and lowering of symmetry in the coordinational surroundings of the palladium atom. The significance of the latter is particularly noticeable when taking into account that the nematic transition temperature in compound **3b**, with minimal symmetry disturbance, is more than 100 °C lower than could be expected in comparison with the sym-

metric square-planar palladium chelates with a very similar shape and structural elements.[2c]

It is interesting to note that crystal-to-nematic transition temperatures, when **3a** is compared with **3b**, and **4a** with **4b**, have only small distinctions. At the same time their clearing points are substantially different (see Table 2). These complexes are differerent from each other by the length of a rigid core in only one of the ferrocenophane-containing azomethine ligands. Thus, greater anisotropy of polarizabilty when adding a phenylenecarboxyl unit into one of the azomethine ligands in complexes **3b** and **4b** causes a significant increase in the thermal stability of the nematic phase. The combination of the relatively low melting point with the higher clearing point in compound **3b** leads to a broad mesophase of 130 °C by width, which is outstanding for heteropolynuclear metallomesogens considering the presence of bulky ferrocene fragments in the molecule of the complex.

Conclusions

A new series of mesogenic heteropolynuclear organopalladium complexes has been synthesized using ferrocenophane-containing Schiff's bases and β-aminovinyl ketone as ligands. Smectic A and nematic mesophases were observed in the obtained compounds. It was demonstrated that using heteroannularly bridged ferrocene, and introducing symmetry disturbances into the palladium(II) coordinational surroundings, enables heteropolynuclear metallomesogens with enhanced liquid crystalline properties to be obtained.

Experimental Section

Materials and Instrumental Methods: Melting points were determined by the capillary method where applicable. Liquid crystalline properties were studied using the polarising optical microscope "Olympus BH-2" equipped with a heating stage HS1 (INSTEC) and remote temperature controller RTC1 (INSTEC). DSC analyses of the phase transitions were performed on the differential scanning calorimeter (TA instruments Q-10) at the scanning rate 5 °C/min. The temperatures of the phase transitions are given on the base of the DSC curves. IR spectra were recorded using a Perkin–Elmer Paragon 1000 instrument. UV and visible spectra in the region of 250–600 nm were recorded with the Lambda-14 (Perkin–Elmer) spectrophotometer in CH_2Cl_2. ^1H NMR spectra were measured with the ARX 300 (Bruker) spectrometer with TMS as internal standard. Dried and distilled solvents were used in all cases. Cyclopalladated complexes were synthesized by adapting the procedures developed by Baena et al. for azomethine ligands.[8d]

Complex 1a: Schiff's base $\mathbf{L_1H}$ (0.7067 g, 1.20 mmol) and palladium(II) acetate (0.2690 g, 1.20 mmol) in glacial acetic acid (15 mL) were stirred at 55 °C for 24 h. The precipitate of organopalladium complex **1a** was filtered, washed several times with cold acetone and dried. Yield 0.7296 g (81%) of brown powder. ^1H NMR (main product is the *trans* isomer; minor amount of *cis* isomer occurs) (300 MHz, $CDCl_3$, 25 °C): δ = 0.89 (t, 3 H, CH_3), 1.25–1.30, (m, 16 H, CH_2), 1.55–1.75 (m, 4 H, CH_2), 1.85 (s, 3 H, CH_3COO), 1.90–2.10 (m, 6 H, C_3H_6 bridge), 3.36 (m, 1 H, C_5H_3Fe), 3.52 (m, 1 H, CH_2O), 3.72 (m, 1 H, CH_2O), 3.89 (m, 1 H, C_5H_3Fe), 4.13 (m, 1 H, C_5H_3Fe), 4.18 (m, 2 H, C_5H_4Fe), 4.49 (m, 2 H, C_5H_4Fe), 6.03 (m, 1 H, C_6H_3Pd), 6.58 (m, 1 H, C_6H_3Pd), 6.66 (m, 2 H, C_6H_4), 7.13 (m, 1 H, C_6H_3Pd), 7.18 (m, 2 H, C_6H_4), 7.52 (s, 1 H, CH=N) ppm. IR (KBr): $\tilde{\nu}$ = 2922 (C–H), 2850 (C–H), 1605 (C=N), 1569, 1534, 1410, 1263, 1224, 1202, 1032, 840, 810, 685, 611, 513 cm^{-1}. $C_{80}H_{98}Fe_2N_2O_6Pd_2$ (1508.18): calcd. C 63.71, H 6.55, N 1.86; found C 63.56, H 6.58, N 1.82.

Complex 1b: Organopalladium complex **1b** was obtained in the same manner as complex **1a** from Schiff's base $\mathbf{L_2H}$ (0.6734 g, 0.95 mmol) and palladium(II) acetate (0.2132 g, 0.95 mmol) in glacial acetic acid (20 mL). Yield 0.6677 g (80%) of brown powder. ^1H NMR (main product is the *trans* isomer; minor amount of *cis* isomer occurs) (300 MHz, $CDCl_3$, 25 °C): δ = 0.89 (t, 6 H, CH_3), 1.25–1.30 (m, 36 H, CH_2), 1.45–1.65 (m, 4 H, CH_2), 1.74 (s, 3 H, CH_3COO), 1.76 (s, 3 H, CH_3COO), 1.80–2.00 (m, 12 H, C_3H_6 bridge), 3.28 (m, 2 H, C_5H_3Fe), 3.80 (m, 4 H, C_5H_4Fe), 4.02 (m, 4 H, CH_2O), 4.09 (m, 6 H, overlapped signals of C_5H_3Fe and C_5H_4Fe), 4.25 (m, 2 H, C_5H_3Fe), 6.03 (m, 1 H, C_6H_3Pd), 6.49 (d, 1 H, C_6H_3Pd), 6.90 (m, 4 H, C_6H_4), 7.00–7.10 (m, 6 H, overlapped signals of C_6H_4 and C_6H_3Pd), 7.10–7.20 (m, 4 H, C_6H_4), 7.28 (m, 2 H, C_6H_3Pd), 7.69 (s, 1 H, CH=N), 7.68 (s, 1 H, CH=N), 8.28 (m, 4 H, C_6H_4) ppm. IR (KBr): $\tilde{\nu}$ = 2922 (C–H), 2850 (C–H), 1728 (C=O), 1605 (C=N), 1567, 1509, 1413, 1256, 1233, 1162, 1067, 842, 763, 690, 648, 582, 511 cm^{-1}. $C_{94}H_{106}Fe_2N_2O_{10}Pd_2$ (1748.40): calcd. C 64.57, H 6.11, N 1.60; found C 64.81, H 6.08, N 1.56.

Complex 2a: A solution (1.3 M) of HCl in MeOH (0.35 mL, 0.45 mmol) was added dropwise to a stirred solution of the μ-acetato-bridged dimer **1a** (0.6054 g, 0.40 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was stirred for 12 h at room temperature and then carefully evaporated with a rotary vacuum evaporator from the solvents and small amounts of acetic acid generated from the reaction. The obtained residue was eluted by CH_2Cl_2 through a silica gel column. The eluate was concentrated and the μ-chloro-bridged complex **2a** was precipitated from a dichloromethane solution by adding ethanol, and then underwent further removal of the more volatile CH_2Cl_2. Yield 0.4210 g (75%) of orange powder. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.89 (t, 3 H, CH_3), 1.23–1.28, (m, 18 H, CH_2), 1.60–1.65 (m, 2 H, CH_2), 1.85–2.10 (m, 6 H, C_3H_6 bridge), 3.43 (m, 1 H, C_5H_3Fe), 3.89 (m, 3 H, overlapped signals of CH_2O and C_5H_3Fe), 4.14 (m, 1 H, C_5H_3Fe), 4.23 (m, 2 H, C_5H_4Fe), 4.51 (m, 2 H, C_5H_4Fe), 6.54 (m, 1 H, C_6H_3Pd), 6.80 (m, 1 H, C_6H_3Pd), 7.13–7.25 (m, 3 H, overlapped signals of C_6H_4 and C_6H_3Pd), 7.39 (m, 2 H, C_6H_4), 7.82 (s, 1 H, CH=N) ppm. IR (KBr): $\tilde{\nu}$ = 2920 (C–H), 2849 (C–H), 1605 (C=N), 1579, 1540, 1451, 1310, 1263, 1202, 1025, 840, 796, 585, 511 cm^{-1}. $C_{76}H_{92}Cl_2Fe_2N_2O_2Pd_2$ (1461.00): calcd. C 62.48, H 6.35, N 1.92; found C 62.55, H 6.31, N 1.89.

Complex 2b: The μ-chloro-bridged complex **2b** was prepared in the same manner as complex **2a** from complex **1b** (0.51 g, 0.29 mmol). Yield 0.3097 g (62%) of orange powder. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.90 (t, 3 H, CH_3), 1.25–1.35 (m, 16 H, CH_2), 1.40–1.52 (m, 2 H, CH_2), 1.81 (m, 2 H, CH_2CH_2O), 1.96 (m, 6 H, C_3H_6 bridge), 3.36 (m, 1 H, C_5H_3Fe), 3.77 (m, 1 H, C_5H_3Fe), 3.98 (m, 2 H, CH_2O), 4.08 (m, 3 H, overlapped signals of C_5H_3Fe and C_5H_4Fe), 4.44 (m, 2 H, C_5H_4Fe), 6.83 (d, 2 H, C_6H_4), 6.96 (m, 1 H, C_6H_3Pd), 7.09 (m, 1 H, C_6H_3Pd), 7.25 (m, 2 H, C_6H_4), 7.33 (m, 1 H, C_6H_3Pd), 7.39 (d, 2 H, C_6H_4), 7.95 (s, 1 H, CH=N), 7.98 (m, 2 H, C_6H_4) ppm. IR (KBr): $\tilde{\nu}$ = 2920 (C–H), 2850 (C–H), 1729 (C=O), 1606 (C=N), 1508, 1466, 1263, 1237, 1162, 1061, 839, 760, 580, 516 cm^{-1}. $C_{90}H_{100}Cl_2Fe_2N_2O_6Pd_2$ (1701.21): calcd. C 63.54, H 5.92, N 1.65; found C 63.78, H 5.87, N 1.59.

Complex 3a: Complex **2a** (0.0773 g, 0.053 mmol), Schiff's base $\mathbf{L_3H}$ (0.0768 g, 0.106 mmol) and potassium carbonate (≈0.2 g) were

stirred at room temperature for 24 h in dichloromethane (10 mL). The resulting mixture was filtered through Celite and the filtrate was concentrated with a rotary evaporator. The product was precipitated by adding ethanol to a concentrated solution, and dichloromethane was removed. Yield 0.1423 g (94.71%) of orange powder. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.89 (t, 3 H, CH_3), 0.89 (t, 3 H, CH_3), 1.23–1.33, 1.33–1.56 (m, 36 H, CH_2), 1.75–2.10 (m, 16 H, overlapped signals of C_3H_6 bridge and CH_2CH_2O), 3.32 (m, 2 H, CH_2O), 3.39 (m, 1 H, C_5H_3Fe), 3.48 (m, 1 H, C_5H_3Fe), 3.84 (m, 1 H, C_5H_3Fe), 3.90 (m, 1 H, C_5H_3Fe), 4.02 (t, 2 H, CH_2O), 4.11 (m, 1 H, C_5H_3Fe), 4.14 (m, 1 H, C_5H_3Fe), 4.17 (m, 2 H, C_5H_4Fe), 4.21 (m, 2 H, C_5H_4Fe), 4.47 (m, 2 H, C_5H_4Fe), 4.54 (m, 2 H, C_5H_4Fe), 5.49 (d, $J_{H,H}$ = 2.36 Hz, 1 H, C_6H_3Pd), 6.41 (m, 3 H, overlapped signals of C_6H_3OPd and C_6H_3Pd), 6.91 (d, $J_{H,H}$ = 9.00 Hz, 2 H, C_6H_4), 7.18 (d, $J_{H,H}$ = 8.37 Hz, 1 H, C_6H_3Pd), 7.23 (m, 1 H, C_6H_3OPd), 7.28 (d, $J_{H,H}$ = 8.65 Hz, 2 H, C_6H_4), 7.39 (d, $J_{H,H}$ = 8.66 Hz, 2 H, C_6H_4), 7.48 (2 overlapped d, $J_{H,H}$ = 8.66 Hz, $J_{H,H}$ = 8.65 Hz, 4 H, C_6H_4), 7.97 (s, 1 H, CH=N), 8.05 (s, 1 H, CH=N), 8.10 (d, $J_{H,H}$ = 9.00 Hz, 2 H, C_6H_4) ppm. IR (KBr): $\tilde{\nu}$ = 2920 (C–H), 2849 (C–H), 1731 (C=O), 1605 (C=N), 1577, 1517, 1433, 1312, 1251, 1199, 1166, 1149, 1118, 1059, 982, 840, 809, 764, 611, 512 cm^{-1}. $C_{83}H_{96}Fe_2N_2O_5Pd$ (1419.78): calcd. C 70.21, H 6.81, N 1.97; found C 69.95, H 6.76, N 2.01.

Complex 3b: Complex **3b** was prepared in the same manner as complex **3a** from the μ-chloro-bridged complex **2b** (0.0307 g, 0.018 mmol) and Schiff's base **L_3H** (0.0262 g, 0.036 mmol). Yield 0.0495 g (89%) of orange powder. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.89 (2 overlapped t, 6 H, CH_3), 1.25–1.43 (m, 32 H, CH_2), 1.43–1.54 (m, 4 H, CH_2), 1.78–1.87 (m, 4 H, CH_2CH_2O), 1.91–2.08 (m, 12 H, C_3H_6 bridge), 3.37 (m, 1 H, C_5H_3Fe), 3.48 (m, 1 H, C_5H_3Fe), 3.83 (m, 1 H, C_5H_3Fe), 3.86 (m, 1 H, C_5H_3Fe), 4.01 (2 overlapped t, 4 H, CH_2O), 4.05 (m, 1 H, C_5H_3Fe), 4.12 (m, 1 H, C_5H_3Fe), 4.14 (m, 1 H, C_5H_4Fe), 4.15 (m, 1 H, C_5H_4Fe), 4.17 (m, 2 H, C_5H_4Fe), 4.34 (m, 1 H, C_5H_4Fe), 4.38 (m, 1 H, C_5H_4Fe), 4.56 (m, 2 H, C_5H_4Fe), 5.43 (d, $J_{H,H}$ = 2.19 Hz, 1 H, C_6H_3Pd), 6.39 (d, $J_{H,H}$ = 2.30 Hz, 1 H, C_6H_3OPd), 6.42 [dd, $J_{H,H}$ (1) = 8.72 Hz, $J_{H,H}$ (2) = 2.30 Hz, 1 H, C_6H_3OPd], 6.79 (d, $J_{H,H}$ = 8.97 Hz, 2 H, C_6H_4), 6.81 [dd, $J_{H,H}$ (1) = 8.05 Hz, $J_{H,H}$ (2) = 2.19 Hz, 1 H, C_6H_3Pd] 6.91 (d, $J_{H,H}$ = 9.02 Hz, 2 H, C_6H_4), 7.23 (d, $J_{H,H}$ = 8.72 Hz, 1 H, C_6H_3OPd), 7.29 (d, $J_{H,H}$ = 8.62 Hz, 2 H, C_6H_4), 7.31 (d, $J_{H,H}$ = 8.05 Hz, 1 H, C_6H_3Pd), 7.35 (q of AB system, $J_{H,H}$ = 8.95 Hz, 4 H, C_6H_4), 7.49 (d, $J_{H,H}$ = 8.62 Hz, 2 H, C_6H_4), 7.80 (d, $J_{H,H}$ = 8.93 Hz, 2 H, C_6H_4), 8.04 (s, 1 H, CH=N), 8.09 (s, 1 H, CH=N), 8.09 (d, $J_{H,H}$ = 8.95 Hz, 2 H, C_6H_4) ppm. IR (KBr): $\tilde{\nu}$ = 2921 (C–H), 2850 (C–H), 1731 (C=O), 1605 (C=N), 1577, 1548, 1517, 1467, 1437, 1314, 1250, 1164, 1122, 1063, 1008, 983, 895, 842, 811, 762, 692, 632, 562, 513 cm^{-1}. $C_{90}H_{100}Fe_2N_2O_7Pd$ (1539.89): calcd. C 70.20, H 6.55, N 1.82; found C 70.43, H 6.52, N 1.80.

Complex 4a: μ-Chloro-bridged complex **2a** (0.0662 g, 0.045 mmol) and β-aminovinyl ketone **L_4H** (0.0572 g, 0.091 mmol) in CH_2Cl_2 (15 mL) were stirred for 24 h at room temperature in the presence of potassium carbonate (≈0.2 g). The resulting mixture was treated as described in the previous syntheses. Yield 0.1012 g (89%) of yellow powder. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.89 (t, 3 H, CH_3), 0.90 (t, 3 H, CH_3), 1.20–1.34 (m, 34 H, CH_2), 1.38–1.45 (m, 2 H, CH_2), 1.46–1.54 (m, 2 H, CH_2), 1.71–1.77 (m, 2 H, CH_2CH_2O), 1.86–2.13 (m, 12 H, C_3H_6 bridge), 3.29 (t, 2 H, CH_2O), 3.41 (m, 1 H, C_5H_3Fe), 3.49 (m, 1 H, C_5H_3Fe), 3.88 (t, 2 H, CH_2O), 3.89 (m, 1 H, C_5H_3Fe), 3.94 (m, 1 H, C_5H_3Fe), 4.10 (m, 1 H, C_5H_3Fe), 4.17 (m, 1 H, C_5H_3Fe), 4.20 (m, 2 H, C_5H_4Fe), 4.28 (m, 2 H, C_5H_4Fe), 4.44 (m, 2 H, C_5H_4Fe), 4.55 (m, 2 H, C_5H_4Fe), 5.59 (d, $J_{H,H}$ = 2.37 Hz, 1 H, C_6H_3Pd), 5.70 (d, $J_{H,H}$ = 7.05 Hz, 1 H, CH=CH), 6.42 [dd, $J_{H,H}$ (1) = 2.37 Hz, $J_{H,H}$ (2) = 8.35 Hz, 1 H, C_6H_3Pd], 6.69 (d, $J_{H,H}$ = 9.01 Hz, 2 H, C_6H_4), 7.18 (d, $J_{H,H}$ = 8.35 Hz, 1 H, C_6H_3Pd), 7.28 (d, $J_{H,H}$ = 9.01 Hz, 2 H, C_6H_4), 7.29 (d, $J_{H,H}$ = 8.63 Hz, 2 H, C_6H_4), 7.33 (d, $J_{H,H}$ = 8.69 Hz, 2 H, C_6H_4), 7.36 (d, $J_{H,H}$ = 8.69 Hz, 2 H, C_6H_4), 7.46 (d, $J_{H,H}$ = 7.05 Hz, 1 H, CH=CH), 7.47 (d, $J_{H,H}$ = 8.63 Hz, 2 H, C_6H_4), 8.01 (s, 1 H, CH=N) ppm. IR (KBr): $\tilde{\nu}$ = 2922 (C–H), 2850 (C–H), 1603 (C=N), 1578, 1559, 1542, 1519, 1492, 1466, 1438, 1402, 1345, 1247, 1194, 1171, 840, 810, 764, 514 cm^{-1}. $C_{78}H_{94}Fe_2N_2O_3Pd$ (1325.71): calcd. C 70.67, H 7.15, N 2.11; found C 70.74, H 7.19, N 2.09.

Complex 4b: The reaction of μ-chloro-bridged complex **2b** (0.1200 g, 0.070 mmol) and β-aminovinyl ketone **L_4H** (0.0890 g, 0.141 mmol), carried out in the same manner as that for complex **4a**, afforded the mixed-ligand complex **4b**. Yield 0.1775 g (87%) of light-orange powder. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.89 (2 overlapped t, 6 H, CH_3), 1.25–1.36 (m, 34 H, CH_2), 1.70–1.78 (m, 2 H, CH_2CH_2O), 1.78–1.87 (m, 2 H, CH_2CH_2O), 1.88–2.12 (m, 12 H, C_3H_6 bridge), 3.37 (m, 1 H, C_5H_3Fe), 3.49 (m, 1 H, C_5H_3Fe), 3.84 (m, 1 H, C_5H_3Fe), 3.88 (t, 2 H, CH_2O), 3.94 (m, 1 H, C_5H_3Fe), 4.00 (t, 2 H, CH_2O), 4.01 (m, 1 H, C_5H_3Fe), 4.14 (m, 2 H, C_5H_4Fe), 4.18 (m, 1 H, C_5H_4Fe), 4.28 (m, 2 H, C_5H_4Fe), 4.32 (m, 1 H, C_5H_4Fe), 4.36 (m, 1 H, C_5H_4Fe), 4.56 (m, 2 H, C_5H_4Fe), 5.45 (d, $J_{H,H}$ = 2.18 Hz, 1 H, C_6H_3Pd), 5.70 (d, $J_{H,H}$ = 6.98 Hz, 1 H, CH=CH), 6.69 (d, $J_{H,H}$ = 8.99 Hz, 2 H, C_6H_4), 6.77 (d, $J_{H,H}$ = 9.01 Hz, 2 H, C_6H_4), 6.83 [dd, $J_{H,H}$ (1) = 2.18 Hz, $J_{H,H}$ (2) = 8.11 Hz, 1 H, C_6H_3Pd], 7.28–7.32 (overlapped m, 8 H, C_6H_4), 7.32 (d, $J_{H,H}$ = 8.11 Hz, 1 H, C_6H_3Pd), 7.29 (d, $J_{H,H}$ = 8.63 Hz, 2 H, C_6H_4), 7.33 (d, $J_{H,H}$ = 8.69 Hz, 2 H, C_6H_4), 7.36 (d, $J_{H,H}$ = 8.69 Hz, 2 H, C_6H_4), 7.45 (d, $J_{H,H}$ = 6.98 Hz, 1 H, CH=CH), 7.49 (d, $J_{H,H}$ = 8.63 Hz, 2 H, C_6H_4), 7.80 (d, $J_{H,H}$ = 9.01 Hz, 2 H, C_6H_4), 8.13 (s, 1 H, CH=N) ppm. IR (KBr): $\tilde{\nu}$ = 2922 (C–H), 2850 (C–H), 1733 (C=O), 1604 (C=N), 1586, 1559, 1517, 1492, 1466, 1436, 1401, 1345, 1247, 1163, 1069, 841, 812, 763, 514 cm^{-1}. $C_{85}H_{98}Fe_2N_2O_5Pd$ (1445.82): calcd. C 70.61, H 6.83, N 1.94; found C 70.83, H 6.77, N 1.92.

Supporting Information (see also the footnote on the first page of this article): DSC curves of compounds **1**–**4** are shown in Figures S1–S8. Examples of liquid crystalline textures observed under a polarization microscope are represented by Figures S9 and S11. ^{1}H NMR patterns of **1**–**4** are shown in Figures S12–S18. Explanations are given for the appearance of ^{1}H NMR signals for the diastereotopic protons in **1a**, and for the signals of four different diastereomeric pairs in **1b**.

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