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Dinuclear *ortho*-Metallated Palladium(II) Complexes with Acetato and Chloro Bridges as Liquid Crystals

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In this article we present the preparation and the investigation of the liquid crystal properties of a series of dinuclear acetato- and chloro-bridged ortho-metallated Pd(II) complexes bearing six alkoxy peripheral chains in the molecule. Their structures were assigned based on elemental analysis, Infrared (IR), and ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, whereas the thermal behavior was investigated by polarizing optical microscopy and differential scanning calorimetry. All these complexes show mesomorphic behavior with smectic A phases being displayed. The acetato complexes exhibit a monotropic smectic A phase with transition temperatures from the isotropic state depending on the alkyl chain lengths, whereas the chloro complexes decompose on melting from the crystalline state to an SmA phase.

Keywords Liquid crystals; metallomesogens; orthometallation; palladium; smectic

Introduction

Liquid-crystalline materials that contain metal ions (metallomesogens) are typical examples where the unique properties of anisotropic fluids are combined with the specific properties of metals such as color, polarizability, and electrical and magnetic properties. The organometallic compounds of palladium(II) based on *ortho*-metallated complexes with imine ligands have been extensively studied, in particular due to the design flexibility and possibility of varying their chemical and physical properties by systematic change of the ligands around the palladium ion. These type of complexes are thermally stable and consist of both dinuclear and mononuclear organometallic species [1,2]. The dinuclear *ortho*-metallated palladium(II) complexes show various liquid-crystalline phases depending on the number of peripheral chains and the nature of the bridging group. Previous studies on the dinuclear acetato-bridged Pd(II) complexes with four peripheral chains revealed

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the absence of mesomorphism, because the acetate bridge was found to be ineffective in promoting mesomorphism in such systems, in particular due to the formation of nonplanar complexes [3–5]. On the other hand, it is well known that the analogous dimeric chloro compounds with *ortho*-palladated imine with two long alkyl chains form smectic A and C phases at high temperatures [6].

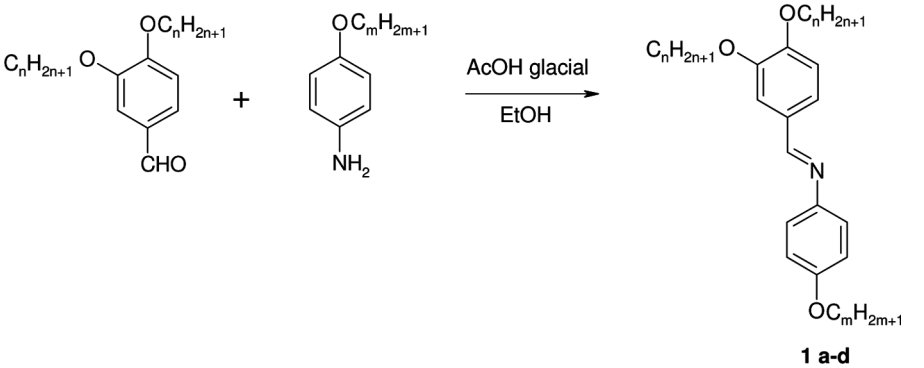
Additional chains in the molecule produce more disc-like shape. Thus, whereas the dinuclear μ-chloro-bridged palladium *ortho*-metallated complexes with six peripherial chains show smectic A and C phases [7], the related compounds with eight alkyl chains, due to their sheet-like shape, show a nematic discotic mesophase [8].

We were interested to study the influence of the nature of the bridging group as well as the alkyl chain length on the mesomorphic behavior of dinuclear palladium(II) complexes with six peripherial alkoxy chains with the aim of extending our previous studies on organometallic palladium(II) complexes with imine ligands, including a thermally stimulated depolarization currents (TSDC) method [9–11]. In this article we present the synthesis, characterization, and the liquid-crystalline phase behavior of six novel palladium mesogens that contain six alkoxy chains in the molecule and acetato or chloro bridges.

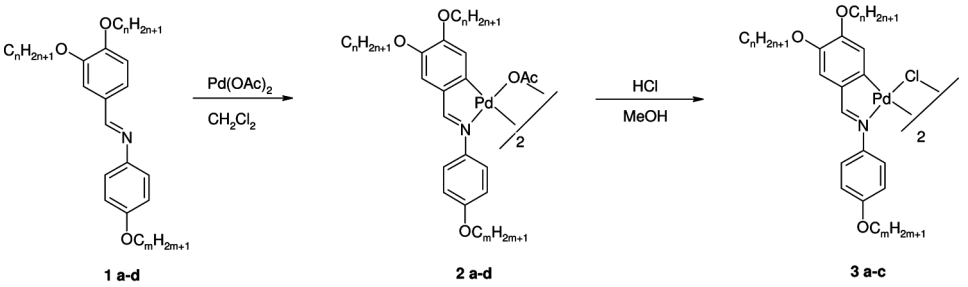
Results and Discussion

The synthetic pathway used to prepare the imine ligands and the palladium(II) complexes is depicted in Schemes 1 and 2. The dinuclear acetato-bridged palladium complex **2** was obtained by the *ortho*-palladation reaction of the imine **1**, by using palladium(II) acetate, with good yields. The crude product obtained by the *ortho*-metallation of imine **1** with palladium acetate was used in the next step without further purification, by reacting it with HCl in methanolic solution in order to prepare the chloro-bridged analogue **3**. The new complexes were characterized by elemental analysis, Infrared (IR), and ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, whereas their liquid-crystal properties were investigated by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM).

These dinuclear complexes can show both *cis* and *trans* isomers depending on how the nitrogen atoms are positioned in respect to the bridge, although, in general, the acetato- and chloro-bridged palladium(II) systems were found to exist as single *trans* compounds. The ^{1}H NMR spectra indicate the presence of only one isomer in solution by the presence of only one set of signals. This can be observed, in



Scheme 1. Preparation of the imine ligands.



a: m = 6, n = 8
b: m = 6, n = 10
c: m = 8, n = 8
d: m = n = 10

Scheme 2. Preparation of dinuclear Pd(II) *ortho*-metallated complexes.

particular, for the iminic proton and for the two singlets assigned to the aromatic protons of the Pd-substituted phenyl ring.

Thermal Behavior

The DSC data and the type of mesophases observed by microscopy are presented in Table 1.

Table 1. Thermal data for dinuclear palladium(II) complexes

Compound	Transition	T (°C)	ΔH (kJ mol^{-1})
1a	Cr-Cr′	35	22.3
	Cr-I	68	48.1
1b	Cr-Cr′	57	36.1
	Cr-I	74	57.6
1c	Cr-I	64	46.7
1d	Cr-I	74	
2a	Cr-I	79	56.3
	(I-SmA)	(76)	(4.8)
2b	Cr-Cr′	50	20.9
	Cr′-I	88	18.0
	(I-SmA)	(70)	(5.6)
2c	Cr-Cr′	76	50.3
	Cr′-Cr′	96	32.4
	Cr′-I	109	26.1
	(I-SmA)	(74)	(5.9)
2d	Cr-I	110	64.8
	(I-SmA)	(75)	(4.3)
3a	Cr-Cr′	111	40.7
	Cr′-SmA(dec.)	175	33.7
3b	Cr-SmA(dec.)	152	42.7
3c	Cr-Cr′	108	45.8
	Cr′-SmA(dec.)	177	36.2

The imine ligands with three alkoxy chains used as ligands do not show any liquid crystal properties and they melt from the crystalline phase straight to the isotropic liquid (**1a**: Cr-I, 74°C, **1b**: Cr-I, 73°C, **1c**: Cr-I, 71°C).

Both acetate- and chloro-bridged dinuclear palladium(II) complexes with six alkoxy chains show mesomorphic behavior. The acetato complexes exhibit a monotropic smectic A phase that could be detected easily by the typical separation as battonets from the isotropic liquid and by the fan-like texture, which can be aligned homeotropically (Figs. 1 and 2) [12], whereas the chloro complexes show extensive decomposition on melting from the crystalline state to the SmA phase. An interesting thermal behavior is seen for complex **2c,** which exhibits three succesive crystalline phases on the first heating run (Fig. 3a). On cooling, the transition to the smectic phase at 74°C is accompanied by a glass transition followed on the next heating run by crystallization and only one crystalline phase (Fig. 3b).

The transition temperatures are significantly lower for the acetato-bridged complexes compared to their chloro-bridged analogues, and this mesophase destabilization can be attributed to the nonplanarity of the molecules induced by the acetate ion. On the other hand, the introduction of an additional alkoxy group on the imine ligand has a great effect on promoting the mesomorphic behavior. There is a clear tendency of increasing the melting points of the acetato complexes with the increase in chain length either on the Pd-substituted ring or on the aniline ring of the imine ligand. However, the temperature of the I-SmA transition does not follow the same trend. The shortest chain homologue, **2a**, shows the highest temperature of

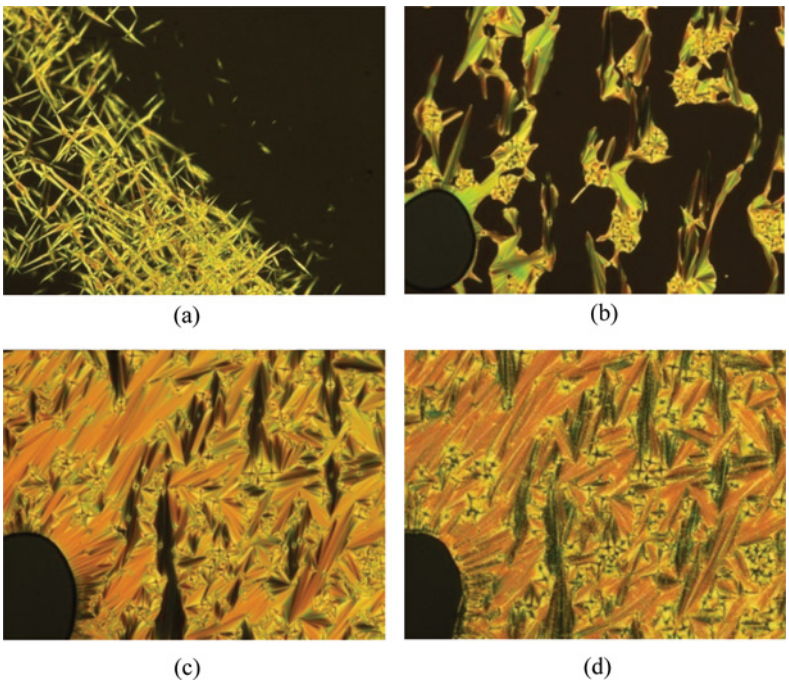


Figure 1. Optical microphotographs of compound **2a** (200×): transition from isotropic liquid to the SmA phase, separation of battônets from isotropic liquid (a) SmA phase at 76°C (b) fan-shaped texture of the SmA phase at 67°C (c) and crystallisation occurs below 40°C (d).

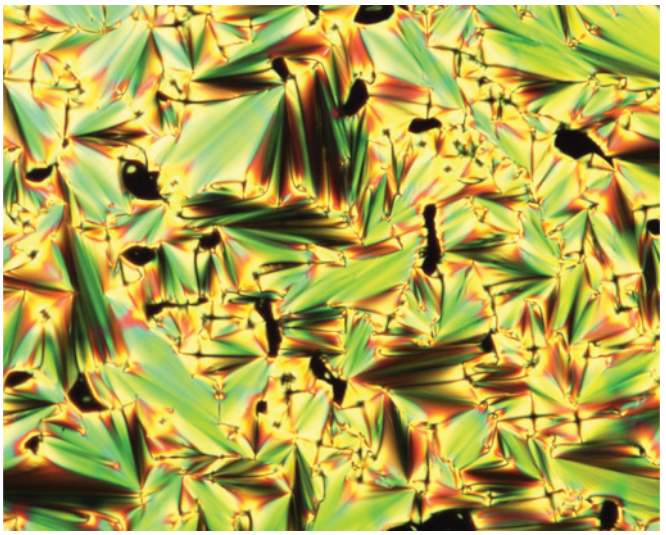


Figure 2. The fan-shaped texture of the SmA phase of complex **2b** at 67°C.

the I-SmA transition; increasing the chain lengths of the alkoxy groups on the Pd-substituted ring leads to a decrease of 6°C of this transition, whereas the increase of the alkoxy chain length of the aniline ring produces only a 2°C decrease; when all alkoxy groups, both on the Pd-substituted ring and on the aniline ring, are substituted with decyloxy groups, the I-SmA is almost unchanged compared to the shortest analogue. The temperatures corresponding to the Cr-SmA transition of the chloro-bridged palladium complexes bearing six alkoxy chains are higher than the temperatures reported for the chloro-bridged palladium(II) complex with four decyloxy chains and two hexyl chains, previously reported in the literature, but this fact can be explained by the presence of two alkyl chains on the aniline rings instead of alkoxy chains in the latter case [7].

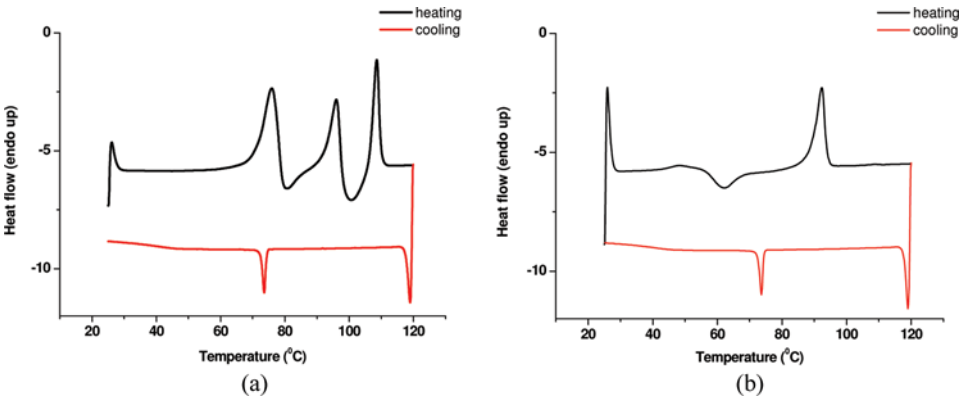


Figure 3. DSC thermogram of compound **2c** showing the first (a) and second (b) heating and cooling cycles.

Experimental

Dichloromethane was distilled from phosporus pentoxide; other chemicals were used as supplied (Merck). The IR spectra were recorded using a BioRad FTS-135 spectrometer. Proton and carbon NMR spectra were recorded on a Bruker DFX spectrometer (Sigma-Aldrich) operating at 270 MHz, using $CDCl_3$ as solvent. ^1H chemical shifts were referenced to the solvent peak position, δ 7.26.

Transition temperatures were measured using A Linkam THMS600 hot stage and a TMS94 temperature controller attached to a Nikon 50i Pol polarizing microscope. These temperatures were confirmed by differential scanning calorimetry (Perkin-Elmer Diamond instrument using 10°C/min or 5°C/min heating rate). Two or more heating/cooling cycles were performed on each sample. The mesophases were assigned by their optical texture.

Synthesis of Imine Ligands 1

The imine ligands were prepared by the condensation reaction between the corresponding aldehydes and anilines, catalyzed by glacial acetic acid, in absolute ethanol. The preparation of **1b** is presented below. To a solution of *p*-hexyloxyaniline (0.193 g, 1 mmol) in ethanol (10 ml), 3,4-didecyloxybenzaldehyde (0.387 g, 1 mmol) followed by five drops of glacial acetic acid was added. The mixture was heated under reflux for 2 h and then cooled to −25°C to give the crude product. Recrystallization from hot ethanol gave the analytically pure product as off-white crystals. The preparation and characterization of **1a** and **1d** were reported elsewhere [11,13].

Compound 1b. Yield 47%, off-white crystals, m.p. 73°C. Anal. Calc. for $C_{39}H_{63}NO_3$: C, 78.9; H, 10.7; N, 2.4; Found: C, 78.7; H, 11.0; N, 2.1. ^1H NMR (300 MHz, $CDCl_3$): 8.35 (s, 1H, CH=N), 7.60 (d, broad, 1H), 7.27 (dd, $J = 1.8$ Hz and $J = 8.3$ Hz, 1H), 7.19 (AA′XX′ system, $J = 8.9$ Hz, 2H aniline ring), 6.91 (d, $J = 8.9$ Hz, 2H, aniline ring), 4.12–4.03 (m, 4H, $2OCH_2$ groups), 3.97 (t, $J = 6.5$ Hz, 2H, OCH_2), 1.90–1.25 (m, 40H, CH_2 groups), 0.95–0.85 (m, 9H, CH_3 groups). ^{13}C NMR: 158.0, 157.4, 151.8, 149.3, 129.5, 123.7, 121.9, 114.8, 112.4, 111.1, 69.0, 68.2, 31.7, 29.1, 29.0, 25.9, 22.5, 14.0. IR (cm^{-1}): 2926 vs, 2856 s, 1621 m, 1599 m, 1574 m, 1513 vs, 1468 m, 1432 m, 1391 m, 1293 m, 1266 vs, 1243 vs, 1168 w, 1135 m, 1024 m, 870 w, 831 s, 723 w, 617 w.

Compound 1c. Yield 55%, off-white crystals, m.p. 64°C. Anal. Calc. for $C_{37}H_{59}NO_3$: C, 78.5; H, 10.5; N, 2.5; Found: C, 78.1; H, 10.9; N, 2.3. ^1H NMR (300 MHz, $CDCl_3$): 8.36 (s, 1H, CH=N), 7.57 (d, broad, 1H), 7.26 (dd, $J = 1.8$ Hz and $J = 8.3$ Hz, 1H), 7.19 (AA′XX′ system, $J = 8.8$ Hz, 2H aniline ring), 6.91 (AA′XX′ system, $J = 8.8$ Hz, 2H, aniline ring), 4.12–4.03 (m, 4H, $2OCH_2$ groups), 3.97 (t, $J = 6.6$ Hz, 2H, OCH_2 group), 1.90–1.25 (m, 36H, CH_2 groups), 0.95–0.85 (m, 9H, CH_3 groups). ^{13}C NMR: 158.0, 157.4, 151.8, 149.3, 129.5, 123.7, 121.9, 114.8, 112.4, 111.1, 69.0, 68.2, 31.7, 29.1, 25.9, 22.5, 14.0. IR (cm^{-1}): 2956 s, 2922 vs, 2851 s, 1623 m, 1601 m, 1577 m, 1511 vs, 1467 m, 1433 m, 1390 m, 1267 vs, 1237 vs, 1170 w, 1136 m, 1017 m, 866 w, 830 s, 723 w, 614 w.

Synthesis of Acetato-Dinuclear Palladium(II) Complexes 2a-c

The following is the typical procedure for acetato-bridged palladium dinuclear complexes. The imine ligand (2.5 mmol) was dissolved in dichloromethane (30 ml)

and palladium acetate (0.83 mmol) was added. The resulting mixture was stirred at room temperature for 18 h, after which the solvent was removed in vacuo. The residue was crystallized from a mixture of dichloromethane–ethanol several times to give the yellow crystalline products, which were washed with cold ethanol and dried under vacuum. The preparation and characterization of **2d** was reported elsewhere [11]. The yields and elemental analysis results are presented below. The ^{1}H and ^{13}C NMR spectra are identical for the three Pd(II) complexes, except the different integration values corresponding to the signals in the 1.52–1.24 ppm region of the ^{1}H NMR spectra, assigned to hydrogens form the alkoxy chains of imine ligands.

Compound 2a. Yield 63%, yellow crystals. Anal. Calc. for $C_{74}H_{114}N_2O_{10}Pd_2$: C, 63.3; H, 8.2; N, 2.0; Found: C, 63.0; H, 8.5; N, 1.8. ^{1}H NMR (300 MHz, $CDCl_3$): 7.43 (s, 1H, HC=N), 6.82 (s, 1H, Pd-substituted phenyl ring), 6.65 (q, $J = 7.0$ Hz, 4H, aniline ring), 5.99 (s, 1H, Pd-substituted phenyl ring), 3.99–3.45 (m, 6H), 1.89 (s, 3H, CH_3 acetate group), 1.78 (m, 6H), 1.52–1.24 (m, 26H), 0.95–0.85 (m, 9H). ^{13}C NMR: 180.2, 170.1, 158.1, 151.1, 150.7, 145.7, 141.3, 136.8, 124.0, 115.6, 114.3, 113.5, 70.8, 68.3, 32.0, 29.5, 26.3, 24.3, 22.8, 14.3. IR (cm^{-1}): 2927 vs, 2856 s, 1654 m, 1597 s, 1517 vs, 1453 m, 1291 vs, 1259 s, 1186 m, 1149 m, 1058 w, 1019 w, 832 w, 723 w.

Compound 2b. Yield 71%, yellow crystals. Anal. Calc. for $C_{82}H_{130}N_2O_{10}Pd_2$: C, 64.9; H, 8.6; N, 1.8; Found: C, 64.5; H, 8.9; N, 1.6.

Compound 2c. Yield 68%, yellow crystals. Anal. Calc. for $C_{78}H_{122}N_2O_{10}Pd_2$: C, 64.1; H, 8.4; N, 1.9; Found: C, 63.8; H, 8.8; N, 1.6.

Synthesis of Chloro-Dinuclear Palladium(II) Complexes 3a-c

In the case of chloro-bridged dinuclear palladium(II) complex, the corresponding acetato-bridged complex was used in the next step without further purification. Thus, the crude product obtained as previously described was treated with 1 mL of HCl in 10 mL of methanol. The mixture was further stirred for 8 h, after which the solvent was removed in vacuo. The residue was crystallized several times from a mixture of dichloromethane–ethanol to give the yellowish-brown crystalline chloro-bridged dinuclear palladium(II) complexes. The yields, elemental analysis results, as well as ^{1}H and ^{13}C NMR data are presented below.

Compound 3a. Yield 47%, yellow-brown crystals. Anal. Calc. for $C_{70}H_{108}Cl_2N_2O_6Pd_2$: C, 63.7; H, 8.5; N, 1.9; Found: C, 63.5; H, 9.0; N, 1.6.^{1}H NMR (300 MHz, $CDCl_3$): 8.15 (s, 1H, HC=N), 8.00 (s, 1H, Pd-substituted phenyl ring), 7.97 (s, 1H, Pd-substituted phenyl ring), 6.97 (AA′XX′ system, $J = 8.8$ Hz, 2H aniline ring), 6.87 (AA′XX′ system, $J = 8.8$ Hz, 2H aniline ring), 4.42 (m, 2H, OCH_2), 4.07 (t, $J = 6.6$ Hz, 2H, OCH_2), 3.87 (t, $J = 6.3$ Hz, 2H, OCH_2), 1.95–1.20 (m, 32H, CH_2 groups), 0.94–0.86 (m, 9H, CH_3 groups).^{13}C NMR: 160.4, 158.3, 150.1, 145.2, 129.6, 122.5, 119.4, 115.7, 113.8, 112.3, 70.4, 69.7, 68.6, 32.0, 29.5, 29.0, 26.4, 26.1, 22.8, 14.2. IR (cm^{-1}): 2925 vs, 2857 s, 1653 m, 1599 s, 1515 vs, 1466 m, 1450 m, 1392 w, 1285 vs, 1253 s, 1180 m, 1148 s, 1012 w, 832 w, 810 w, 722 w.

Compound 3b. Yield 40%, yellowish-brown crystals. Anal. Calc. for $C_{78}H_{124}Cl_2N_2O_6Pd_2$: C, 63.7; H, 8.5; N, 1.9; Found: C, 63.3; H, 9.0; N, 1.7. ^{1}H NMR

(300 MHz, $CDCl_3$): 8.16 (s, 1H, HC=N), 7.95 (s, 1H, Pd-substituted phenyl ring), 7.92 (s, 1H, Pd-substituted phenyl ring), 6.97 (AA′XX′ system, $J = 8.5$ Hz, 2H aniline ring), 6.90 (AA′XX′ system, $J = 8.8$ Hz, 2H aniline ring), 4.23 (m, 2H, OCH_2), 4.09 (t, $J = 6.8$ Hz, 2H, OCH_2), 3.91 (t, $J = 6.6$ Hz, 2H, OCH_2), 1.97–1.20 (m, 40H, CH_2 groups), 0.92–0.87 (m, 9H, CH_3 groups). ^{13}C NMR: 160.4, 158.3, 150.1, 145.2, 129.6, 122.5, 119.4, 115.7, 113.8, 112.3, 70.4, 69.7, 68.6, 32.0, 29.5, 29.0, 28.8, 26.4, 26.1, 22.8, 14.2. IR (cm^{-1}): 2926 vs, 2857 s, 1653 m, 1599 s, 1515 vs, 1466 m, 1449 m, 1392 w, 1285 vs, 1253 s, 1179 m, 1148 s, 1015 w, 832 w, 807 w, 722 w.

Compound 3c. Yield 52%, yellow-brown crystals. Anal. Calc. for $C_{74}H_{116}Cl_2N_2O_6Pd_2$: C, 62.9; H, 8.3; N, 2.0; Found: C, 62.4; H, 8.8; N, 1.7. ^{1}H NMR (300 MHz, $CDCl_3$): 8.19 (s, 1H, HC=N), 7.99 (s, 1H, Pd-substituted phenyl ring), 7.96 (s, 1H, Pd-substituted phenyl ring), 6.97 (AA′XX′ system, $J = 8.8$ Hz, 2H aniline ring), 6.88 (AA′XX′ system, $J = 8.8$ Hz, 2H aniline ring), 4.41 (m, 2H, OCH_2), 4.08 (t, $J = 6.6$ Hz, 2H, OCH_2), 3.89 (t, $J = 6.3$ Hz, 2H, OCH_2), 1.95–1.20 (m, 36H, CH_2 groups), 0.94–0.86 (m, 9H, CH_3 groups). ^{13}C NMR: 160.4, 158.4, 150.1, 145.2, 129.6, 122.5, 119.4, 115.7, 113.8, 112.2, 70.5, 69.7, 68.6, 32.0, 29.5, 29.0, 26.4, 26.1, 22.8, 14.2. IR (cm^{-1}): 2926 vs, 2858 s, 1653 m, 1599 s, 1515 vs, 1470 m, 1449 m, 1392 w, 1285 vs, 1253 s, 1180 m, 1148 s, 1015 w, 830 w, 807 w, 722 w.

Conclusions

The imines **1a-c** with three alkoxy chains used as ligands do not show any liquid-crystalline properties. Increasing the alkoxy chain lengths, either at the aniline or benzaldehyde unit, leads to a decrease of transition temperatures, higher in the case of increasing the two alkoxy chains lengths from the benzaldehyde phenyl ring. The stability of the SmA phase is higher for chloro-bridged Pd(II) complexes compared to their acetate-bridged analogues. It is clear that the mesogenic behavior of acetato-bridged *ortho*-metallated Pd(II) complexes is destabilized due to the promotion of nonplanarity in such complexes leading to monotropic mesogenic behavior.

Acknowledgments

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