

# Ferroelectric Metallomesogenic Palladium(II) Complexes Derived from Bidentate Schiff Bases

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The synthesis and characterization of four new chiral palladium(II) complexes ( $\text{PdL}_2$ ) derived from chiral Schiff bases of the ligands (L) are reported. The complexes are of the type  $\{\text{Pd}\{-4-(\text{C}_{n\text{H}_{2n+1}\text{O})C}_6\text{H}_3(\text{O})\text{CH}=\text{NC}_6\text{H}_4\text{ZR}^*\}_2\}$ , where  $n = 5, 10$ ;  $\text{Z} = -\text{CH}=\text{CHCOO}-, -\text{COO}-, -\text{O}-$ ;  $\text{R}^* = -\text{C}^*\text{H}(\text{CH}_3)\text{COOC}_4\text{H}_9$ . The mesogenic properties of both ligands and complexes have been studied by DSC and optical microscopy. Although only two of the ligands exhibited mesogenic properties, all of the complexes were liquid crystals. Some of these materials display the potentially chiral ferroelectric smectic C phase in addition to a smectic A or cholesteric mesophase. The spontaneous polarization ( $P_s$ ) values were measured in the pure compounds. The values obtained are in the range of 40–98 nC/cm<sup>2</sup>. The relationship between molecular structure and ferroelectric properties is investigated.

## Introduction

The synthesis of liquid-crystalline compounds incorporating transition metals is of considerable interest,<sup>1,2</sup> and our group has published a number of papers on the subject.<sup>3</sup> To date the typical ferroelectric liquid crystals that have been described are chiral rodlike organic molecules.<sup>4</sup> However, recently, we have described a ferroelectric liquid-crystal material consisting of an ortho-palladated azine dimer complex where the chirality is introduced by means of chiral carboxylate bridges<sup>5</sup> (Figure 1a) and paramagnetic ferroelectric liquid crystals of copper(II) and oxovanadium(IV) complexes derived from a chiral Schiff base<sup>6</sup> (Figure 1b). Interest in the preparation of materials showing chiral smectic C phases over the past few years, apart from their ferroelectric properties, is in their potentially nonlinear optical (NLO) properties.<sup>7</sup> Ferroelectric metallomesogens are good materials for NLO studies due to the fact that the high electron density of

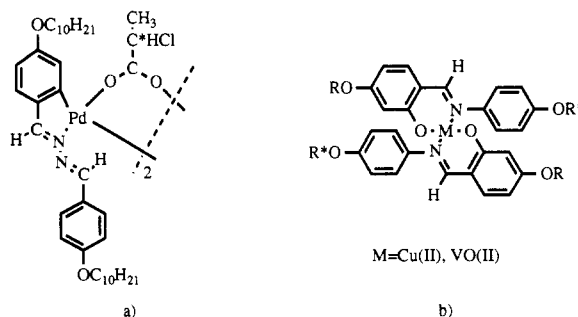
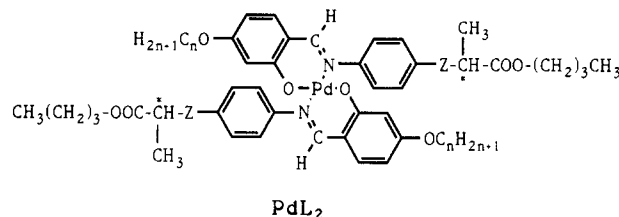


Figure 1.



Compound	Z	n
Pd-5-A	-CH=CH-COO-	5
Pd-10-A	-CH=CH-COO-	10
Pd-10-B	-COO-	10
Pd-10-C	-O-	10

Figure 2. Complexes synthesized.

the metallic center may lead to an increase in polarizability and high birefringence, and under the right conditions these complexes may exhibit a NLO response.<sup>8</sup>

In this paper we present the synthesis of chiral liquid-crystal palladium(II) complexes ( $\text{PdL}_2$ ) using bidentate chiral Schiff bases as ligands with the general structure shown in Figure 2.

We also have studied the influence of different types of aromatic anilines on the mesogenic behavior of the chiral

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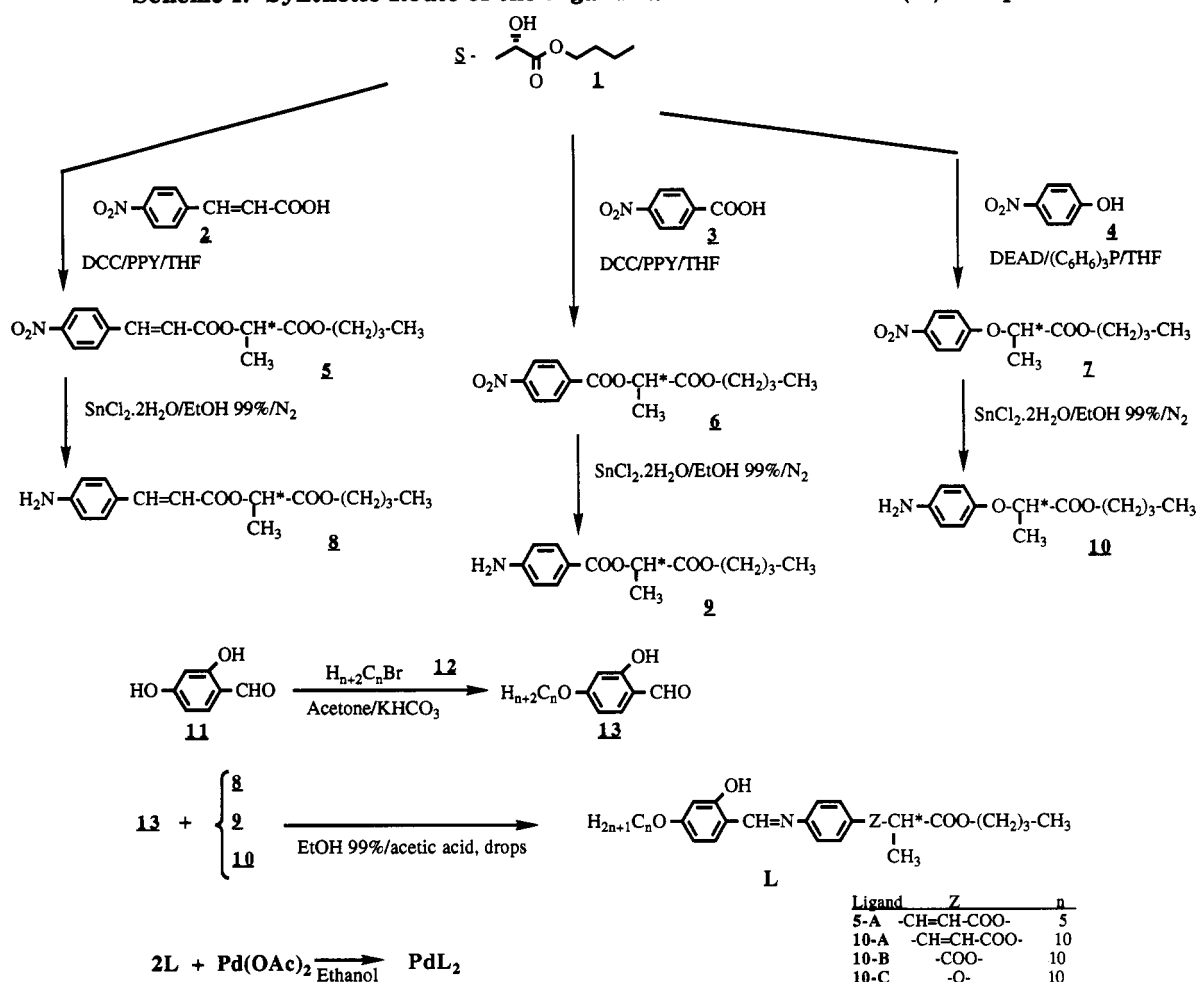
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Scheme I. Synthetic Route of the Ligands and of the Palladium(II) Complexes



complexes and the ligands. Some physical studies of these materials were carried out in order to establish their ferroelectric character. These studies are designed to determine the spontaneous polarization of the complexes and their response time.

### Experimental Section

**Synthesis.** The synthetic route used to prepare the ligands and the palladium(II) complexes is shown in Scheme I. The chiral Schiff bases were synthesized from the appropriate aldehyde and the chiral aniline following Scheme I. The starting material was (S)-(-)-butyl lactate commercially available from Fluka in 97% enantiomeric purity.

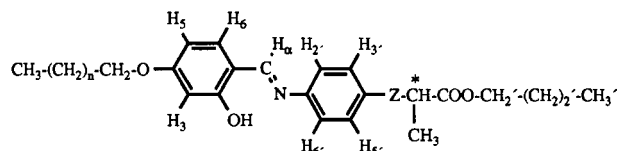
**Preparation of the Aldehydes.** The 4-alkoxy-2-hydroxybenzaldehydes 13 were synthesized as previously described.<sup>9</sup>

**Preparation of the Chiral Anilines.** Chiral amines 8–10 were obtained from the appropriate nitro derivatives by reduction with  $SnCl_2 \cdot 2H_2O$  in ethanol under an inert atmosphere following the Bellamy method<sup>10</sup> and used without further purification.

(S)-(-)-Butyl 2-(4-nitro-(E)-cinnamoyloxy)propanoate (5) and (S)-(-)-butyl 2-(4-nitrobenzoyloxy)propanoate (6) were obtained by the coupling of (S)-(-)-butyl lactate (1) to 4-nitrocinnamic acid (2) or 4-nitrobenzoic acid (3, 71.8 mmol) with dicyclohexylcarbodiimide (DCC, 79 mmol) as an esterification agent and 4-pyrrolidinopyridine (PPY, 7.18 mmol) as a catalyst in dry tetrahydrofuran (THF, 20 mL) according to the method described by Hassner and Alexanian.<sup>11</sup> The products were purified by flash chromatography (dichloromethane), (5, 39% yield; 6, 36% yield).

(R)-(-)-Butyl 2-(4-nitrophenyloxy)propanoate (7) was obtained using the Mitsunobu method<sup>12</sup> by condensation of (S)-(-)-butyl lactate (1) (60.9 mmol) and 4-nitrophenol (4, 60.9 mmol), with diethyl azodicarboxylate (DEAD, 60.9 mmol) and triphenylphosphine ( $(C_6H_5)_3P$ , 60.9 mmol) in dry THF. It was purified by flash chromatography (hexane/ethyl acetate, 20/1), 42% yield. This reaction proceeds with inversion of configuration.

**Preparation of Chiral Schiff Bases.** L: 10-A, 5-A, 10-B, 10-C. The Schiff bases were synthesized by mixing an ethanolic solution of chiral anilines 8–10 (5.7 mmol) with the appropriate



ligand	Z
10-A	CH=CH-COO
5-A	CH=CH-COO
10-B	COO
10-C	O

aldehyde 13 (5.7 mmol) and two drops of acetic acid as a catalyst, and purified by recrystallization from ethanol. The ligands were characterized by C, H, N analyses and IR (Table I) and <sup>1</sup>H NMR (Table II) spectroscopy.

**Preparation of the Chiral Complexes:**  $PdL_2$ . An ethanolic solution containing palladium acetate (1 mmol) was added to a hot ethanolic solution of L (2 mmol). The color of the reaction solution changed from yellow to brown. The solution was refluxed

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**Table I. Elemental Analysis (Calculated Values in Parentheses), the Most Relevant IR Data, and Yields for Ligands and Palladium(II) Complexes**

compound	% C	% H	% N	$\nu(\text{C}=\text{O})$ , $\text{cm}^{-1}$	$\nu(\text{C}=\text{N})$ , $\text{cm}^{-1}$	$\nu(\text{CH}=\text{CH})$ , $\text{cm}^{-1}$	yield, %
10-A	72.2(71.9)	8.1(8.2)	2.4(2.5)	1752, 1719	1630 <sup>a</sup>	1630 <sup>a</sup>	48
5-A	69.4(69.9)	7.2(7.3)	3.1(2.9)	1750, 1720	1633 <sup>a</sup>	1633 <sup>a</sup>	46
10-B	70.6(70.9)	8.5(8.2)	2.8(2.7)	1750, 1726	1628		51
10-C	72.2(72.4)	8.4(8.7)	2.8(2.8)	1732	1623		59
Pd-10-A	65.6(65.4)	7.8(8.1)	2.4(2.5)	1755, 1719	1606	1633	56
Pd-5-A	62.9(62.9)	7.3(7.6)	2.6(2.7)	1757, 1717	1606	1634	53
Pd-10-B	64.2(64.5)	7.5(7.3)	2.5(2.4)	1753, 1720	1606		49
Pd-10-C	65.4(65.8)	8.5(8.9)	2.6(2.6)	1752	1610		51

<sup>a</sup> Overlapping signals.**Table II. <sup>1</sup>H NMR Data for Ligands<sup>a</sup> ( $\delta$  (ppm), Multiplicities,<sup>b</sup>  $J$ (Hz))**

H <sup>c</sup>	10-A	5-A	10-B	10-C
OH	13.52(s)	13.49 (s)	13.4 (s)	13.81 (s)
H <sub>α</sub>	8.52 (s)	8.53 (s)	8.52 (s)	7.24 (s)
H <sub>2</sub> ', H <sub>6</sub> '	7.55 (d, 8.4)	7.56 (d, 8.4)	7.27 (d, 8.6)	7.22 (d, 8.8)
H <sub>3</sub> ', H <sub>5</sub> '	7.30–7.20 (m) <sup>d</sup>	7.40–7.10 (m) <sup>d</sup>	8.11 (d, 8.6)	6.88 (d, 8.8)
H <sub>6</sub>	7.30–7.20 (m) <sup>d</sup>	7.40–7.10 (m) <sup>d</sup>	7.26 (d, 8.8)	7.18 (d, 9.0)
H <sub>3</sub> , H <sub>5</sub>	6.42–6.56 (m) <sup>e</sup>	6.40–6.56 (m) <sup>e</sup>	6.42–6.56 (m)	6.48–6.40 (m)
PhCH=	7.73 (d, 16.1)	7.73 (d, 16.3)		
=CHCOO	6.42–6.56 (m) <sup>e</sup>	6.40–6.56 (m) <sup>e</sup>		
C*H	5.20 (c, 6.9)	5.19 (c, 7.0)	5.30 (c, 7.1)	4.74 (c, 6.8)
CH <sub>2</sub> '	4.16 (t)	4.16 (t)	4.16 (t)	4.15 (m)
CH <sub>2</sub>	3.98 (t)	3.98 (t)	3.98 (t)	3.97 (t)
C*CH <sub>3</sub>	1.53 (d)	1.55 (d)	1.62 (d)	1.61 (d)
CH <sub>3</sub> '	0.92 (t)	0.92 (t)	0.90 (t)	0.87 (t)
CH <sub>3</sub>	0.86 (t)	0.91 (t)	0.86 (t)	0.86 (t)

<sup>a</sup> Spectra recorded in CDCl<sub>3</sub> at 300 MHz. <sup>b</sup> s, singlet; d, doublet; t, triplet; c, quartet; m, multiplet. <sup>c</sup>  $-(\text{CH}_2)_n-$  and  $-(\text{CH}_2)_2'-$  protons appeared in the range  $\delta$  1.84–1.20 (m). <sup>d</sup> H<sub>3</sub>', H<sub>5</sub>', H<sub>6</sub> overlapped signals. <sup>e</sup> H<sub>3</sub>, H<sub>5</sub>, =CH- overlapped signals. <sup>f</sup> Ph = aromatic ring.**Table III. <sup>1</sup>H NMR Data for Palladium(II) Complexes<sup>a</sup> ( $\delta$  (ppm), Multiplicities,<sup>b</sup>  $J$ (Hz))**

H <sup>c</sup>	Pd-10-A	Pd-5-A	Pd-10-B	Pd-10-C
H <sub>3</sub> ', H <sub>5</sub> '	7.57 (d, 8.6)	7.57 (d, 8.4)	8.12 (d, 8)	6.86 (d, 8.8)
H <sub>α</sub>	7.54 (s)	7.54 (s)	7.53 (s)	7.54 (s)
H <sub>2</sub> ', H <sub>6</sub> '	7.35 (d, 8.4)	7.35 (d, 8.4)	7.39 (d, 8.3)	7.20 (d, 9.0)
H <sub>6</sub>	7.30 (d, 8.7)	7.03 (d, 9.0)	7.30 (d, 9.0)	7.00 (d, 8.8)
PhCH=	7.79 (d, 15.9)	7.79 (d, 15.9)		
=CHCOO	6.5 (d, 15.9)	6.52 (d, 15.9)		
H <sub>5</sub>	6.2 (dd, 2.0, 9.0)	6.2 (dd, 2.0, 9.0)	6.2 (d, 8.6)	6 (dd 2.0, 9.0)
H <sub>3</sub>	5.47 (d, 2.0)	5.47 (d, 2.0)	5.48 (s, 1 H)	5.62 (d, 2.1)
C*H	5.21 (c, 7.0)	5.21 (c, 7.2)	5.32 (c, 7.0)	4.75 (c, 6.8)
CH <sub>2</sub> '	4.17 (t)	4.17 (t)	4.30–4.10 (m)	4.70–4.00 (t)
CH <sub>2</sub>	3.72 (t)	3.72 (t)	3.84–3.70 (m)	3.80 (t)
C*CH <sub>3</sub>	1.57 (d)	1.57 (d)	1.25 (d)	1.62 (d)
CH <sub>3</sub> '	0.92 (t)	0.92 (t)	0.91 (t)	0.89 (t)
CH <sub>3</sub>	0.86 (t)	0.86 (t)	0.86 (t)	0.86 (t)

<sup>a</sup> Spectra recorded in CDCl<sub>3</sub> at 300 MHz. <sup>b</sup> s, singlet; d, doublet; t, triplet; c, quartet; m, multiplet. <sup>c</sup>  $-(\text{CH}_2)_n-$  and  $-(\text{CH}_2)_2'-$  protons appeared in the range  $\delta$  1.75–1.20 (m). <sup>f</sup> Ph = aromatic ring.

for 1 h and then cooled. The precipitate was collected by filtration and recrystallized from toluene/ethanol (1/3).

The complexes were characterized by C, H, N analyses and IR and <sup>1</sup>H NMR spectroscopy.

The elemental analyses, yields and the most relevant IR data for the ligands and complexes are given in Table I. The <sup>1</sup>H NMR data for the ligands and complexes are gathered in Tables II and III respectively.

**Techniques.** Microanalysis was performed with a Perkin-Elmer 240 B microanalyzer. Infrared spectra for all the complexes were obtained by using a Perkin-Elmer 1600 (FTIR) spectrophotometer in 400–4000-cm<sup>-1</sup> spectral range. <sup>1</sup>H NMR spectra were recorded on a Varian Unity 300-MHz spectrometer in deuteriochloroform solutions.

The textures of the mesophases were studied with an optical microscope (Nikon) equipped with polarized light, a Mettler FP82 hot stage, and a Mettler central processor.

Measurements of transition temperatures were made using a Perkin-Elmer DSC-7 differential scanning calorimeter with a heating or cooling rate of 10 K/min. The apparatus was calibrated with indium (156.6 °C, 28.44 J/g) and tin (232.1 °C, 60.5 J/g).

The spontaneous polarization and the response time were obtained simultaneously using the triangular waveform method.<sup>13</sup> In the experimental setup the triangular wave voltage is supplied by a HP3245A function generator. The current-voltage cycles are recorded by a digital acquisition system tech ADC488/16A. All the equipment is interfaced to a microcomputer. Cells for measurements are 4 μm thick with indium tin oxide (ITO) electrodes and coated with polyimide.

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## Results and Discussion

**Synthesis.** The readily available chiral starting material for the compounds presented in this paper is (*S*)-(-)butyl lactate (Fluka). The syntheses of both ligands and complexes are shown in Scheme I. Schiff bases synthesized by condensation of the appropriate aldehyde with the corresponding chiral amine (see Experimental Section), react with palladium acetate in a 2:1 molar ratio affording green, brown, or green-brown complexes.

All the compounds synthesized, both the ligands and the complexes, were characterized by elemental analyses and IR and  $^1\text{H}$  NMR spectra and the data obtained are in full agreement with the proposed structures (Tables I–III).

The Schiff bases exhibit a stretching vibration within the infrared region  $1633\text{--}1623\text{ cm}^{-1}$  assigned to the  $\text{C}=\text{N}$  bond. This band is shifted to a lower wavenumber ( $1606\text{--}1610\text{ cm}^{-1}$ ) upon chelation, indicating that the azomethine N atom is involved in the metal–nitrogen bond formation. The infrared spectra of type A and B ligands also show two stretching bands between  $1732\text{--}1752$  and  $1719\text{--}1726\text{ cm}^{-1}$  regions which were assigned to ester groups. Ligand 10-C only shows a stretching band at  $1732\text{ cm}^{-1}$  assigned to the ester group of the lactate unit. In addition to the  $\text{C}=\text{N}$  band, two bands within the regions of  $1753\text{--}1757$  and  $1720\text{--}1717\text{ cm}^{-1}$  corresponding to ester groups of complexes type A and B are observed. In the case of complex Pd-10-C this band appears at  $1739$  and  $1725\text{ cm}^{-1}$ . The band corresponding to the  $\text{C}=\text{C}$  bond of the type A ligands derived from cinnamic acid overlaps with the  $\text{C}=\text{N}$  band. After chelation these two bands split, the band corresponding to the  $\text{C}=\text{N}$  bond being shifted  $24\text{ cm}^{-1}$  lower. The  $\text{C}=\text{C}$  bond remains unchanged during the chelation process.

$^1\text{H}$  NMR spectra of the ligands show a signal at  $13.4\text{--}13.8\text{ ppm}$  corresponding to the proton of the OH group which disappears after chelation was carried out, indicating that a metal–oxygen bond was formed. The hydrogen signal of the imine group appears at  $8.5\text{ ppm}$  for ligands 10-A, 5-A, and 10-B and at  $7.2\text{ ppm}$  for ligand 10-C. This signal undergoes a downfield shift of  $1\text{ ppm}$  for type A and B complexes and an upfield shift of  $0.3\text{ ppm}$  for complex Pd-10-C.

**Mesophase Characterization.** The mesophases were identified according to their textures which were observed by optical microscopy.<sup>14</sup>

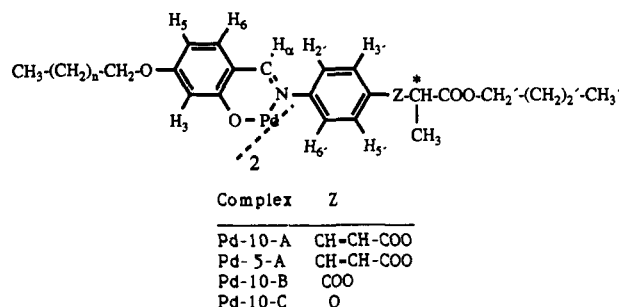
The cholesteric phase (Ch) showed by complex Pd-10-C was identified by the typical focal-conic texture (and oily streak texture was observed when the sample was manipulated). On cooling the Ch focal conic phase transforms in a chiral smectic C\* phase ( $\text{S}_\text{C}^*$ ) which exhibit broken fan-shaped texture. Dechiralization lines were observed. Smectic A mesophase ( $\text{S}_\text{A}$ ) present in ligands 10-A and 5-A and in complexes Pd-10-A, Pd-5-A, and Pd-10-C was clearly identified by its fan-shaped texture, which appears when the sample is cooled from the isotropic liquid and the phase becomes homeotropic when the sample is submitted to mechanical stress.

Smectic C\* ( $\text{S}_\text{C}^*$ ) (present in ligand 10-A and complexes Pd-10-A and Pd-10-C) showed broken fan-shaped texture on cooling the fan-shaped  $\text{S}_\text{A}$  phase. Dechiralization lines

Table IV. Transition Temperatures for Ligands and Palladium Complexes

ligands			complexes		
compound	transition <sup>a</sup>	temp (°C)	compound	transition	temp (°C)
10-A	$\text{C} \rightarrow \text{S}_\text{C}^*$	51.7	Pd-10-A	$\text{C}_1 \rightarrow \text{C}_2$	117.4
	$\text{S}_\text{C}^* \rightarrow \text{S}_\text{A}^b$	92		$\text{C}_2 \rightarrow \text{S}_\text{C}^*$	132.2
	$\text{S}_\text{A} \rightarrow \text{I}$	113.3		$\text{S}_\text{C}^* \rightarrow \text{S}_\text{A}^b$	156
5-A	$\text{C} \rightarrow \text{S}_\text{A}$	59.4		$\text{S}_\text{A} \rightarrow \text{I}$	183.4
	$\text{S}_\text{A} \rightarrow \text{I}$	116.4	Pd-5-A	$\text{C} \rightarrow \text{S}_\text{A}$	195.0
10-B	$\text{C} \rightarrow \text{I}$	87.9		$\text{S}_\text{A} \rightarrow \text{I}$	232.0
				$\text{C} \rightarrow \text{Ch}$	123.6
10-C				$\text{Ch} \rightarrow \text{I}$	126.5
			Pd-10-B	$\text{Ch} \rightarrow \text{S}_\text{C}^{*c}$	114.0
				$(\text{C}_1 + \text{C}_2) \rightarrow (\text{C}_2 + \text{I})$	78.0
				$(\text{C}_2 + \text{I}) \rightarrow \text{I}$	108.8
				$\text{I} \rightarrow \text{S}_\text{A}$	73.2
				$\text{S}_\text{A} \rightarrow \text{S}_\text{C}^{*b,c}$	33.5

<sup>a</sup> C = crystal,  $\text{S}_\text{C}^*$  = chiral smectic C,  $\text{S}_\text{A}$  = smectic A, Ch = cholesteric, I = isotropic. <sup>b</sup> Optical data. <sup>c</sup> Monotropic transition.



were observed in the ferroelectric mesophase. A pseudohomeotropic texture can be obtained on applying mechanical stress to the sample.

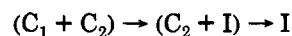
The textures observed for ligands and complexes are optically similar; however, the mesophases showed by the complexes were more viscous than the corresponding mesophase exhibited by the ligands, especially the smectic C\* of complex Pd-10-C.

**Mesogenic Properties.** The optical and thermal data of the ligands and complexes are gathered in Table IV.

**Ligands.** As can be observed, only the ligands derived from cinnamate (10-A, 5-A) are mesogens exhibiting a  $\text{S}_\text{A}$  mesophase when the aldehyde terminal chain is short ( $n = 5$ ) and the ferroelectric  $\text{S}_\text{C}^*$  phase together with the  $\text{S}_\text{A}$  mesophase when the aldehyde terminal chain has ten carbon atoms ( $n = 10$ ). Ligands 10-B and 10-C do not exhibit mesomorphism at all.

**Complexes.** Three of the palladium complexes synthesized show the potentially ferroelectric  $\text{S}_\text{C}^*$  mesophase, enantiotropic for Pd-10-A (in addition to a  $\text{S}_\text{A}$  mesophase) and monotropic for Pd-10-B and Pd-10-C. Pd-10-B also exhibits a cholesteric mesophase at a higher temperature, and apparently this is the first time that a Ch phase has been reported for a metallomesogen. Pd-5-A only presents a enantiotropic  $\text{S}_\text{A}$  phase.

Complex Pd-10-C shows crystalline polymorphism during the first heating process, the sequence of transitions observed follows the scheme



On cooling the isotropic liquid (I) a monotropic smectic A mesophase and a monotropic chiral smectic C phase appeared. It was observed that complex Pd-10-C solidified keeping the texture of the smectic C\* phase.

(14) (a) Demus, D.; Richter, L. *Textures of liquid Crystals*; Verlag-Chemie: Weinheim, New York, 1978. (b) Gray, G. W.; Goodby, J. W. G. *Smectic Liquid Crystals Textures and Structures*; Leonard Hill: Glasgow, 1984.

**Table V.** Spontaneous Polarization Values ( $P_s$ , nC/cm<sup>2</sup>), Switching Time ( $\mu$ s V  $\mu$ m<sup>-1</sup>), and Rotational Viscosity (Pas)

	$P_s(\text{max})$	sign	$P_s^a$	$\tau^a$	$\gamma^a$
Pd-10-A	44	-	33	2306	0,45
Pd-10-B	80	+	76	4286	1,86
Pd-10-C	98 <sup>b</sup>		70*		

<sup>a</sup>  $P_s$  values, switching times,  $\tau$ , and viscosities,  $\gamma$ , 10 °C below the transition. <sup>b</sup> Data obtained by extrapolation of the  $P_s$  values measured in a mixture of compound Pd-10-C 10 mol % with a nonchiral S<sub>C</sub> compound 90 mol %.

As can be observed from Table IV, the coordination of the ligands to a palladium atom gives rise to the appearance of mesogenic properties when the ligands (in the case of ligands B or C) are not liquid crystals. Unlike the type B and C complexes, the type A complexes show shorter mesophase ranges than their respective ligands.

The differences between the three types of ligand or their respective complexes are, on the one hand, the distance of the chiral centre from the mesogenic unit and, on the other hand, the type of bond joining the chiral centre to the central core: -CH=CHCOO- (cinnamate) for the type A compounds, -COO- (benzoate) for the type B ligand and complex and -O- (ether) for the type C ligand and complex.

The introduction of a cinnamate group determines the appearance of mesogenic behavior in the type A ligands and enantiotropic behaviour in the complexes. The presence of the group CH=CHCOO increases the polarizability anisotropy of the ligands and complexes and consequently the intermolecular interaction which leads to the appearance of mesophases.

The proximity of the chiral center to the central core gives rise to a loss of stability in the ligands (thus compound B (-COO-) and C (-O-) are not liquid crystals) as well as in the complexes. The effect of the proximity in the type B and C complexes leads to lower transition temperatures than in the type A complexes.

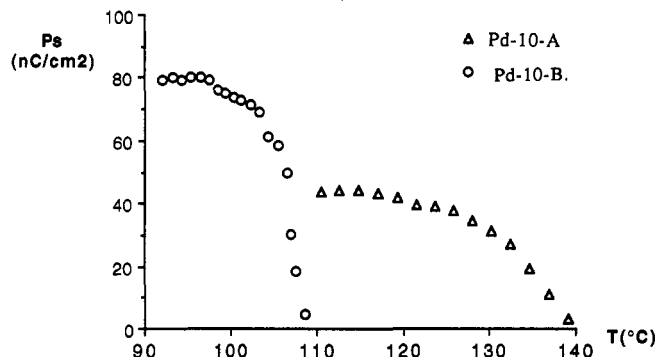
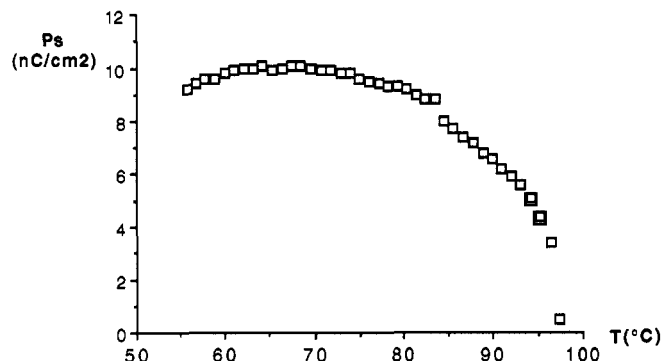
The length of the terminal chain in the aldehyde part, like the ligands, determines the type of mesophase. The shortest chain shows smectic A ( $n = 5$  in complex Pd-5-A) and the longest ( $n = 10$  in complex Pd-10-A) causes a more ordered mesophase (smectic C\*) to appear. There is also a decrease in the transition temperatures as the length of the terminal chain increases.

**Ferroelectric Properties.** The spontaneous polarization  $P_s$ , the switching time  $\tau$  and the rotational viscosity  $\gamma$  were measured for complexes Pd-10-A and Pd-10-B. The monotropic character of the S<sub>C</sub>\* phase of complex Pd-10-C as well the fact that it shows up at low temperatures and its short mesophase range made it impossible for  $P_s$  to be evaluated in a pure sample. For this reason, a study of the physical properties of complex Pd-10-C was carried out by the preparation of a mixture consisting of 10 mol % of the chiral compound (Pd-10-C) and 90 mol % of a nonchiral S<sub>C</sub> material: 4-pentyloxy-*N*-(4-(decyloxy)-2-hydroxybenzilidene)aniline (C 71.2 °C, S<sub>C</sub> 115 °C, N 117 °C, I).

All three magnitudes ( $P_s$ ,  $\tau$ ,  $\gamma$ ) were determined simultaneously by the triangular wave method<sup>13</sup> using 4- $\mu$ m cells in an electric field of 16 V peak to peak and a frequency of 20 Hz.

Data related to the ferroelectric properties of the complexes are gathered in Table V.

The complexes exhibit switching in the millisecond range, comparable to the switching time exhibited by the

**Figure 3.** Temperature dependence of spontaneous polarization of Pd-10-A and Pd-10-B complexes.**Figure 4.** Temperature dependence of spontaneous polarization of a 10 mol % mixture of Pd-10-C complex and 4-(pentyloxy)-*N*-(4-(decyloxy)-2-hydroxybenzilidene)aniline.

ferroelectric metallomesogens previously described<sup>6</sup> and exhibited by some polymeric ferroelectric liquid crystals,<sup>15</sup> but slightly longer than that of most ferroelectric organic liquid crystals, which are normally in the range of microseconds.

Figure 3 shows the dependence of spontaneous polarization against temperature: complexes Pd-10-A and Pd-10-B display different behavior of their corresponding  $P_s$  values as temperature decreases. Complex Pd-10-B, with a first-order phase transition, i.e., Ch-S<sub>C</sub>\*, shows a steep slope of the  $P_s$  vs temperature plot when the ferroelectric mesophase appears, reaching the  $P_s$  saturation value a few degrees below the transition. However, the second-order transition S<sub>A</sub>-S<sub>C</sub>\* in complex Pd-10-A gives rise to a continuous increase in the  $P_s$  as the material cools, and so the  $P_s$  saturation value is reached just before crystallization.

Figure 4 shows the variation of  $P_s$  as a function of temperature for the mixture consisting of 90 mol % of a nonchiral S<sub>C</sub> compound and 10 mol % of Pd-10-C. The value for extrapolated  $P_s(\text{max})$  for the pure compound is ca. 98 nC/cm<sup>2</sup> and the extrapolated value for the  $P_s$  at a temperature 10 °C below the transition to Ch-S<sub>C</sub> is 70 nC/cm<sup>2</sup>.

With regard to the molecular structure-spontaneous polarization relationship, we want to emphasize two aspects.

First, the considerable increase in the  $P_s$  value when the C=C group is eliminated: the benzoate derivative (Pd-10-B, 80 nC/cm<sup>2</sup>) shows a  $P_s(\text{max})$  value almost twice the value obtained for the cinnamate derivative (Pd-10-A, 44 nC/cm<sup>2</sup>). Taking into account the results mentioned, we

(15) Poths, H.; Schönfeld, A.; Zentel, R.; Kremer, F.; Siemsmeyer, K. *Adv. Mater.* 1992, 4, 351.

note the importance of the intramolecular coupling of molecular dipoles in the same way as it occurs in organic FLC materials. As the chiral center gets closer to the rigid mesogenic nucleus, i.e., complex Pd-10-B, the free independent rotation of the asymmetric part of the molecule is made more difficult, and so its dipole is more coupled to other dipoles in the molecule. Complex Pd-10-C, with the asymmetric center even closer to the rigid core, gives rise to a higher  $P_s$  value (98 nC/cm<sup>2</sup>). Complex Pd-10-C is an example of how mesogenic and ferroelectric properties are not always favored by the same structural factors: the approach of the asymmetric center to the rigid core is to the detriment of the S<sub>C</sub>\* phase stability making difficult the experimental conditions for  $P_s$  evaluation.

The second aspect is concerned with the fact that the  $P_s(\text{max})$  value of complex Pd-10-A turned out to be the same as the one of its corresponding ligand (44 nC/cm<sup>2</sup>), and twice the  $P_s$  value of its analogous copper (23 nC/cm<sup>2</sup>)

and oxovanadium (22 nC/cm<sup>2</sup>) derivatives, as reported in our previous paper.<sup>6</sup> More exhaustive studies on the influence of the type of transition metal on the ferroelectric properties of metallomesogens containing chiral Schiff bases are now in progress.

### Conclusions

New ferroelectric metalloorganic liquid crystals incorporating palladium(II) atoms in their structure have been synthesized and characterized. The results reported in this paper show that stable low-temperature ferroelectric metallomesogen materials can be obtained exhibiting high spontaneous polarization values.

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