

Monomeric and dimeric *ortho*-metallated palladium(II)-imine systems as liquid crystals

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Abstract

Several types of *ortho*-palladated complexes derived from the imines $HL_n = p-C_nH_{2n+1}O-C_6H_4-CH=N-C_6H_4-OC_nH_{2n+1}-p$ ($n = 2, 4, 6, 8$ and 10) have been prepared and their mesogenic properties studied. The types include the dinuclear complexes $[Pd(\mu-X)L_n]_2$ with $X = Cl, OAc, (R)-2-Cl\text{-propionato}$ or $(S)-2-Br\text{-propionato}$, and the mononuclear complexes $[Pd(acac)L_n]$ and $[Pd(NHacac)L_n]$ ($NHacac = 4\text{-amino-3-penten-2-onate}$). Most of the complexes (except the acetato derivatives and some others with very short alkoxy chains) show liquid-crystal behavior. Nematic, smectic A and smectic C phases are found. Most of the derivatives with chiral carboxylates display double melting behavior.

Keywords: Palladium; Cyclometallation; Imine; Mesogenic properties; Liquid crystal

1. Introduction

Transition metal-containing liquid crystals (TMLCs) have attracted increasing attention in recent years [1]. Only a minority are organometallic compounds, no doubt because the requirement of thermal stability for thermotropic behavior (liquid-crystal behavior on heating) is at variance with the thermal instability often associated with organometallic compounds. Many of the TMLC-containing M–C bonds are of the cyclometallated type, a class of organometallics that is particularly stable and has a favorable geometry for the production of either calamitic or discotic molecules. In 1982, Ghedini et al. [2] described the first cyclopalladated derivatives showing liquid-crystal behavior, using azobenzene derivatives as ligands. Later, imines [3], azines [4] and phenylpyrimidines [5] were used for the production of such systems, which have since been extensively studied. Despite this, systematic studies of the influence of the chain length on the mesogenic properties are scarce. For the present work we chose imines having the same chain (*n*-alkoxy) on the *para* position of both aryl rings of the imine, because previous studies [6] have demon-

strated that alkoxy chains and a phenyl ring linked to the nitrogen atom both bestow good mesogenic properties on the cyclometallated complexes. We describe the syntheses and mesogenic behavior of several molecular types of *ortho*-palladated imine derivatives, with the alkoxy chain length varied systematically for each type.

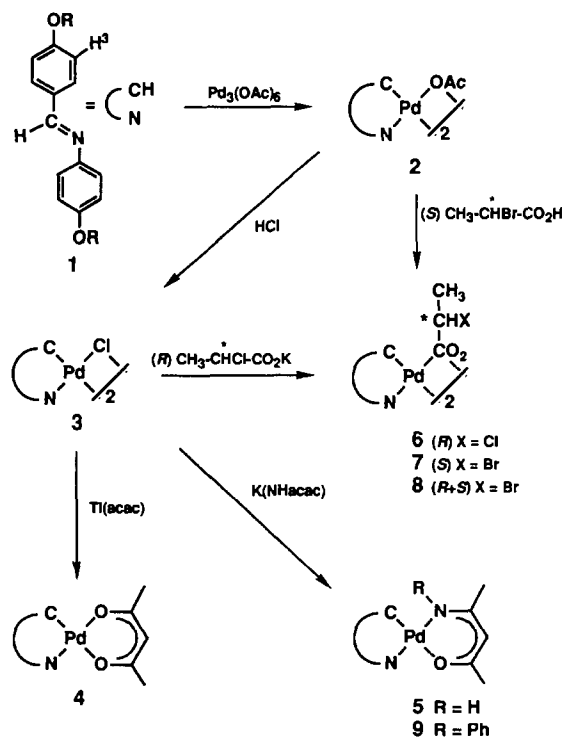
2. Results and discussion

2.1. Syntheses and structures

The imines **1** were readily prepared with good yields by condensation of the corresponding aldehydes and anilines. For simplicity, we represent these ligands as HL_n , where n is the number of carbon atoms on both terminal chains. Their cyclopalladated complexes were synthesized as depicted in Scheme 1.

Slight modifications of the method described by Onoue and Moritani [7] allowed us to obtain **2** without any decomposition to black Pd and with almost quantitative yields. Treatment with HCl afforded the chloro-bridged dimers **3**, which were precursors for the monomeric derivatives with acetylacetonate (**4**) or aminoenonate (**5**). β -Diketones have been used previously as chelating ligands in cyclopalladated mesogens

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Scheme 1.

[8–10], but there are no examples of similar complexes containing β -enaminoketones. Such ligands have been reported to give mesogenic metal (bis)chelate complexes [11]. Chiral carboxylate derivatives were obtained either by treatment of **3** with potassium (*R*)-2-chloropropionate (**6**), or by displacement of acetic acid from **2** by use of (*S*)-2-bromopropionic acid (**7** and **8**). All the imines [12], as well as three complexes (**2** [3], **3** [3] and **4** [9] with L10), have been previously described.

All the compounds were characterized by satisfactory CHN analyses, and IR (see Section 4) and ^1H NMR spectroscopy. The reactions can be readily monitored by ^1H NMR spectroscopy. Both the iminic proton and H^3 (see Scheme 1) are very sensitive to changes in the molecular structure. The ^1H NMR parameters for compounds of the types **1–9** with L6 are listed in Table 1. These parameters are the same for the rest of ligands within less than ± 0.03 ppm for the chemical shifts, and less than ± 0.02 Hz for the coupling constants; the only changes are in the integrals for the chain hydrogen atoms, and the multiplicities for the ethoxy signals in L2. The insolubility of **3** with L2 precluded the recording of its NMR spectra.

The acetato-bridged complexes **2** are obtained mainly as the *trans* isomers, with a small amount (about 4%) of the *cis* isomer, which is detected easily in the corresponding imine hydrogen signal. We have shown previously that this open-book-shaped (or butterfly-shaped) structure is rigid on the NMR time scale [13]. The

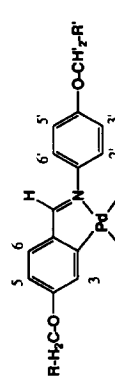
reaction with HCl produces the planar complex **3** exclusively as the *trans* isomer.

Only one isomer is possible for complexes of type **4**. In the derivatives **5**, only one of the two possible isomers (*N,N-trans* and *N,N-cis*) is formed. The ^1H NMR signals corresponding to the enaminoketonate ligand show coupling of the NH proton to both the CH in the enaminoketonate moiety, and the methyl group close to the amino group. In order to assign the structure of the complexes of type **5**, the corresponding complex **9** with 4-phenylamino-3-penten-2-one was prepared. In this case both H^3 and the first methylene of the alkoxy group attached to the cyclometallated ring show strong upfield shifts ($\delta(\text{H}^3) = 5.09$ ppm with $\Delta\delta = 1.6$ ppm; $\delta(\text{OCH}_2) = 3.51$ ppm with $\Delta\delta = 0.5$ ppm) owing to the anisotropic field created by the phenyl ring of the aminoenonate ligand. This proves the *trans* arrangement of the nitrogen atoms in the molecule. Consequently **5** are assigned the *N,N-trans* structure, as shown in Scheme 1. Similar results have been reported for the *N*-(phenyl)-2-salicylideneaminato ligand [14], although in that case a mixture of *N,N-trans* and *N,N-cis* (5 : 1) isomers is formed.

The use of chiral carboxylates as bridges gives rise to a number of diastereomers [13]. For 100% enantiomerically pure carboxylates (for instance *R*) there are two reasons for the formation of the diastereomers: (i) the presence of *trans* and *cis* isomers from the arrangement of the two imines in the dimer and (ii) the chirality of the *trans* isomer, that leads to two enantiomers (Λ and Δ ; the *cis* isomer is not chiral). Thus in the case of the azine derivatives (*cis*: *trans* ratio of 30 : 70) a mixture of *cis-R,R*: *trans- Δ R,R*: *trans- Λ R,R* (30 : 35 : 35) was obtained [15]. In the case of **6**, with pure (*R*)-2-chloropropionic acid and a *cis*: *trans* ratio of 4 : 96, a mixture of *cis-R,R*: *trans- Δ R,R*: *trans- Λ R,R* (4 : 48 : 48) was obtained.

The study of **7** proved to be more complicated owing to the low optical purity of the commercial carboxylic acids [16], which leads to the formation of *R,R*, *S,S* and *R,S* combinations in the complexes that can be verified in their 300 MHz ^1H NMR spectra. Fig. 1 shows all possible diastereomers (excluding enantiomers), and the number of signals expected for H^3 and for CHBr. Complexes **7** were made from the purest commercially available form of the acid, (*S*)-2-bromopropionic acid (93.25% *S*; 6.75% *R*). In order to confirm the assignment of the signals, **8** was prepared using a racemic mixture of (*R*)- and (*S*)-2-bromopropionic acid. The approximate compositions expected for the mixtures **7** and **8**, assuming a *trans*: *cis* ratio of 96 : 4, are shown in Table 2.

Fig. 2 shows the 300 MHz ^1H NMR signals for the most sensitive nuclei, H^3 and the proton on the chiral carbon atom. Only signals arising from the more abundant *trans* isomers are seen in this region (the signals

Table 1
1H NMR data for 1–9^a


Complex	H	H ³	H ⁵	H ⁶	H ^{2',6'}	H ^{3',5'}	O-CH ₂ and O-CH' ₂	Others ^b
1	8.39(s)	6.94 [8.8]	6.53(dd) [8.3, 2.4]	(+H ²) 7.81 [8.8]	7.18 [9.0]	6.90 [9.0]	4.01, 3.96(t) [6.2]	—
2	7.44(s) ^c	6.05(d) [2.4]	6.54(dd) [8.3, 2.3]	7.10(d) [8.3]	7.25 [8.8]	6.66(s)	4.13–3.49(m)	1.87(s)MeCO ₂
3	7.75(s)	6.84(d)	6.59(dd) [8.3, 2.4]	7.19(d) [8.3]	7.33 [9.0]	6.84 [8.8]	3.93(t) [6.3]	—
4	7.95(s)	7.10(d) [2.4]	6.59(dd) [8.1, 2.2]	7.27(d) [8.3]	7.38(d) [9.0]	6.87 [9.0]	4.14–3.90(m)	5.33(s)CH; 2.07, 1.87(s)Me
5	8.06(s)	6.69(d) [2.2]	6.56(dd) [8.3, 2.2]	7.36(d) [8.1]	—	6.89 [9.0]	4.11–3.90(m)	6.16(br)NH; 4.93(d) [2.3] CH;
6	7.48(s) ^c	5.99, 5.98(d) [2.5]	6.55(dd) [8.3, 2.3]	7.13(d) [8.3]	—	6.61(s)	3.95–3.41(m)	2.11(d) [0.6] Me; 1.87(s)Me
7	7.47(s) ^c	5.98, 5.97(d) [2.5]	6.55(dd) [8.3, 2.3]	7.13(d) [8.3]	—	6.62(s)	3.95–3.42(m)	4.33, 4.29(q) [6.8] C*H;
8 ^c	7.47(s) ^c	5.98, 5.97(d) [2.5]; 6.00, 5.96(d) [2.5]	6.55(dd) [8.3, 2.3]	7.13(d) [8.3]	—	6.62(s)	3.95–3.42(m)	1.52, 1.51(d) [6.8] MeC*
9 ^c	7.91(s)	5.09(d) [2.3]	6.40(dd) [8.2, 2.3]	—	—	6.88 [9.0]	3.51, 3.99(t)	4.36, 4.33 (q) [6.8]; 4.36, 4.32 (q) [6.8]; 1.69, 1.68(d) [6.8]; 1.69, 1.68(d) [6.8] MeC*

^a In CDCl₃ at 80.13 MHz (300.13 MHz for 6–8).^b Aliphatic protons (R and R') appear in the range 1.75–0.8 ppm.^c Signals for the cis isomers are observed at about 7.60 ppm.^d Overlapped with 3',5'.^e See text.^f Overlapped with PhNacac.

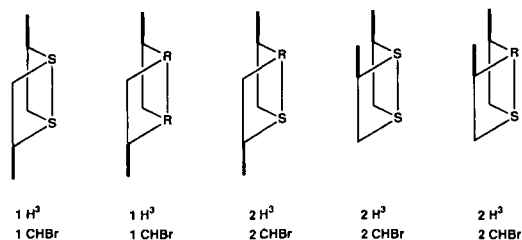


Fig. 1. Schematic representation of the possible diastereomers for the 2-bromopropionic-bridged complexes. The bar indicates the $N-C_6H_4-OR$ moiety. R or S indicates the conformation of the carboxylate ligand in that position. The number of H^3 or $CHBr$ NMR signals predicted for each isomer are given under the structure.

for the minor *cis* isomers are seen in the imine protons region). For **7**, where the (*S*)-carboxylate dominates, two doublets are obtained in the aromatic region, each corresponding to each of the two dominant diastereomers *trans*- $\Delta S,S$ and $\Lambda S,S$ (plus a small amount of their enantiomers *trans*- $\Lambda R,R$ and $\Delta R,R$, indistinguishable from their main enantiomers). In addition, two more doublets, less intense, are expected from the diastereomer *trans*- R,S (whether Λ or Δ , since both are enantiomers), each coming from the H^3 proton close to the (*R*)-carboxylate and from the H^3 proton close to the (*S*)-carboxylate; only the external signals can be seen, whereas the internal signals are obscured by those from the dominant diastereomers. Increasing the (*R*)-enantiomer content (**8**), the R,S signals increase (as well as R,R signals, but these are enantiomers and do not produce any observable effect), leading to four doublets of equal intensity. The same effect might be detected in principle for the $CHBr$ signals. However, these signals are quartets and, for **7**, only the two quartets of the main diastereomers can be observed. In **8**, the two quartets of the *trans*- R,S diastereomer can also be observed, although there is overlapping of some signals.

2.2. Mesogenic properties

The mesogenic properties of the compounds are shown in Tables 3 and 4, and compared in Figs. 3 and 4. The textures shown by the organometallic mesogens are similar to those observed for organic mesogens, although noticeably more viscous. The imines **1** have been previously reported [12], but their thermal and

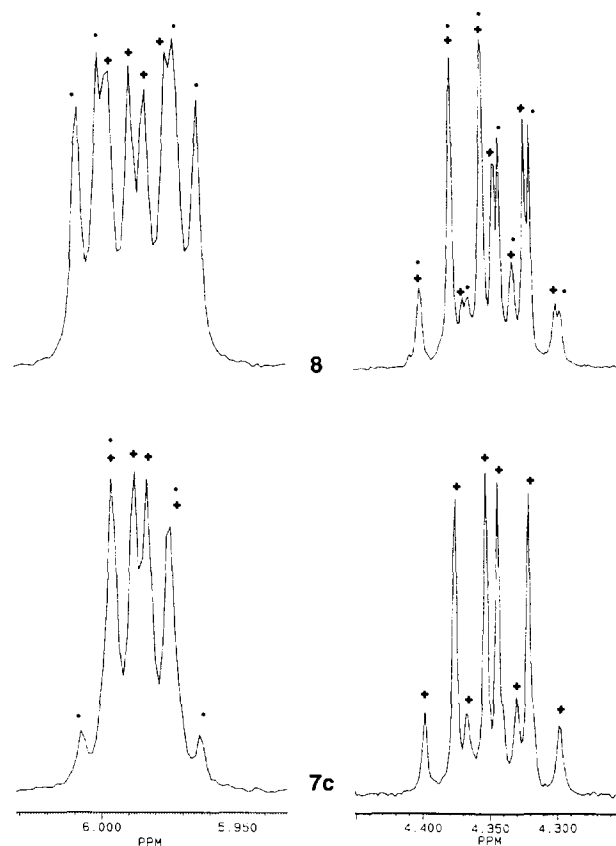


Fig. 2. 1H NMR spectra in the range of the H^3 (left) and $CHBr$ (right) signals for **7c** (down) and **8** (up): +, signals associated with the *trans*- $\Delta S,S$ and *trans*- $\Lambda S,S$ diastereomers (plus their enantiomers); ●, *trans*- R,S diastereomer ($\Lambda + \Delta$, both are enantiomers).

thermodynamic data are included for comparison. They show low melting and clearing temperatures, narrow mesophase ranges and a poor polymesomorphism; only nematic (*N*) and/or smectic *C* (S_C) phases are found.

The planar molecules **3** show mesogenic behavior and are characterized by high melting and clearing temperatures, usually with decomposition at the clearing point, and smectic polymorphism. Complex **3** with L2 exhibits smectic *A* (S_A) and nematic (*N*) phases in a narrow range, but at this point decomposition is severe. The mesogenic properties are very much better for the mononuclear acetylacetonate complexes **4**, which have mesogenic properties even better than those of the free ligands. The change from the dinuclear complexes **3** to

Table 2
Percentage of the different diastereomers for **7** and **8**

Diastereomer	Amount (%)	
	7	8
<i>trans</i> - $\Delta S,S$ (plus its enantiomer <i>trans</i> - $\Lambda R,R$)	41.95	24
<i>trans</i> - $\Lambda S,S$ (plus its enantiomer <i>trans</i> - $\Delta R,R$)	41.95	24
<i>trans</i> - R,S (all possible combinations are enantiomers)	12.1	48
<i>cis</i> - S,S (plus its enantiomer <i>cis</i> - R,R)	3.5	2
<i>cis</i> - R,S (plus its enantiomer <i>cis</i> - S,R)	0.5	2

Table 3
Optical, thermal and thermodynamic data for **1**, **3**, **4** and **5**

Compound	<i>L</i> <i>n</i>	Transition ^a	<i>T</i> (°C)	ΔH (kJ mol ⁻¹)
1a	L2	C-I	147.4	31.8
		I-N ^b	143.5	-1.6
		N-C	126.2	-23.3
1b	L4	C-I	123.5	32.0
		I-N ^b	120.0	-31.5 ^c
		N-C	119.1	
1c	L6	C-N	104.4	30.3
		N-I	113.0	1.7
1d	L8	C-S _C	100.6	36.8
		S _C -N	109.7	8.0 ^c
		N-I	112.5	
1e	L10	C-S _C	102.6	51.3
		S _C -I	112.1	10.9
3a	L2	C-S _A	258.7	61.5
		S _A -N-I ^d	270.0 ^e	-
3b	L4	C-S _A	181.0	22.2
		S _A -I	271.0 ^e	2.5
3c	L6	C-S _A	175.3	18.0
		S _A -I	261.0 ^e	2.7
3d	L8	C-S _C	175.3	15.4
		S _C -S _A ^d	205.0	-
		S _A -I	270.0 ^e	1.7
3e	L10	C-S _C	123.8	15.3
		S _C -S _A ^d	204.0	-
		S _A -I	265.0 ^e	2.9
4a	L2	C-I	187.0	41.2
		I-N ^b	146.4	-1.3
		N-C	130.4	-31.3
4b	L4	C-I	137.8	31.7
		I-N ^b	131.4	-1.3
4c	L6	C-S _A	73.5	31.8
		S _A -N	107.4	1.9
		N-I	127.8	1.0
4d	L8	C-S _A	63.2	35.8
		C'-S _A	84.6	1.9
		S _A -N	123.7	3.7 ^c
		N-I	124.6	
4e	L10	C-S _A	63.0	53.5
		C'-S _A	72.8	4.9
		S _A -I	124.3	5.7
5a	L2	C-I	201.9	46.6
		I-N-C ^b	111.7	-23.8

Table 3 (continued)

Compound	<i>L</i> <i>n</i>	Transition ^a	<i>T</i> (°C)	ΔH (kJ mol ⁻¹)
5b	L4	C-I	161.8	36.3
		I-N ^b	118.9	-2.1
		N-(N+C)	83.7	-5.5
		(N+C)-C	50.8	-1.1
5c	L6	C-N	112.4	38.2 ^c
		N-I	115.9	
5d	L8	C-N	94.1	41.2
		N-I	115.6	1.3
5e	L10	C-S _A	92.0	20.4
		S _A -N	110.5	4.8 ^c
		N-I	113.7	

^a C, crystal; N, nematic; S_A, smectic A; S_C, smectic C; I, isotropic liquid.

^b Monotropic transition.

^c Combined enthalpies.

^d Optical microscopy data; a sequence of three phases, such as S_A-N-I, indicates that a transient phase (the one in the middle, N in this example) is observed which immediately changes to the next mode.

^e Decomposition.

the mononuclear complexes **4** involves a change in the molecular shape that leads to a large decrease in both melting and clearing temperatures at the expense of narrower mesophase ranges. It is note worthy that the mononuclear complexes **4** retain mesophase ordering on cooling to give glassy solids (except for L2, which crystallizes). As a consequence of the low transition temperatures, there is no decomposition at the clearing point and the complexes can safely be repeatedly heated and cooled. The properties are quite similar for the new type of derivatives **5**, but in this case the mesophase ranges are smaller and the phases are less ordered (mainly nematic). Many complexes **4** and **5** show different crystalline phases, either on cooling or on heating from their glassy states, and this leads to more complicated thermograms for the second heating. Although some irregularities are found, an increase in length of the alkoxylic chains in general produces a reduction in the transition temperatures, especially for the melting points, leading to a stabilization of the mesophases.

The properties of the carboxylato-bridged complexes deserve comment. Complexes **2**, as expected from previous studies, exhibit high melting temperatures and do not show mesogenic behavior. This can be attributed to their markedly non-planar structure which hinders good molecular packing and so leads to the absence of mesomorphism. Surprisingly the mesogenic behavior is restored (except for the shortest chain) in complexes of the types **6** and **7** in which the carboxylato group is even bulkier. This suggests that the new dipolar mo-

Table 4

Optical, thermal and thermodynamic data for the carboxylato complexes **2**, **6** and **7**

Complex	Ln	Transition ^a	T (°C)	ΔH (kJ mol ⁻¹)
2a	L2	C–I	249.1 ^b	37.3
2b	L4	C–I	245.5 ^b	48.1
2c	L6	C–I	217.0 ^b	56.2
2d	L8	C–I	206.6 ^b	57.7
2e	L10	C–I	200.5 ^b	62.7
6a	L2	C–I	208.4	53.82
		I–C' ^c	215.0	–
		C'–I ^c	265.0 ^b	–
6b	L4	C–I	205.2	37.87 ^d
		I–S' _A ^c	207.0	–
		S' _A –I ^c	237.0 ^d	–
6c	L6	C–S _A	151.2	22.8
		S _A –I	192.9	5.3
		I–S' _A ^c	203.0	–
		S' _A –I ^c	236.0 ^b	–
6d	L8	C–S _A	146.0	40.96
		S _A –I	191.1	8.5
		I–S' _A ^c	212.0	–
		S' _A –I ^c	240.0 ^b	–
6e	L10	C–S _A	102.3	–
		C'–S _A ^c	110.5	–
		S _A –I	174.7	9.0
		I–S' _A ^c	200.0	–
		S' _A –I ^c	235.0 ^b	–
7a	L2	C–I	178.5	24.3
		I–C' ^c	182.0	–
		C'–I ^c	265.0 ^b	–
7b	L4	C–I	182.7	25.4
		I–S' _A ^c	187.0	–
		S' _A –I ^c	237.0 ^b	–
7c	L6	C–S _A	119.8	21.9
		S _A –I	189.2	0.4
		I–S' _A ^c	191.3	–
		S' _A –I ^c	240.0 ^b	–
7d	L8	C–S _A	138.2	37.1
		S _A –I	190.1	0.8
		I–S' _A ^c	191.0	–
		S' _A –I ^c	239.0 ^d	–
7e	L10	C–S _A	93.8	35.5
		S _A –I	183.3	2.2
		I–S' _A ^c	190.0	–
		S' _A –I ^c	227.0 ^d	–

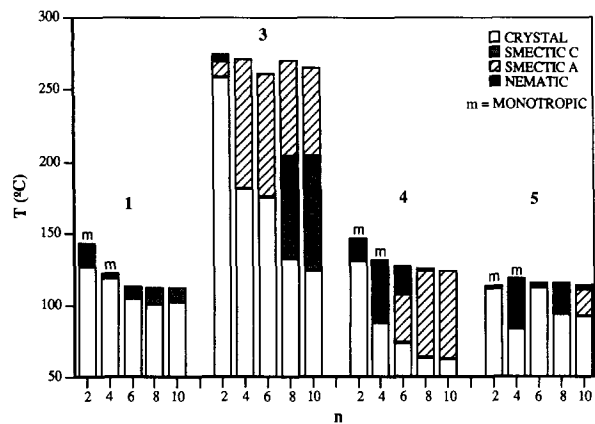
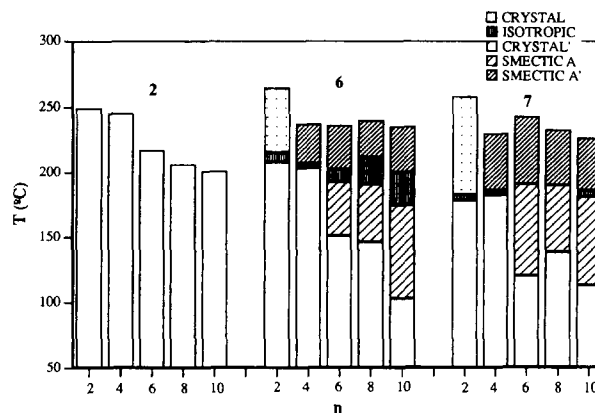
^a C, C', crystal; S_A, S'_A, smectic A; S_C, smectic C; I, isotropic liquid.^b Decomposition.^c Optical microscopy data.^d Combined enthalpies.

Fig. 3. Thermal behavior of compounds of types 1, 3, 4 and 5.

ments introduced by C–Cl or C–Br bonds are strong enough to compensate for the unfavorable shape of the molecules and maintain the intermolecular forces leading to mesophase formation. If this were the only effect, however, one would expect a clearly larger effect for the smaller and more polar C–Cl bond, whereas the effects for **6** and **7** are quite similar. We suggest that this can be attributed to either of the two following reasons: (i) the fact that **7** is present as more complex isomeric mixtures than **6**, and it is well known that mixtures often induce the appearance of mesophases or (ii) if the halogens are disposed preferentially towards the chains (below the line of the hinge of the molecule) they might contribute to fill the empty space and improve the molecular packing, helping to keep the chains extended after their melting, this effect being better for the bulkier halogen. This should also help to stabilize the mesophase.

These complexes are also unusual in their “double melting behavior”. This is a kinetic effect, extensively studied by Ohta et al. in copper (II) β-diketonates [17], and more recently [18] in ferrocenyl derivatives. It is based on the existence of several crystalline forms of different thermal stabilities. As a kinetic effect, this

Fig. 4. Thermal behavior of compounds of types 2, 6 and 7. Smectic A' is used to label the second S_A phase produced on heating.

phenomenon is markedly dependent on the scanning rate and can be observed only if the heating is sufficiently fast (in our case, $25^{\circ}\text{C min}^{-1}$); if the heating is slow, interchange between these crystalline forms takes place, and the phenomenon disappears. It should be noted that at the first clearing point there is no decomposition (or slight), but at the second clearing point (far above 200°C) it is severe. Thus the differential scanning calorimetry data provide little information, and most data come from use of the microscope.

3. Conclusions

The following conclusions can be drawn from the results in this work.

(1) An increase in the length of the alkoxy chains produces in general a stabilization of the mesophases in all the molecules studied, whether monomeric or dimeric. This improvement is mainly due to the decrease in melting point associated with that change.

(2) The use of bulkier 2-halopropionato bridges unexpectedly induces mesogenic behavior in complexes that do not form liquid crystals when they contain acetato bridges. The effect cannot be attributed to a decrease in melting point (although this in fact occurs) produced by the bulkier group, since most of the 2-halopropionato complexes also show mesophases at temperatures above the melting points of some of the acetato complexes. It can be the result of a combination of factors such as the new dipole moments introduced, the formation of isomeric mixtures and more efficient space filling in the melt.

(3) β -Aminoenonates appear to provide a very promising alternative to β -diketonates for the production of monomeric complexes with improved liquid-crystal behavior.

4. Experimental section

4.1. Techniques

Elemental analyses were carried out with a Perkin–Elmer 2400 microanalyzer. IR spectra were recorded on a Perkin–Elmer 833 spectrophotometer with KBr pellets unless otherwise noted. ^1H NMR spectra were recorded with CDCl_3 solutions at 80.13 MHz or 300.13 MHz on Bruker AC-80 or AC-300 instruments. The textures of the mesophases were studied with a Leitz Laborlux-D polarizing microscope, equipped with a Leitz 350 hot stage. Transition temperatures and enthalpies were measured by differential scanning calorimetry, with a Perkin–Elmer DSC-7 operated at a scanning rate of $5^{\circ}\text{C min}^{-1}$ ($25^{\circ}\text{C min}^{-1}$ for **6** and **7**) on heating. The

apparatus was calibrated by use of indium (156.6°C ; 28.5 J g^{-1}).

4.2. Materials

Published methods were used for the preparation of 4-alkoxyanilines [19], $\text{Pd}_3(\text{OAc})_6$ [20], $\text{Ti}(\text{acac})_3$ [21], 4-amino-3-penten-2-one [22] and potassium (*R*)-2-chloropropionate [23]. (*R*)- and (*S*)-2-bromopropionic acids and 4-alkoxybenzaldehydes were obtained from commercial sources and used as received.

4.3. Synthesis of the ligands (HLn) (1)

The Schiff bases were made by acetic-acid-catalyzed condensation of the 4-alkoxybenzaldehydes and the 4-alkoxyanilines in absolute ethanol, as described elsewhere [24]. Yields: HL2 (**1a**), 77%; HL4 (**1b**), 80%; HL6 (**1c**), 95%; HL8 (**1d**), 74%; HL10 (**1e**), 75%. Anal. Found: C, 76.05; H, 7.11; N, 5.13. $\text{C}_{17}\text{H}_{19}\text{NO}_2$ (**1a**) Calc.: C, 75.81; H, 7.11; N, 5.20%. Anal. Found: C, 77.69; H, 8.38; N, 4.30. $\text{C}_{21}\text{H}_{27}\text{NO}_2$ (**1b**) Calc.: C, 77.50; H, 8.36; N, 4.30%. Anal. Found: C, 78.99; H, 8.92; N, 3.73. $\text{C}_{25}\text{H}_{35}\text{NO}_2$ (**1c**) Calc.: C, 78.70; H, 9.24; N, 3.67%. Anal. Found: C, 79.89; H, 10.11; N, 3.16. $\text{C}_{29}\text{H}_{43}\text{NO}_2$ (**1d**) Calc.: C, 79.59; H, 9.90; N, 3.20%. Anal. Found: C, 80.58; H, 10.53; N, 2.87. $\text{C}_{33}\text{H}_{51}\text{NO}_2$ (**1e**) Calc.: C, 80.27; H, 10.41; N, 2.84%. IR (KBr): $\nu(\text{C}=\text{N})$ 1627; $\nu(\text{aryl})$ 1606, 844; $\nu(\text{C}-\text{O}-\text{C})$ 1251, 1029 cm^{-1} .

4.4. Synthesis of the complexes

4.4.1. $[\text{Pd}(\mu\text{-OAc})\text{Ln}]_2$ (2)

To a suspension of 1 g (1.48 mmol) of palladium acetate ($\text{Pd}_3(\text{OAc})_6$) 15 ml of acetic acid, was added the appropriate amount of the Schiff base **1** (4.45 mmol; Pd:imine, 1:1), and the stirred mixture was kept in a thermostat bath at 50°C for 14 h and then allowed to cool the yellow precipitate of **2** was filtered off, washed with cold acetone and air dried. No trace of metallic palladium was observed. Yields: **2a**, 95%; **2b**, 94%; **2c**, 95%; **2d**, 94%; **2e**, 94%. Anal. Found: C, 52.84; H, 4.92; N, 3.14. $\text{Pd}_2\text{C}_{38}\text{H}_{42}\text{N}_2\text{O}_8$ (**2a**) Calc.: C, 52.61; H, 4.88; N, 3.23%. Anal. Found: C, 56.51; H, 5.96; N, 2.77. $\text{Pd}_2\text{C}_{46}\text{H}_{58}\text{N}_2\text{O}_8$ (**2b**) Calc.: C, 56.39; H, 5.97; N, 2.86%. Anal. Found: C, 59.53; H, 6.89; N, 2.49. $\text{Pd}_2\text{C}_{54}\text{H}_{74}\text{N}_2\text{O}_8$ (**2c**) Calc.: C, 59.40; H, 6.83; N, 2.56%. Anal. Found: C, 62.04; H, 7.62; N, 2.25%. $\text{Pd}_2\text{C}_{62}\text{H}_{90}\text{N}_2\text{O}_8$ (**2d**) Calc.: C, 61.84; H, 7.53; N, 2.33%. Anal. Found: C, 64.09; H, 8.19; N, 2.12%. $\text{Pd}_2\text{C}_{70}\text{H}_{106}\text{N}_2\text{O}_8$ (**2e**) Calc.: C, 63.89; H, 8.12; N, 2.13%. IR (KBr): $\nu(\text{C}=\text{N})$ 1611; $\nu(\text{C}=\text{O})$ 1574, 1418; $\nu(\text{aryl})$ 1590, 836; $\nu(\text{C}-\text{O}-\text{C})$ = 1251, 1034 cm^{-1} .

4.4.2. $[Pd(\mu\text{-Cl})Ln]_2$ (**3**)

A solution of hydrochloric acid in methanol (Pd : HCl, 1 : 1) was cautiously added to a stirred solution of 1.48 mmol of **2** in 40 ml of dichloromethane. As the reaction proceeded, the initially red solution became yellow. After 1 h the solution was evaporated to dryness, and the residue was chromatographed on a silica column with dichloromethane as eluant. Addition of acetone to the eluates and evaporation of the dichloromethane gave **3** as yellow crystals, which were washed with acetone and air dried. Yield: **3a**, 95%; **3b**, 94%; **3c**, 94%; **3d**, 94%; **3e**, 96%. Anal. Found: C, 49.69; H, 4.32; N, 3.27. $Pd_2C_{34}H_{36}N_2O_4Cl_2$ (**3a**) Calc.: C, 49.78; H, 4.42; N, 3.41%. Anal. Found: C, 54.26; H, 5.57; N, 2.88. $Pd_2C_{42}H_{52}N_2O_4Cl_2$ (**3b**) Calc.: C, 54.09; H, 5.26; N, 3.00%. Anal. Found: C, 57.66; H, 6.58; N, 2.55. $Pd_2C_{50}H_{68}N_2O_4Cl_2$ (**3c**) Calc.: C, 57.48; H, 6.56; N, 2.68%. Anal. Found: C, 60.37; H, 7.33; N, 2.38. $Pd_2C_{58}H_{84}N_2O_4Cl_2$ (**3d**) Calc.: C, 60.21; H, 7.32; N, 2.42%. Anal. Found: C, 62.69; H, 7.97; N, 2.01. $Pd_2C_{66}H_{100}N_2O_4Cl_2$ (**3e**) Calc.: C, 62.46; H, 7.94; N, 2.21%. IR (KBr): $\nu(C=N)$ 1609; $\nu(\text{aryl})$ 1582, 830; $\nu(C-O-C)$ 1250, 1028; $\nu(Pd-Cl)$ 248 (Nujol mull) cm^{-1} .

4.4.3. $[Pd(\text{acac})Ln]$ (**4**)

Solid $Tl(\text{acac})$ (0.48 mmol) was added to the solution of **3** (0.24 mmol) in 25 ml of dichloromethane (Pd : acac, 1 : 1), and the mixture was stirred in the dark for 30 min. The $TlCl$ was filtered off, and ethanol was added to the solution. Evaporation of the dichloromethane gave **4** as pale-yellow crystals, which were filtered off, washed with ethanol and air dried. Yields: **4a**, 91%; **4b**, 85%; **4c**, 85%; **4d**, 85%; **4e**, 90%. Anal. Found: C, 55.98; H, 5.37; N, 2.91. $PdC_{22}H_{25}NO_4$ (**4a**) Calc.: C, 55.77; H, 5.32; N, 2.96%. Anal. Found: C, 59.30; H, 6.22; N, 2.63. $PdC_{26}H_{33}NO_4$ (**4b**) Calc.: C, 58.93; H, 6.28; N, 2.64%. Anal. Found: C, 62.13; H, 7.04; N, 2.36. $PdC_{30}H_{41}NO_4$ (**4c**) Calc.: C, 61.48; H, 7.05; N, 2.39%. Anal. Found: C, 64.14; H, 7.66; N, 2.17. $PdC_{34}H_{49}NO_4$ (**4d**) Calc.: C, 63.59; H, 7.69; N, 2.18%. Anal. Found: C, 65.71; H, 8.20; N, 2.05. $PdC_{38}H_{57}NO_4$ (**4e**) Calc.: C, 65.36; H, 8.23; N, 2.00%. IR (KBr): $\nu(C=N)$ 1610; $\nu(C=O)$ + $\nu(\text{aryl})$ 1581, 1537; $\nu(C-O-C)$ 1263, 1030 cm^{-1} .

4.4.4. $[Pd(NH\text{acac})Ln]$ (**5**)

To a solution of **3** (0.17 mmol) in 25 ml of dichloromethane was added a slight excess of 4-amino-3-penten-2-one (0.37 mmol) (Pd : NHacac, 1 : 1.1) and an excess of potassium carbonate. The mixture was stirred overnight and the solvent then evaporated off. The residue was extracted with dichloromethane and the extract was filtered (to remove insoluble potassium chloride and potassium NHacac); ethanol was then added to the filtrate. Evaporation of the dichloromethane gave

5 as pale-yellow crystalline solids, which were filtered off, washed with ethanol and air dried. Yields: **5a**, 87%; **5b**, 78%; **5c**, 88%; **5d**, 85%; **5e**, 87%. Anal. Found: C, 55.60; H, 5.41; N, 5.92. $PdC_{22}H_{26}N_2O_3$ (**5a**) Calc.: C, 55.88; H, 5.54; N, 5.92%. Anal. Found: C, 59.02; H, 6.37; N, 5.33. $PdC_{26}H_{34}N_2O_3$ (**5b**) Calc.: C, 59.04; H, 6.48; N, 5.30%. Anal. Found: C, 61.77; H, 7.07; N, 4.65. $PdC_{30}H_{42}N_2O_3$ (**5c**) Calc.: C, 61.59; H, 7.23; N, 4.78%. Anal. Found: C, 63.67; H, 7.59; N, 4.49. $PdC_{34}H_{50}N_2O_3$ (**5d**) Calc.: C, 63.69; H, 7.86; N, 4.39%. Anal. Found: C, 65.59; H, 8.14; N, 4.03. $PdC_{38}H_{58}N_2O_3$ (**5e**) Calc.: C, 65.46; H, 8.38; N, 4.02%. IR (KBr): $\nu(C=N)$ 1602; $\nu(N-H)$ 3362; $\nu(C=O)$ + $\nu(\text{aryl})$ 1575, 1535; $\nu(C-O-C)$ 1243, 1031 cm^{-1} .

4.4.5. $[Pd(\mu\text{-}(R)CH_3\text{-CHCl-CO}_2)Ln]_2$ (**6**)

A suspension of 1.22 mmol of the chloro complexes **3** and a slight excess of potassium (*R*)-2-chloropropionate (2.7 mmol; Pd : carboxylate, 1 : 1.1) in 25 ml of a mixture of dichloromethane : acetone (1 : 1 v/v) was stirred for 12 h during which the initially yellow suspension became red. The solvent was evaporated off and the residue extracted with dichloromethane. The extract was filtered and ethanol was added to the red filtrate. Evaporation of the dichloromethane gave yellow crystals of **6** which were washed with ethanol and air dried. Yields: **6a**, 92%; **6b**, 96%; **6c**, 95%; **6d**, 94%; **6e**, 98%. Anal. Found: C, 49.97; H, 4.56; N, 2.48. $Pd_2C_{40}H_{44}N_2O_8Cl_2$ (**6a**) Calc.: C, 49.81; H, 4.60; N, 2.90%. Anal. Found: C, 53.99; H, 5.61; N, 2.22. $Pd_2C_{48}H_{60}N_2O_8Cl_2$ (**6b**) Calc.: C, 53.75; H, 5.26; N, 2.61%. Anal. Found: C, 56.88; H, 6.32; N, 2.29. $Pd_2C_{56}H_{76}N_2O_8Cl_2$ (**6c**) Calc.: C, 56.57; H, 6.44; N, 2.36%. Anal. Found: C, 59.40; H, 7.13; N, 2.17. $Pd_2C_{64}H_{92}N_2O_8Cl_2$ (**6d**) Calc.: C, 59.08; H, 7.13; N, 2.15%. Anal. Found: C, 61.56; H, 7.72; N, 2.06. $Pd_2C_{72}H_{108}N_2O_8Cl_2$ (**6e**) Calc.: C, 61.19; H, 7.70; N, 1.98%. IR (KBr): $\nu(C=N)$ 1611; $\nu(C=O)$ 1574; $\nu(\text{aryl})$ 1590, 836; $\nu(C-O-C)$ 1251, 1034 cm^{-1} .

4.4.6. $[Pd(\mu\text{-}(S)CH_3\text{-CHBr-CO}_2)Ln]_2$ (**7**)

In a typical procedure, (*S*)-2-bromopropionic acid (25.4 μ l, 0.28 mmol) was added to a suspension of **2** (0.13 mmol) in acetone (Pd : carboxylate, 1 : 1.1); the mixture was stirred for 2 h and then allowed to cool. The orange-yellow products were filtered off and re-crystallized from dichloromethane-ethanol. The crystals were filtered off, washed with cold ethanol and air dried. Yields: **7a**, 71%; **7b**, 89%; **7c**, 80%; **7d**, 81%; **7e**, 91%. Anal. Found: C, 45.73; H, 3.86; N, 2.83. $Pd_2C_{40}H_{44}N_2O_8Br_2$ (**7a**) Calc.: C, 45.61; H, 4.21; N, 2.66%. Anal. Found: C, 49.87; H, 4.76; N, 2.30. $Pd_2C_{48}H_{60}N_2O_8Br_2$ (**7b**) Calc.: C, 49.46; H, 5.19; N, 2.40%. Anal. Found: C, 53.256; H, 5.80; N, 2.24. $Pd_2C_{56}H_{76}N_2O_8Br_2$ (**7c**) Calc.: C, 52.64; H, 5.99; N, 2.19%. Anal. Found: C, 55.81; H, 6.34; N, 2.33.

$\text{Pd}_2\text{C}_{64}\text{H}_{92}\text{N}_2\text{O}_8\text{Br}_2$ (**7d**) Calc.: C, 55.30; H, 6.67; N, 2.01%. Anal. Found: C, 58.04; H, 6.68; N, 1.91.
 $\text{Pd}_2\text{C}_{72}\text{H}_{108}\text{N}_2\text{O}_8\text{Br}_2$ (**7e**) Calc.: C, 57.57; H, 7.25; N, 1.86%. IR (KBr): $\nu(\text{C}=\text{N})$ 1607; $\nu(\text{C}=\text{O})$ 1573, 1397; $\nu(\text{aryl})$ 1582, 829; $\nu(\text{C}-\text{O}-\text{C})$ 1245, 1031 cm^{-1} .

4.4.7. Reaction of $[\text{Pd}(\mu\text{-OAc})\text{L6}]_2$ with (*R* + *S*) $\text{CH}_3\text{-CHBr-CO}_2\text{H}$ (**8**)

A racemic mixture of (*R* + *S*) $\text{CH}_3\text{-CHBr-CO}_2\text{H}$ made from the commercial (*R*)-2-bromopropionic acid (19.2 μl , 0.21 mmol) and (*S*)-2-bromopropionic acid (16.7 μl , 0.18 mmol) was added to a suspension of **2c** (**L6**) (0.19 mmol) in acetone (Pd:carboxylate, 1:1.1). The mixture was stirred for 2 h, the acetone then evaporated, and the crude product recrystallized from dichloromethane ethanol. The orange–yellow crystals of **8** were filtered off, washed with cold ethanol and air dried. Yield: 64%. Anal. Found: C, 57.66; H, 6.58; N, 2.55. $\text{Pd}_2\text{C}_{56}\text{H}_{76}\text{N}_2\text{O}_8\text{Br}_2$ (**8**) Calc.: C, 57.48; H, 6.56; N, 2.68%. IR (KBr): $\nu(\text{C}=\text{N})$ 1607; $\nu(\text{C}=\text{O})$ 1572, 1397; $\nu(\text{aryl})$ 1582, 830; $\nu(\text{C}-\text{O}-\text{C})$ 1245, 1030 cm^{-1} .

4.4.8. $[\text{Pd}(\text{PhNacac})\text{L6}]$ (**9**)

The complex was prepared as described for derivatives **5** and isolated as a yellow crystals. Yield: 85%. Anal. Found: C, 65.67; H, 7.11; N, 4.49. $\text{PdC}_{36}\text{H}_{46}\text{N}_2\text{O}_3$ (**9**) Calc.: C, 65.40; H, 7.01; N, 4.24%. IR (KBr): $\nu(\text{C}=\text{N})$ 1602; $\nu(\text{C}=\text{O}) + \nu(\text{aryl})$ 1575, 1535; $\nu(\text{C}-\text{O}-\text{C})$ 1243, 1031 cm^{-1} .

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- [16] Unexpected differences between **7** made with the (*R*) and (*S*) acids were found. At our request, Janssen Chimica analyzed the optical purity of their commercial chiral carboxylic acids, finding the following composition: *S*-2-bromopropionic acid; 99.2% chemical purity, 93.25% (*S*) plus 6.75% (*R*). (*R*)-2-bromopropionic acid; 99.4% chemical purity, 87.73% (*R*) plus 12.27% (*S*). Thus we decided not to use the *R* derivatives. We thank Albert Vanneste (Janssen Chimica) for these analyses.
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