

Mesogens based on palladium orthometalated complexes with carboxylato bridges: tuning and shaping a non-planar molecule

Laura Díez, Pablo Espinet*, Jesús A. Miguel, M. Paz Rodríguez-Medina

Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain

Received 20 July 2004; accepted 13 September 2004

Abstract

The binuclear cyclopalladated compounds $[\text{Pd}_2(\mu\text{-OH})_2(\text{L}^n)_2]$ (**1**) derived from imines $\text{HL}^n = p\text{-C}_n\text{H}_{2n+1}\text{O-C}_6\text{H}_4\text{-CH=N-C}_6\text{H}_4\text{-OC}_n\text{H}_{2n+1-p}$ ($n = 6, 10$) react with carboxylic acids to give the derivatives $[\text{Pd}_2(\mu\text{-ox})_2(\text{L}^n)_2]$ (**2**) with a planar core for oxalic acid, and $[\text{Pd}_2(\mu\text{-OOCR})_2(\text{L}^n)_2]$ (**3–7**) compounds with a non-planar ridge tent structure for other RCOOH acids: (**3**) $\text{R} = \text{C}_m\text{H}_{2m+1}$ ($m = 1, 3, 5, 7, 9, 11, 13, 15, 17$); (**4**) $\text{R} = \text{CH}_2(\text{OCH}_2\text{CH}_2)_p\text{OCH}_3$ ($p = 1, 2$); (**5**) $\text{R} = \text{CH}_2\text{-C}_6\text{H}_4\text{-OC}_q\text{H}_{2q+1-p}$ ($q = 2, 4, 6, 8, 10, 12$); (**6**) $\text{R} = \text{C}_6\text{H}_4\text{-OC}_r\text{H}_{2r+1-p}$ ($r = 4, 10$); (**7**) $\text{R} = \text{C}^*\text{H}(\text{OH})\text{CH}_3$. The acids used were designed to explore the effect on the thermal properties of the compounds prepared of systematic variations in the type of carboxylato ligand, which induce structure, packing, and polarity changes, and in the length of the carboxylato chain. Most of the complexes prepared, even when far from planar, show liquid crystal behavior and display nematic, smectic A and smectic C phases.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Metallomesogens; Palladium; Orthometalated imine; Carboxylato; Liquid crystals

1. Introduction

The tendency for a given molecule to display a given liquid-crystalline superstructure is usually strongly related to its shape [1]. Thus, rod-like molecules preferentially assemble into nematic or smectic mesophases, whereas disc-like molecules tend to display columnar phases. Notwithstanding that, materials with columnar phases can be generated also from molecules which are not disc-shaped, and there are compounds showing calamitic phases with molecular structures rather different from rod-like.

Dinuclear and mononuclear ortho-palladated compounds are one of the most widely studied class of metallomesogens [2]. Some pioneering discoveries in metallomesogens have been made within this kind of mesogenic materials [3–5]. In dimeric molecules

$[\text{Pd}_2(\mu\text{-X})_2\text{L}^n_2]$ ($\text{L}^n =$ orthopalladated imines and azines) the X-bridges determine the basic molecular shape, and consequently have a marked influence on the mesogenic or lack of mesogenic properties of the material. Thus, thiocyanato, chloro and bromo bridges produce planar dimeric structures prone to give mesomorphism [2g,2h,6–9]. Carboxylato bridges force the molecule into a non-planar ridge-tent (or open-book) structure (Fig. 1). According to single crystal X-ray diffraction studies [10], the dihedral angle between the two coordination planes is about 30° and there is some Pd...Pd bonding interaction. The aspect ratio of this structure is not propitious to give rise to mesophases, as empty spaces in the direction of the ridge of the tent (symbolized as a grey volume in Fig. 1) should produce an inefficient space filling if the alkyl chains remained stretched (as represented in the Fig. 1). As a consequence, a curling of the chains must occur to fill that otherwise empty space, leading to a shorter length/width ratio and disfavoring mesogenic behavior.

* Corresponding author. Tel.: +34 9834 23231; fax: +34 9834 23013.
E-mail address: espinet@qi.uva.es (P. Espinet).

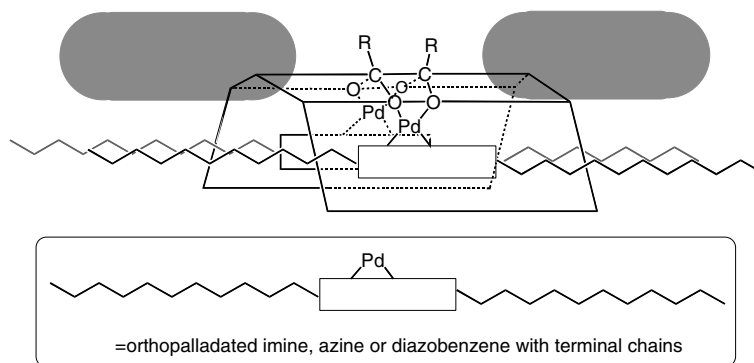


Fig. 1. Non-planar structures in dimeric molecules with carboxylato bridges: the grey volume in the direction of the ridge of the tent highlights the empty spaces.

The recent availability of $[\text{Pd}_2(\mu\text{-OH})_2\text{L}_2^n]$ ($\text{HL}^n = p\text{-C}_n\text{H}_{2n+1}\text{O-C}_6\text{H}_4\text{-CH=N-C}_6\text{H}_4\text{-OC}_n\text{H}_{2n+1}\text{-p}$, $n = 2, 6$ and 10) towards protic substrates [11], has provided us with an extremely convenient general entry to many bridged complexes, by reaction with acidic substrates. Using this preparative approach, we report here the preparation and thermal behavior of a variety of carboxylato bridged dimers $[\text{Pd}_2(\mu\text{-O}_2\text{CR})_2\text{L}_2^n]$ ($n = 6, 10$). The carboxylato groups (oxalato, n -alkylcarboxylato, n -oxaalkylcarboxylato, p -alkoxyphenylacetato, p -alkoxybenzoato and chiral carboxylato) are chosen to produce different structural effects [12].

2. Results and discussion

2.1. Syntheses and structures

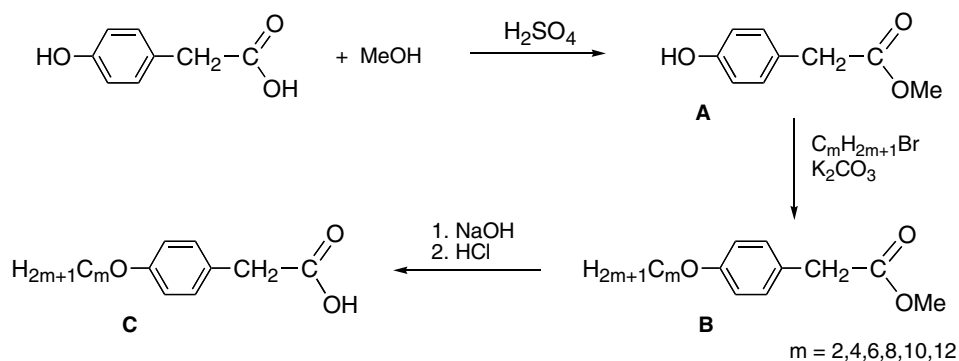
The complexes $[\text{Pd}_2(\mu\text{-OH})_2\text{L}_2^n]$ were prepared by published methods [11]. The acids employed were obtained from commercial sources, except for p -alkoxy-substituted-phenylacetic acids, which were synthesized in a three-step reaction as shown in Scheme 1. Commercial 4-hydroxy-phenylacetic acid was transformed into its methyl ester using H_2SO_4 as catalyst. The unsymmet-

rical ethers **B** were obtained in a Williamson ether synthesis using the methyl-(4-hydroxy)-phenylacetate **A** and the corresponding 1-bromoalkane in acetone. Finally, saponification with NaOH followed by acidification with cold concentrated hydrochloric acid afforded the acids **C**.

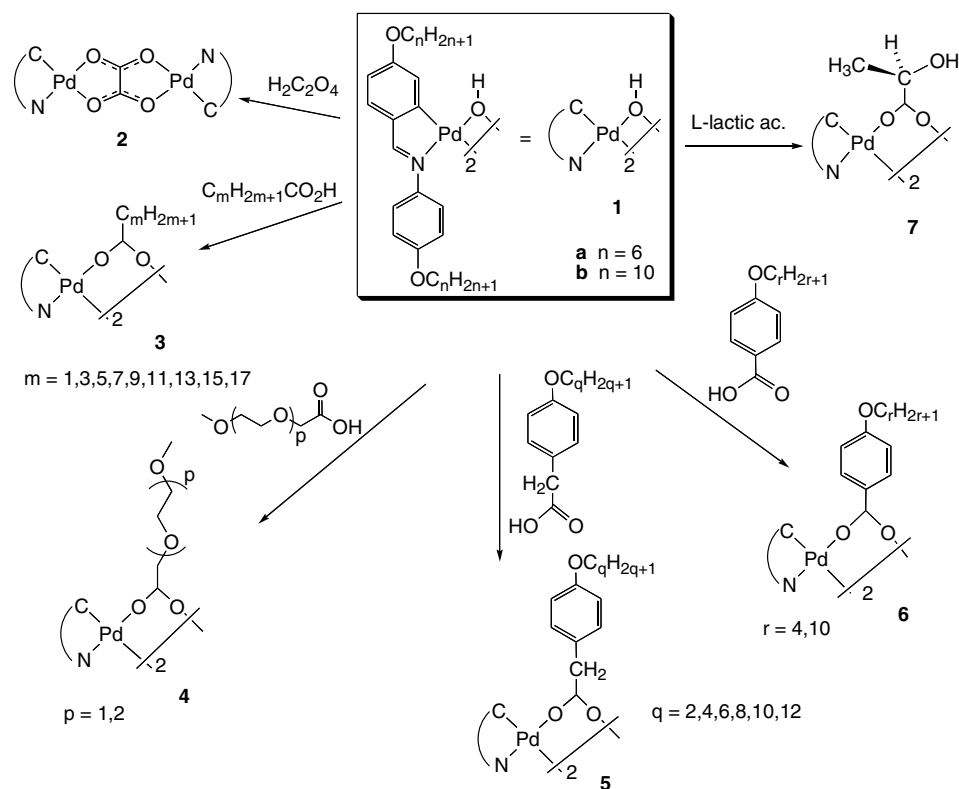
The dinuclear complexes **2–7** were obtained from the hydroxo complexes **1** and the appropriate acid, at room temperature in dichloromethane (Scheme 2). All the complexes were isolated in good yield and characterized by IR, ^1H NMR and elemental microanalyses.

The oxalato-bridged group in complexes **2** prefers the chelating coordination to give five-membered metalacycles, and forces the molecules into a strictly coplanar $\text{Pd}(\mu_2\text{-oxalato})\text{Pd}$ geometry, in accordance with structures found for similar complexes by X-ray diffraction studies in the literature [13]. The ^1H NMR spectra of complexes **2** show a mixture of *cis* (or *syn*) and *trans* (or *anti*) isomers (relative to the imine arrangement in each half of the molecule) in a 40:60 ratio. Only the *trans* isomer (presumed to be the major component in the mixtures) is depicted in Scheme 2.

The carboxylato-bridged complexes **3–7** were obtained as the *trans* isomers, with a small amount (about 4%) of the *cis* isomers. The ^1H NMR parameters (partic-



Scheme 1.



Scheme 2.

Table 1
Parameters of ^1H NMR for compounds 2–7^a

Compounds	H	H ³	H ⁵	H ⁶	H ^{2'6'} , H ^{3'5'} ^b	OCH ₂	OCH ₂ '	Others ^c
2	7.88 s ^d	6.85 d (2.3)	6.61 dd ^e (8.3)	7.22 d	7.36, 6.93 (8.9)	4.01		
3	7.45 s ^d	6.02 d (2.3)	6.55 dd (8.3, 2.3)	7.11 d (8.3)	7.66, 6.62 (8.9)	3.71 m 3.48 m	3.88 m, (6.6)	2.12 m O ₂ CCH ₂ ;
4	7.46 s ^d	6.01 d (2.3)	6.56 dd (8.3, 2.0)	7.12 d (8.3)	6.64, 6.62 (9.4)	3.74 m 3.53 m	3.88 m	3.88 m O ₂ CCH ₂ ; 3.53 m O(CH ₂) ₂ O; 3.38 s OCH ₃
5	7.40 s ^d	5.73 d (2.4)	6.49 dd (8.3, 2.0)	7.06 d (8.3)	6.58, 6.50 (9.1)	3.39 m 3.12 m	3.89 m (6.6)	3.39 m O ₂ CCH ₂ ; 7.07, 6.75 ^b (9.0) C ₆ H ₄ ; 3.89 m OCH ₂ ;
6	7.55 s ^d	5.97 d (2.3)	6.50 dd (8.3, 2.3)	7.14 d (8.3)	6.70, 6.44 (8.8)	2.33 m 2.92 m	3.78 m 3.67 m	8.01, 6.78 (8.8) C ₆ H ₄ ; 3.95 t (6.5) OCH ₂
7	7.51 s 7.49 s	5.89 d 5.81 d (2.2)	^f	7.17 d 7.16 d (8.3)	6.60 m	3.96 m 3.75 m 3.52 m		4.08 m CH; 3.19 m OH; 1.22 d, 1.18 d (6.8) CH ₃

^a In CDCl₃ at 300.13 MHz; the numbers in parentheses correspond to $J(^1\text{H}-^1\text{H})$ in Hz; s, singlet; d, doublet; t, triplet; m, multiplet.^b (AB)₂ spin system.^c Aliphatic protons appear in the range $\delta = 0.8$ –1.9 ppm.^d Signals for the *cis* isomers are observed at 7.89 s (2), 7.59 (3); 7.57 (4); 7.54 (5); 7.54 (6).^e The signal for the *cis* isomer is observed at 6.63 dd.^f Overlapped with H^{2'6'}, H^{3'5'}.

ularly the H³ proton resonance appearing around $\delta = 6.0$ ppm, see Table 1) support that they a ridge tent structure, rigid in the NMR time scale as far as inversion

of the folding is concerned [17,14]. This makes the pairs of hydrogen atoms on each half of the molecule diastereotopic, as can be seen in the methylene groups of the

iminic alkoxy chains and in the first methylene group of the carboxylato bridges. The ^1H NMR parameters of the imine moiety (Table 1) are very similar for all the compounds. The larger difference in chemical shifts is observed for the iminic proton and for H^3 , which are very sensitive to structural changes [17,11]. The assignments given in Table 1 for **5** were assessed by COSY and NOESY experiments.

Complexes **7** were made from the commercially available form of (*S*)-lactic acid. The IR band observed at 3605 cm^{-1} , due to $\nu(\text{OH})$, and the chemical shift of H^3 (around $\delta = 5.8$ ppm) are typical of dimers with carboxylato bridges. Several examples of this type of structure have been confirmed by X-ray diffraction for α -hydroxycarboxylates [15]. Since the rigid ridge tent structure is chiral (Λ and Δ enantiomers) [17,14], the use of (*S*)-lactic acid gives rise to *trans*- $\Delta(\text{S,S})$ and *trans*- $\Lambda(\text{S,S})$ diastereomers, which are observed in a 40:60 in the ^1H NMR spectrum.

2.2. Mesogenic behavior

The family of complexes studied here offers a complete and systematic panorama of the effects of changes in the carboxylato bridges. This had been studied only partially on some particular azine or imine systems [4,16–18]. The thermal properties of the complexes were studied using polarized light optical microscopy and differential scanning calorimetry (DSC). The data are summarized in Table 2 and are plotted for direct comparison in Fig. 2.

The bridging oxalate imposes a planar structure to the central bimetallic core of the dimer. Thus the intermolecular interactions are very strong leading to melting points of **2a–b** above $230\text{ }^\circ\text{C}$. That is even higher than for the hydroxo and chloro bridged analogues, which are also planar. Due to the very high transition temperature the compounds decompose at, or just above, their clearing point.

Compounds **3a** ($m = 1, 3, 5, 7, 9, 11, 13, 15, 17$), with imine L^6 , exhibit thermotropic behavior only for the largest chains ($m \geq 11$). They display a smectic A phase, with spherulites and homeotropic zones, and a nematic phase (schlieren texture) in a very short temperature range (about $2\text{ }^\circ\text{C}$ only). In addition, a SmC phase is observed on cooling for $m \geq 13$. A very sharp decrease in melting point is observed on going from $m = 1$ to $m = 3$, which was expected as the increase in length of the carboxylato chain, for short chains, leads to an increase in molecular width and a less efficient packing of the molecules in the crystal state.

As stated in Section 1, the non-planar structure of the complexes is expected to disfavor an efficient molecular packing. X-ray diffraction studies in the mesophase on complexes with orthopalladated azines and carboxylato bridges have shown that these molecules tend to pack by

lateral association, each one sliding over the other neighbors in order to fill the space in the best possible way [16]. A similar packing is expected for the imine complexes, and indeed mesomorphism appears only when the flexible alkyl chains in the carboxylate are long enough to orient themselves along the main axis of the imine ligand (z , molecular length), filling the grey zones in Fig. 1 and providing a more cylindrical shape to the molecule (Fig. 3).

In contrast, complexes **3b**, with imine L^{10} , are liquid crystals except when the bridge is acetate, $m = 1$. Only when the value of the alkyl carboxylato chain is 5 or 7 are the compounds enantiotropic, with a very short temperature range ($2\text{--}4\text{ }^\circ\text{C}$) on heating.

Comparing for identical alkoxy chains the properties of the imine complexes **3b** with related azine complexes reported in our previous study [16], the melting temperatures are about $15\text{ }^\circ\text{C}$ higher for the former. This is somewhat surprising since more extended conjugated aromatic cores usually increase the melting point noticeably. Probably this behavior is due to the different isomeric compositions for the two types of complexes (mixtures lower the transition temperatures). The *trans/cis* mixture is 3/1 for the azines and 96/4 for the imines.

A remarkable variation in thermal properties is produced when some methylene groups in the carboxylato bridges are substituted for oxygen. Thus complexes **4** with 3,6-dioxaheptanoic ($p = 1$) or 3,6,9-trioxadecanoic acids ($p = 2$) display enantiotropic SmA phases. Comparing the two compounds **4a** in Fig. 2 ($p = 1, 2$), a decrease in the melting and the clearing temperature is observed when the length of the polyethers chains increases. A very interesting increase in range of the smectic A phase ($>50\text{ }^\circ\text{C}$) occurs when the length of the imine chains changes from six (**4a**) to ten (**4b**) carbon atoms, which decreases the melting point and increases the clearing temperature for **4b**.

It is known for organic systems that the substitution of one methylene by oxygen in the alkoxylic chains of imines derived from benzylideneanilines lowers the clearing point of smectic and nematic phases [19]. Also, the biphenyl derivatives (4-hexyl,4'-hexyloxy)biphenyl and (4-hexyl,4'-nonyloxy)biphenyl, with alkyl chains, are liquid crystals but the oligoethylene glycol 4,4'-bis[2-(2-methoxy-ethoxy)ethoxy]biphenyl with comparable length is not mesomorphic [20,21], whereas the replacement of alkyl chain linkages by polyethers causes an increase in range of mesophase in biphenylophane derivatives [21], and a decrease in the case of 2- or 5-phenylpyrimidine *para*-cyclophane [22]. This has been explained considering the influence of these structural changes on the amphiphilicity of the molecules. The increase in range of mesophase reported here for complexes **4** can also be explained by the effect that replacing alkyl by polyether chains has on the

Table 2
Phase transition temperatures (°C) and enthalpies (kJ mol⁻¹) (in parentheses) for compounds 2–7^a

Compounds	<i>m/p/q/r</i>	Heating scan
2a		Cr 266 ^b SmA 277 ^{b,c} I
2b		Cr 231.8 (36.1) SmA 257 ^{b,c} I
3a	1	Cr 217.0 ^c (56.2) I
3a	3	Cr 156.9 (37.8) I
3a	5	Cr 146.7 (33.1) I
3a	7	Cr 143.6 (33.9) I
3a	9	Cr 142.4 (59.2) I
3a	11	Cr 51.8 (6.2) Cr' 130 ^b SmA 132.0 (39.6) ^d I
3a	13	Cr 118.8 SmA 121 ^b N 122.9 ^c (34.9) ^d I I 121.3 N 120 ^b (-4.9) ^d SmA 98 ^b (SmC) ^f
3a	15	Cr 62.9 (-12.7) Cr' 108.8 SmA 111 ^b (41.5) ^d N 116.8 ^c (3.9) I I 115.1 N 114 ^b (-4.4) ^d SmA 92 (SmC) ^f
3a	17	Cr 72.4 (-9.4) Cr' 108.1 (46.3) I I 108.1 ^c (N) ^f 108 ^b (-4.3) ^c (SmA) ^f 86.1 (-0.3) (SmC) ^f
3b	1	Cr 205.5 ^c (62.7) I
3b	3	Cr 114.0 (9.2) Cr' 135.7 (31.9) I I 129.2 (-5.3) (SmA) ^f
3b	5	Cr 128 ^b SmA 131.7 ^c (25.9) ^d I
3b	7	Cr 128 ^b SmA 130.4 ^c (31.8) ^d I
3b	9	Cr 95.5 (-13.6) Cr' 129.9 (50.2) I I 119.6 (-5.4) (SmA) ^f
3b	11	Cr 77.5 (-9.8) Cr' 127.1 (56.0) I I 116.3 (-5.4) (SmA) ^f
3b	13	Cr 81.4 (9.5) Cr' 97.7 (-15.8) Cr'' 126.6 (63.9) I I 115.3 (-5.4) (SmA) ^f
3b	15	Cr 81.7 (-15.3) Cr' 117.3 (64.3) I I 114.1 (-5.4) (SmA) ^f 100.8 (-1.5) (SmC) ^f
3b	17	Cr 85.4 (-21.6) Cr' 113.5 (64.7) I I 112.2 (-5.6) (SmA) ^f 98.4 (-1.6) (SmC) ^f
4a	1	Cr 119.6 (18.4) SmA 133.3 (5.3) I
4a	2	Cr 93.1 (16.9) SmA 103.8 (3.7) I
4b	1	Cr 91.6 (9.7) SmA 145.8 (5.8) I
4b	2	Cr 67.8 (13.2) SmA 127.9 (6.7) I
5a	2	Cr 172 ^b SmA 175.8 (37.6) ^d I
5a	4	Cr 164.7 (37.2) SmA 170.5 (5.6) I
5a	6	Cr 136.2 (38.4) SmA 168.1 (8.2) I I 167.9 ^c (-7.4) SmA 139.3 (-0.7) (SmC) ^f
5a	8	Cr 122.9 (23.6) SmC 131.6 (0.6) SmA 162.4 (7.7) I
5a	10	Cr 115.6 (19.8) SmC 123.9 (0.3) SmA 153.3 (7.5) I
5a	12	Cr 115.0 (21.4) SmC 125.8 (0.5) SmA 152.9 (8.7) I
5b	2	Cr 138.5 (20.5) SmA 174.0 (9.7) I I 173.9 (-9.7) SmA 134 ^b (SmC) ^f
5b	4	Cr 125.4 (21.1) Cr' 145.6 (12.5) SmA 165.6 (8.0) I I 163.3 (-8.7) SmA 140 ^b (SmC) ^f
5b	6	Cr 131.2 (28.2) SmC 138.9 (1.4) SmA 159.5 (6.0) I
5b	8	Cr 128.8 (32.8) SmC 133 ^b SmA 153.2 (7.8) I
5b	10	Cr 123.7 (30.3) SmC 129 ^b SmA 148.9 (7.4) I
5b	12	Cr 121.6 SmC 1289 ^b SmA 147.1 (7.3) I
6a	4	Cr 140.8 (30.9) Cr' 174.9 (36.9) I
6a	10	Cr 128.6 (33.9) I
6b	4	Cr 65.6 (-8.7) Cr' 114.7 (21.9) SmC 131 ^b (4.3) SmA 148 ^{b,c} I
6b	10	Cr 133.3 (56.3) I I 128.6 (SmA) ^f
7a		Cr 102.8 (14.2) SmA 176.0 (6.6) I
7b		Cr 85.1 (4.0) SmA 162.9 (7.0) I

^a Cr, Cr', Cr'' = crystalline phase; SmA = smectic A; SmC = smectic C; I = isotropic liquid; N = nematic.

^b Observed by polarized light microscopy.

^c Transition with decomposition.

^d Combined enthalpies.

^e Peak data.

^f Monotropic transition (data for the cooling cycle).

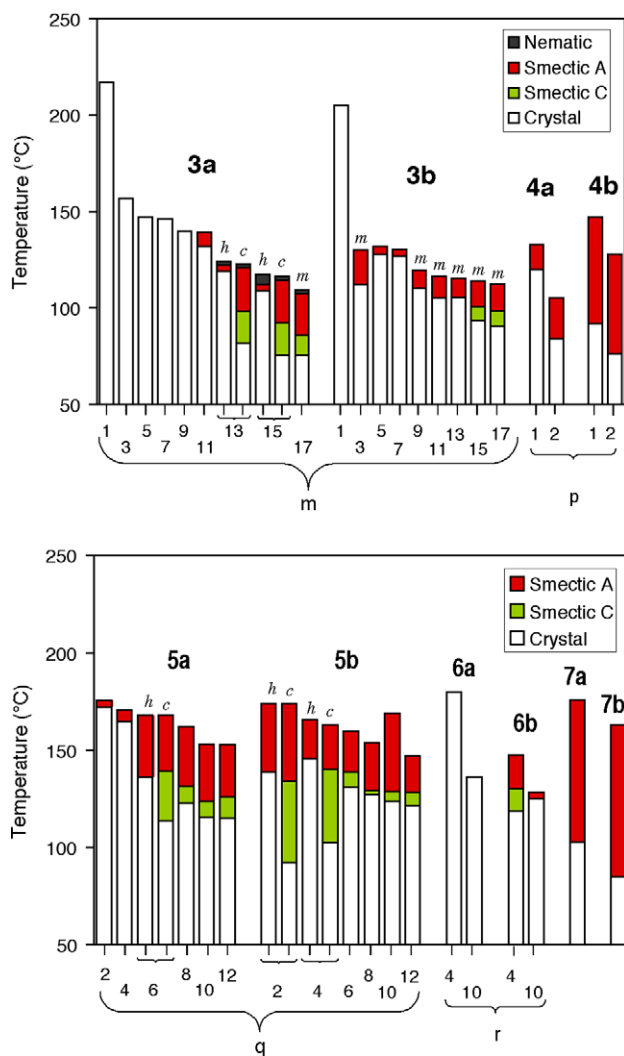


Fig. 2. Thermotropic behavior of Pd complexes 3–7. The number (m , p , q or r) in the x -axes refers to the labels used in Scheme 2. When monotropic transitions are present two bars are shown, one for the heating (h) and one for the cooling (c) cycle; m , monotropic transition.

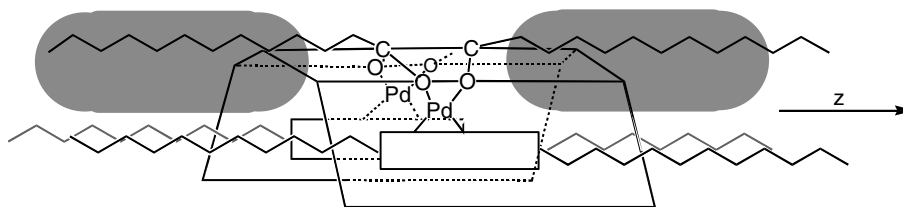


Fig. 3. Schematic representation with the alkyl chains of the carboxylate filling the grey zones.

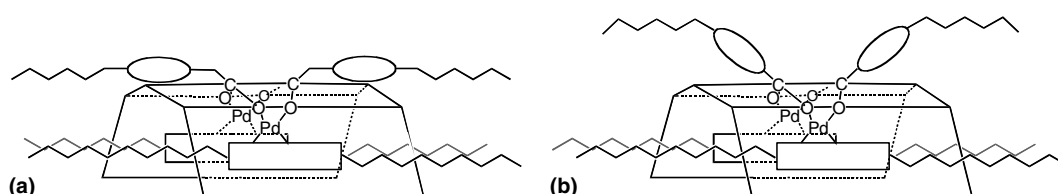


Fig. 4. Schematic representation of the ridge tent-shaped derivatives: (a) $[\text{Pd}(\mu\text{-alkoxyphenyl acetate})\text{L}^n]_2$ (5) and (b) $[\text{Pd}(\mu\text{-alkoxybenzoate})\text{L}^n]_2$ (6).

amphiphilicity of the molecules, and the fact that the microsegregation [23] of the polar regions (rigid cores and polyether chains) from the lipophilic chains should become more efficient.

Complexes 5, derived from 4-alkoxyphenyl acetic acid ($p\text{-C}_m\text{H}_{2m+1}\text{OC}_6\text{H}_4\text{CH}_2\text{CO}_2\text{H}$, $m = 2, 4, 6, 8, 10, 12$), are enantiotropic liquid crystals. The influence of the chain length on the mesogenic properties of the dimer complexes can be seen in Fig. 2. Smectic A phases were found for these complexes. In addition, SmC phases appeared for the complexes with L^6 and the longest alkoxy chains ($m \geq 6$) in the 4-alkoxyphenyl acetate, and for all the complexes with L^{10} (for $m = 2, 4$ the SmC phases are monotropic). The absence of nematic phases is not unexpected, considering the presence of the two additional aryl rings that stabilize the smectic phase. Longer chains, whether on the 4-alkoxyphenyl acetate or on the imine, lower the melting and clearing points. The influence of the chain length of the carboxylate on the thermal behavior is larger for L^6 than for L^{10} . For the compounds with L^6 the increase in the length of the chain from 2 to 12 carbons produces a bigger decrease in melting (59°C) than in clearing points (21°C) and greater ranges of mesogenic behavior are produced. For L^{10} the melting and clearing points are similarly reduced and the mesophase ranges are maintained.

The thermal behavior observed is consistent with the model proposed in Fig. 1. In the p -alkoxyphenylacetate bridged complexes (compounds 5, Fig. 4a) we presume that the aryl moiety (depicted as an ellipse) and the long chain can immediately arrange more or less parallel to the molecular long axis, improving the mesogenic properties. When this methylene group is lacking (derivatives 6, Fig. 4b) the rigidity of the aryl group on the carboxylic fragment imposes a less favorable molecular shape.

Finally, the complexes with 2-hydroxypropionate (L -lactate) bridges, 7a and 7b, exhibit a wide range of smec-

tic A phase. Compared to the lack of mesomorphism for the corresponding acetato-bridged complexes, this might look is somewhat surprising, since *L*-lactate is bulkier than acetate and should disturb more the molecular packing in the mesophase. This positive effect on mesogenic properties for bulkier carboxylates has been observed also in 2-halopropionate bridged complexes of palladium [17] and platinum [5] with imines and can be the result of a combination of factors such as the positive influence of the new dipole moment introduced by C–OH bonds, the formation of isomeric mixtures (the chiral carboxylates as bridges gives rise to a number of diastereomers *cis*-*S,S*:*trans*- $\Delta S,S$:*trans*- $\Lambda S,S$ (4:38:58)), and a more efficient space filling in the melt: the halo or hydroxo substituents can be oriented into the empty region close to the hinge of the molecule, thus helping to partially fill this unfavorable gap, while not increasing the width of the molecule. Comparison of the mesogenic behavior of **7a** and **7b** with the chloropropionate analogues of palladium shows that the effect of replacing Cl by OH in the propionate bridges is thermally beneficial, yielding an important decrease in the melting temperatures (up to 50 °C) with only a slight decrease in the clearing temperatures, and producing a wider mesogenic range. Although the phases obtained are not chiral in this case, the use of lactato bridges looks very promising.

3. Conclusions

This study shows that, once the rules of the molecular system are understood, metal-containing compounds with unfavorable molecular shapes can be manipulated and tuned to obtain liquid crystalline compounds. In this case the features of the carboxylato bridges in dimers $[\text{Pd}_2(\mu\text{-OOCR})_2(\text{L}^n)_2]$ are a key factor to control of their thermal behavior. They can be manipulated to shape an essentially inadequate ridge tent-shaped molecule into a more cylindrical form, or to provide extra interactions easing microsegregation.

4. Experimental

4.1. Materials and general methods

Literature methods were used to prepare the imines $[\text{Pd}_2(\mu\text{-OH})_2(\text{L}^n)_2]$ (**1**) [11]. Aliphatic acids $\text{HO}_2\text{CC}_m\text{H}_{2m+1}$, oxalic acid and *L*(+)-lactic acid were obtained from commercial sources and were used without further purification. 3,6-Dioxaheptanoic and 3,6,9-trioxadecanoic acids were supplied by Hoechst AG. C, H, N analyses were carried out on a Perkin–Elmer 2400 microanalyzer. All new compounds gave satisfactory elemental analyses (Table S1, Supplementary Mate-

rials). IR spectra were recorded on a Perkin–Elmer FT-1720X spectrometer using Nujol mulls between polyethylene plates. ^1H NMR spectra were recorded on Bruker AC-300 or ARX-300 MHz spectrophotometers. The textures of the mesophases were studied with a Leitz microscope with polarizers equipped with a Mettler FP82HT hot stage and a Mettler FP90 central processor, at a heating rate of approximately $10\text{ }^\circ\text{C min}^{-1}$. Transition temperatures and enthalpies were measured by differential scanning calorimetry, with a Perkin–Elmer DSC-7 apparatus operated at a scanning rate of $10\text{ }^\circ\text{C min}^{-1}$ on heating. The apparatus was calibrated with indium as standard ($156.6\text{ }^\circ\text{C}$, 28.5 J g^{-1}), the samples were sealed in aluminum capsules in air, and the holder atmosphere was dry nitrogen.

Typical preparation procedures and physical data are given below. All analogous ligands and complexes were prepared in the same way.

4.2. Methyl-(4-hydroxy)phenylacetate (*A*)

To a nitrogen flushed flask containing, *p*-hydroxyphenylacetic acid (5.00 g, 33 mmole) dissolved in 100 ml of anhydrous MeOH was added a catalytic amount of H_2SO_4 , and the mixture was refluxed for 7 h. The reaction mixture was poured into water and extracted three times with ether. The organic layer was separated, acidified with NaHCO_3 , and dried over MgSO_4 . The solvent was evaporated to yield a white solid. Yield: 82%. ^1H NMR (CDCl_3): δ 7.09, 6.76, (AB system $J_{\text{AB}} = 8.7\text{ Hz}$, C_6H_4); 3.69 (s, CH_3); 3.56 (s, CH_2).

4.3. 4-(Decyloxy)phenylacetic acid (*C*, $m = 10$)

To a mixture of 100 ml of acetone–DMSO (90/10) was added methyl-(4-hydroxy)phenylacetate (**A**) (4.5 g, 27.1 mmol), K_2CO_3 (3.7 g, 27.1 mmole) and 1-bromodecane (5.62 ml, 27.1 mmole). The suspension was refluxed for 18 h and then allowed to cool down. The solution was then poured into 500 ml of H_2O , acidified with diluted formic acid until pH = 5, and then extracted with dichloromethane ($3 \times 30\text{ ml}$). The organic phase was separated, dried over MgSO_4 , filtered and the solvent evaporated on a rotary evaporator. The residue was purified by column chromatography (silica gel, hexane/ether 9:1 as eluent). The product obtained after evaporation was a white solid, which was added to a solution of NaOH (5 g) in 100 ml of water. The suspension was refluxed for 2 h until the solid got dissolved. The resulting solution was cooled and acidified with HCl. A white precipitate was formed which was filtered from the solution, washed thoroughly with water and dried. Yield: 5.83 g (60%). ^1H NMR (CDCl_3): δ 7.18, 6.85, (AB system, $J_{\text{AB}} = 8.7\text{ Hz}$, C_6H_4); 3.93 (t, 6.7 Hz, OCH_2); 3.58 (s, CH_2), 1.50–0.85 (m, C_9H_{19}). IR (Nujol, cm^{-1}): $\nu(\text{CO})$ 1703; $\nu(\text{OH})$ 3446.

4.4. $[Pd_2(\mu-O_2CC_5H_{11})_2(L^6)_2]$ (**3a**, $m = 5$)

A mixture of $[Pd_2(\mu-OH)_2(L^6)_2]$ (**1a**) (0.10 mmol) and hexanoic acid (0.025 ml, 0.20 mmole) was stirred in dry dichloromethane (20 ml) for 1 h. The yellow solution was evaporated to ca. 3 ml under reduced pressure. Addition of methanol afforded **3a** as a yellow solid, which was filtered off, washed with cold acetone (2×3 ml) and vacuum dried. Yield: 80%.

4.5. $Pd_2(\mu-O_2CCH(CH_3)OH)_2(L^6)_2$ (**7a**)

To a suspension of $[Pd_2(\mu-OH)_2(L^6)_2]$ (0.10 mmol) in dichloromethane (20 ml) was added of $L(+)$ lactic acid (0.22 mmole). After stirring for 1 h, the solvent was evaporated and the residue was extracted with 15 ml of acetone/ether 1:1. Then, the solution was refrigerated at $-4^\circ C$ and the resulting orange solid was collected on a frit, and dried in vacuum. Yield: 60%.

Acknowledgement

We gratefully acknowledge financial support by the Spanish Comisión Interministerial de Ciencia y Tecnología (Project MAT2002-00562), and the Junta de Castilla y León (Project VA050/02).

Appendix A. Supplementary material

Table of yields, elemental analysis and relevant IR data for complexes **2–7**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2004.09.024.

References

- [1] (a) A.M. Giroud-Godquin, P.M. Maitlis, *Angew. Chem. Int. Ed. Engl.* 30 (1991) 375; (b) P. Espinet, M.A. Esteruelas, L.A. Oro, J.L. Serrano, E. Sola, *Coord. Chem. Rev.* 117 (1992) 215; (c) D.W. Bruce, D. O'Hare (Eds.), *Inorganic Materials*, Wiley, Chichester, 1992 (Chapter 8); (d) S.A. Hudson, P.M. Maitlis, *Chem. Rev.* 93 (1993) 861; (e) J.L. Serrano (Ed.), *Metallomesogens*, VCH: Weinheim, Germany, 1996; (f) S.R. Collinson, D.W. Bruce, in: J.P. Sauvage (Ed.), *Transition Metal in Supramolecular Chemistry*, John Wiley and Sons, Chichester, UK, 1999, p. 285 (Chapter 7); (g) B. Donnio, D.W. Bruce, *Struct. Bonding* 95 (1999) 193.
- [2] (a) For representative important examples see: M. Ghedini, M. Longeri, R. Bartolino, *Mol. Cryst. Liq. Cryst.* 84 (1982) 207; (b) M. Ghedini, S. Licoccia, S. Armentano, R. Bartolino, *Mol. Cryst. Liq. Cryst.* 108 (1984) 269; (c) M. Ghedini, D. Pucci, E. Cesarotti, P. Antogniazza, O. Francescangeli, R. Bartolino, *Chem. Mater.* 5 (1993) 883; (d) M. Ghedini, D. Pucci, *J. Organomet. Chem.* 395 (1990) 105; (e) M. Ghedini, D. Pucci, G. de Munno, D. Viterbo, F. Neve, S. Armentano, *Chem. Mater.* 3 (1991) 65;
- (f) M.J. Baena, P. Espinet, M.B. Ros, J.L. Serrano, *Angew. Chem. Int. Ed. Engl.* 30 (1991) 711;
- (g) M.J. Baena, P. Espinet, M.B. Ros, J.L. Serrano, A. Ezcurra, *Angew. Chem. Int. Ed. Engl.* 32 (1993) 1203;
- (h) M.J. Baena, J. Barberá, P. Espinet, A. Ezcurra, M.B. Ros, J.L. Serrano, *J. Am. Chem. Soc.* 116 (1994) 1899;
- (i) M. Ghedini, D. Pucci, F. Neve, *J. Chem. Soc. Chem. Commun.* (1996) 137;
- (j) D.P. Lydon, G.W.V. Cave, J.P. Rourke, *J. Mater. Chem.* 7 (1997) 403;
- (k) K. Praefcke, D. Singer, B. Gündogan, *Mol. Cryst. Liq. Cryst.* 223 (1992) 181;
- (l) B. Neumann, T. Hegmann, R. Wolf, C. Tschierske, *J. Chem. Soc. Chem. Commun.* (1998) 105.
- [3] P. Espinet, J. Etxebarria, M. Marcos, J. Pérez, A. Remón, J.L. Serrano, *Angew. Chem. Int. Ed. Engl.* 28 (1989) 1065.
- [4] M.J. Baena, J. Buey, P. Espinet, H.S. Kitzerow, G. Heppke, *Angew. Chem. Int. Ed. Engl.* 32 (1993) 1201.
- [5] J. Buey, L. Díez, P. Espinet, H.S. Kitzerow, J.A. Miguel, *Chem. Mater.* 8 (1996) 2375.
- [6] J. Barberá, P. Espinet, E. Lalinde, M. Marcos, J.L. Serrano, *Liq. Cryst.* 6 (1987) 833.
- [7] M. Marcos, M.B. Ros, J.L. Serrano, *Liq. Cryst.* 8 (1988) 1129.
- [8] M.B. Ros, N. Ruiz, J.L. Serrano, *Liq. Cryst.* 9 (1991) 77.
- [9] M.J. Baena, P. Espinet, M.B. Ros, J.L. Serrano, *J. Mater. Chem.* 6 (1996) 1291.
- [10] (a) See for example M.T. Pereira, J.M. Vila, E. Gayoso, M. Gayoso, W. Hiller, J. Strahle, *J. Coord. Chem.* 18 (1988) 245; (b) R. Mosteiro, E. Perille, A. Fernández, M. López-Torres, J.M. Vila, A. Suárez, J.M. Ortigueira, M.T. Pereira, J.J. Fernández, *Appl. Organomet. Chem.* 14 (2000) 634; (c) R.B. Bedford, C.S.J. Cazin, S.J. Coles, T. Gelbrich, M.B. Hursthouse, V.J.M. Scordia, *Dalton Trans.* (2003) 3350.
- [11] L. Díez, P. Espinet, J.A. Miguel, *J. Chem. Soc. Dalton Trans.* (2001) 1189.
- [12] (a) For the use of carboxylates as modifiers of liquid crystal properties in very different systems see: J.P. Rourke, F.P. Fanizzi, N.J.S. Salt, D.W. Bruce, D.A. Dunmur, P.M. Maitlis, *J. Chem. Soc. Chem. Commun.* (1990) 229; (b) C.P. Roll, B. Donnio, W. Weigand, D.W. Bruce, *Chem. Commun.* (2000) 709.
- [13] (a) T. Kawato, T. Uechi, H. Koyama, H. Kanatomi, *Inorg. Chem.* 23 (1984) 764; (b) M.J. Arendse, G.K. Anderson, N.P. Rath, *Polyhedron* 20 (2001) 2495; (c) R. Kramer, K. Polborn, W. Beck, *J. Organomet. Chem.* 441 (1992) 333.
- [14] M.A. Ciriano, P. Espinet, J.L. Serrano, *J. Mol. Struct.* 196 (1988) 327.
- [15] See for example P.A. Agaskar, F.A. Cotton, L.R. Falvello, S. Han, *J. Am. Chem. Soc.* 111 (1986) 1214.
- [16] P. Espinet, J. Pérez, M. Marcos, M.B. Ros, J.L. Serrano, J. Barberá, A.M. Levelut, *Organometallics* 9 (1990) 2028.
- [17] J. Buey, P. Espinet, *J. Organomet. Chem.* 507 (1996) 137.
- [18] J. Buey, P. Espinet, G.A. Díez, S. García-Granda, E. Pérez-Carreño, *Eur. J. Inorg. Chem.* (1998) 1235.
- [19] H. Kelker, R. Hatz (Eds.), *Handbook of Liquid Crystal*, Verlag Chemie, Weinheim, 1980, p. 52.
- [20] D. Demus, L. Richter, C.E. Rürup, H. Sackmann, H. Schubert, *J. Physiol. (Paris) Suppl.* 36 (C1) (1975) 349.
- [21] P.R. Aston, D. Joachimi, N. Spencer, J.F. Stoddart, C. Tschierske, A.J.P. White, D. Williams, K. Zab, *Angew. Chem. Int. Ed. Engl.* 33 (1994) 1503.
- [22] B. Neumann, T. Hegmann, C. Wagner, P.R. Ashton, R. Wolf, C. Tschierske, *J. Mater. Chem.* 13 (2003) 778.
- [23] (a) C. Tschierske, *J. Mater. Chem.* 11 (2001) 2647; (b) C. Tschierske, *J. Mater. Chem.* 8 (1998) 1485.