Mesogenic Dinuclear Cyclopalladated Derivatives with Mixed Bridges − Crystal Structure of *cis*-[Bis({4,4′-di-*n*-butoxy}benzylideneaniline-C^2,*N*)-(μ-*n*-butylthiolato)(μ-chloro)dipalladium(II)]

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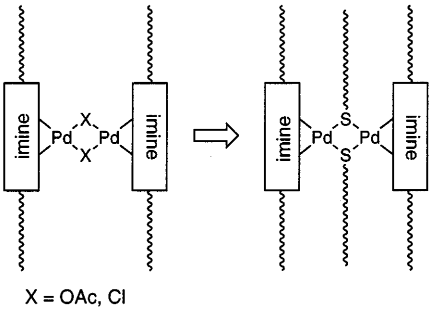
The dinuclear cyclopalladated compounds [Pd(μ-Cl)Ln]$_2$ (**2**) [HLn = p-$C_nH_{2n+1}OC_6H_4CH{=}NC_6H_4OC_nH_{2n+1}$-$p$ (n = 6, 8, and 10)] react with silver thiolates AgSRm (Rm = C_mH_{2m+1}, m = 6, 8, 10, and 18) to give dinuclear derivatives with mixed bridges [Pd$_2$(μ-Cl)(μ-SRm)Ln$_2$] (**3**). Treatment of derivatives **2** with silver acetate (Pd/AgOAc = 2:1) or treatment of [Pd(μ-OAc)Ln]$_2$ (**1**) with thiols HSRm (Pd/thiol = 2:1) affords acetato-thiolato bridged complexes [Pd$_2$(μ-OAc)(μ-SRm)Ln$_2$] (**4**). In addition to their mesogenic behavior, the most interesting feature of these complexes is the *cis* disposition of the palladium-imine moieties, that can be inferred from their ^{1}H-NMR spectra. The *cis* structure as well as the disposition of the bridges was confirmed by the X-ray diffraction study of **3** (n = m = 4).

The synthesis of metal-containing liquid crystals is an area of research which has seen a fast development in the last two decades[1]. Cyclometallated compounds of Pd^{II} with imines and related groups have received much attention due to: i) their thermal stability; ii) the variety of ligands useful for orthometallation leading either to calamitic or to discotic mesogens; and iii) the possibility of tuning the mesogenic properties not only by varying the nature or the length of the chains, but also the nature of the bridges in dinuclear complexes. The imine moiety provides the rigid core and flexible chains needed for liquid-crystal behavior, and two of these moieties are fused together upon orthometallation to give a X-bridged dinuclear complex (Figure 1). We have reported in the last years several types of cyclopalladated imine complexes and studied the structure-mesogenic activity relationships[2][3]. It seems from these studies that the acetato-bridged derivatives [Pd(μ-OAc)Ln]$_2$ (**1**) are rigid non-planar dimers ("open book" or "butterfly" shaped), both in the solid state and in solution. Because of this unfavorable molecular shape the compounds do not display mesogenic behavior (there are, however, a few exceptions: some chiral-carboxylate derivatives[3], as well as certain carboxylate complexes using azine instead of imine as ligand[4], are mesomorphic). Their NMR spectra show that the acetato-bridged complexes are in fact a mixture of two isomers, depending on the relative arrangement of the two imine moieties (ca. 96% *trans* versus 4% *cis*). On the contrary, planar ("H" shaped) chloro-bridged dimers [Pd(μ-Cl)Ln]$_2$ (**2**) contain only the *trans* isomer, and show the widest mesophase ranges (compared to other derivatives with azobenzene or azine as ligands)[5], although both the melting and the clearing points are quite high, above 100 and 200°C respectively. In both structures the separation between the two imine fragments leaves a wide empty space in the central part of the dimer, which could be filled using bridges that contained long alkyl chains. This should have a noticeable effect on the thermal properties of the material.

Figure 1. Sketch of the different space-filling efficiencies for complexes having bridges without or with long alkyl chains



X = OAc, Cl

In this paper we report on the attempt of replacing the chloro or acetato groups by thiolates bearing long alkyl chains. They were chosen taking advantage of the tendency of such ligands to form very stable Pd^{II}- or Pt^{II}-bridged complexes[6]. Furthermore, they could be expected to produce a basically planar dimer[7]. The results have shown that using silver thiolates only one of the chloro bridges is displaced, leading to mixed-bridged derivatives.

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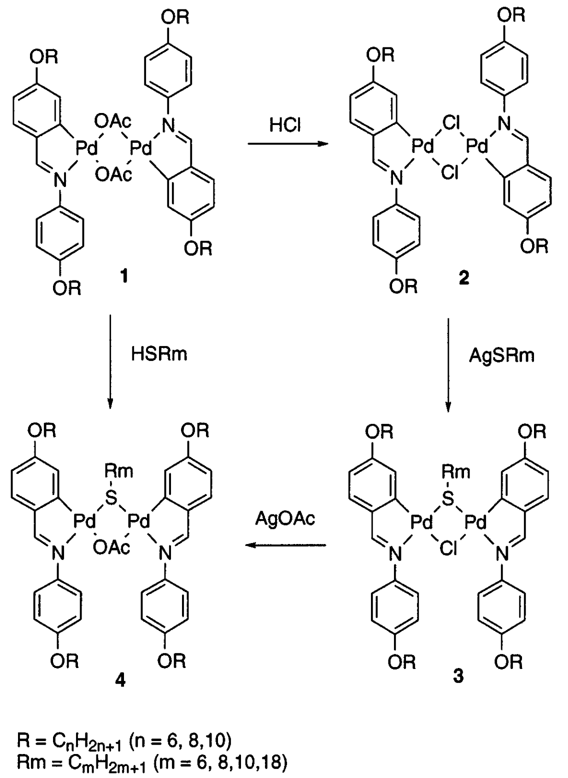
Scheme 1



Results and Discussion

Synthesis of the Complexes

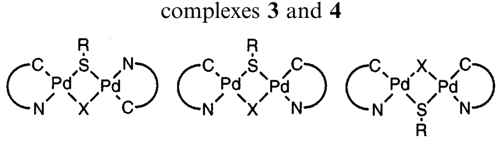
Mixed-bridged chloro-thiolate or acetato-thiolate complexes were prepared as shown in Scheme 1. The syntheses of the precursors **1** and **2** have been recently described by our group[3]. Treatment of $[Pd(\mu\text{-}Cl)Ln]_2$ (**2**) with the appropriate silver thiolate (AgSRm) in CH_2Cl_2 (Pd/thiolate = 2:1.1) afforded $[Pd_2(\mu\text{-}Cl)(\mu\text{-}SRm)Ln_2]$ (**3**) in good yields (73−91%). It should be noted that, regardless of the reaction conditions or the ratio Pd/AgSRm used, only monosubstitution was obtained. The replacement of the second chloro bridge yielding $[Pd_2(\mu\text{-}OAc)(\mu\text{-}SRm)Ln_2]$ (**4**) was achieved by treating derivatives **3** with silver acetate in CH_2Cl_2 (Pd/acetate = 2:1, method A). This kind of complexes could also be obtained by displacement of one acetato bridge in complexes **1** using the corresponding thiol (Pd/thiol = 2:1, method B). Yields were similar (64−86%) in both cases.

All the complexes gave satisfactory elemental analyses, and were characterized by IR and ^{1}H-NMR spectroscopy. The latter is very informative, because both the iminic proton and H^3 are very sensitive to changes in the molecular structure, and the reactions can be monitored using these signals. These ^{1}H-NMR parameters are summarized in Table 2 only for complexes **3** and **4** with $n = m = 6$; the rest of complexes show little variation, within ± 0.03 ppm for the chemical shifts, and unnoticeable for the coupling constants.

Characterization of Complexes 3

The ^{1}H-NMR spectra of these complexes indicate that there is only one thiolato group in the dinuclear molecule. Three isomers are possible (Figure 2), but only one is formed since only one set of signals is observed in the aromatic region.

Figure 2. Sketch of the three possible isomers in mixed-bridged complexes **3** and **4**



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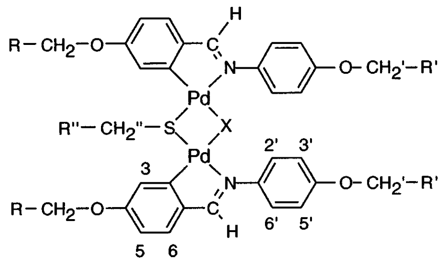
The *trans*-I structure can be discounted since the different environment of the two imines should give rise to two sets of signals. Thus, the disposition of the palladium-imine moieties must be *cis*. The *cis*-II structure is favored because the antisymbiotic behavior of the palladium atom should place the thiolate group *cis* to the metallated carbon

Table 1. ^{1}H-NMR parameters for complexes **3** and **4**[a]



X	H	H^3	H^5	H^6	H$^{2',6'}$[b]	H$^{3',5'}$[b]	O−CH$_2$/O−CH'$_2$[c]	S-CH$_2$''[c]	OTHERS[d]
Cl	7.93 s	7.39 d [2.3]	6.58 dd [8.2, 2.4]	7.28 d [8.3]	7.21 [8.9]	6.80 [8.9]	4.04 t/3.94 t	2.96 t	–
OAc	7.89 s	7.49 d [2.3]	6.48 dd [8.3, 2.3]	7.21 d [8.3]	7.19 [8.9]	6.81 [8.9]	4.00 m/3.88 t	2.46 t	1.62 s MeCO$_2^-$

[a] In CDCl$_3$ at 300.13 MHz; δ values and [*J* in Hz]; key: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; m, multiplet. − [b] Apparent AB system. − [c] Broad signals. − [d] Aliphatic proton signals (R, R', and R'') appear in the range δ = 2.0−0.8.

atom[8]. In fact, this structure has been observed in complexes $[M_2(\mu\text{-Cl})(\mu\text{-SR})Cl_2(PR_3)_2]$ (M = Pd or Pt)[9]: for M = Pd only the *cis* isomer was obtained, whereas for M = Pt a mixture of *cis* and *trans* isomers was found. On the contrary, cycloplatinated complexes similar to **3** lead only to the *cis* isomer[10]. Complexes **3** are expected to be basically planar both in solution and in the solid state and the comparable sizes of the chloro- and sulfur-bridging atoms should lead to an approximately parallel arrangement of the two imines.

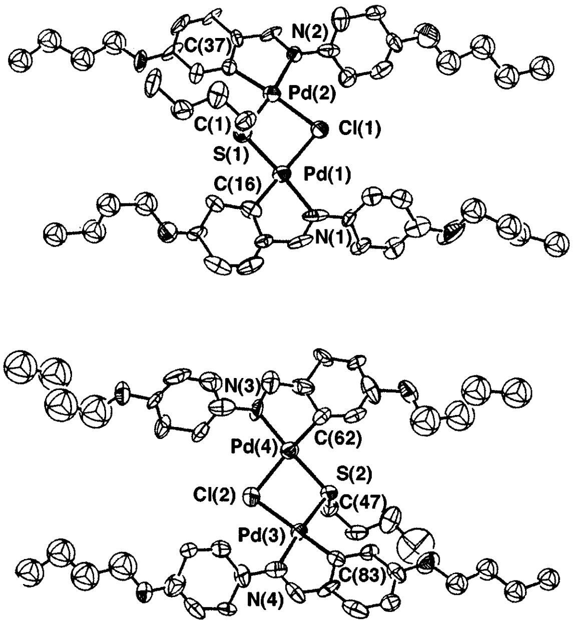
Bridged dimers with orthopalladated ligands either have *trans* structure, or are mixtures of *cis*/*trans* isomers (*cis* being the minor isomer). Thus, these complexes are interesting for they afford isomerically pure *cis*-cyclopalladated derivatives in high yields. The *cis* arrangement is particularly interesting in view of possible application where a net dipolar moment on the material is required. The proposed structure was confirmed by the X-ray crystal analysis of the complex with $n = m = 4$. This is one of the few X-ray crystal structures of a cyclopalladated mesogen[11], probably due to the difficulty to obtain crystals suitable for X-ray analysis when long aliphatic chains are present. This complex displays an S_A mesophase between 175 and 235°C on heating.

The crystal structure consists of four molecules per unit cell, grouped in pairs. There are two different molecules in each pair (labelled as M1 and M2) in a disposition perpendicular to one another, and parallel to the molecules of the other pair. A perspective ORTEP view of these independent molecules is given in Figure 3. Selected bond lengths and angles are listed in Table 2.

Table 2. Selected bond lengths [Å] and angles [°] for complex **3** ($n = m = 4$)

M1		M2	
Pd(1)−C(16)	2.03(2)	Pd(4)−C(62)	1.98(2)
Pd(1)−N(1)	2.11(2)	Pd(4)−N(3)	2.065(13)
Pd(1)−S(1)	2.300(6)	Pd(4)−S(2)	2.307(5)
Pd(1)−Cl(1)	2.483(5)	Pd(4)−Cl(2)	2.464(6)
Pd(2)−C(37)	1.99(2)	Pd(3)−C(83)	1.93(2)
Pd(2)−N(2)	2.142(14)	Pd(3)−N(4)	2.13(2)
Pd(2)−S(1)	2.261(6)	Pd(3)−S(2)	2.266(5)
Pd(2)−Cl(1)	2.444(6)	Pd(3)−Cl(2)	2.444(5)
S(1)−C(1)	1.73(2)	S(2)−C(47)	1.90(2)
C(16)−Pd(1)−N(1)	84.2(6)	C(62)−Pd(4)−N(3)	83.1(6)
C(16)−Pd(1)−S(1)	90.3(5)	C(62)−Pd(4)−S(2)	92.4(5)
C(16)−Pd(1)−Cl(1)	172.9(5)	C(62)−Pd(4)−Cl(2)	174.8(5)
N(1)−Pd(1)−S(1)	174.1(4)	N(3)−Pd(4)−S(2)	175.4(4)
N(1)−Pd(1)−Cl(1)	102.4(4)	N(3)−Pd(4)−Cl(2)	100.6(4)
S(1)−Pd(1)−Cl(1)	83.0(2)	S(2)−Pd(4)−Cl(2)	83.8(2)
C(37)−Pd(2)−N(2)	79.3(8)	C(83)−Pd(3)−N(4)	77.8(7)
C(37)−Pd(2)−S(1)	95.2(6)	C(83)−Pd(3)−S(2)	96.2(5)
C(37)−Pd(2)−Cl(1)	173.2(6)	C(83)−Pd(3)−Cl(2)	177.3(6)
N(2)−Pd(2)−S(1)	174.2(5)	N(4)−Pd(3)−S(2)	173.8(5)
N(2)−Pd(2)−Cl(1)	100.6(4)	N(4)−Pd(3)−Cl(2)	100.8(5)
S(1)−Pd(2)−Cl(1)	84.7(2)	S(2)−Pd(3)−Cl(2)	85.1(2)
Pd(1)−S(1)−Pd(2)	98.1(2)	Pd(3)−S(2)−Pd(4)	97.5(2)

Figure 3. ORTEP view of the two independent molecules, M1 and M2, of complex **3** ($n = m = 4$) showing the atom-labelling scheme



The coordination at each palladium atom is approximately square planar, with maximum deviations from the mean plane of 0.019 (Pd1) and 0.053 (Pd2) Å on M1 and 0.017 (Pd3) and 0.028 (Pd4) Å on M2. The Pd−C bond lengths in the two molecules are slightly different: 2.03(2) and 1.99(2) Å in M1 and 1.93(2) and 1.98(2) Å in M2. They are in good agreement with those described for $[Pd_2(\mu\text{-}Cl)_2(imine)_2]$ 1.97 Å[11]. The distances Pd−Cl and Pd−S are also quite similar to those found in complexes of the type $[Pd_2(\mu\text{-Cl})(\mu\text{-SR})Cl_2(PR'_3)_2]$ (R = alkyl or aryl; R′ = Me, Et, Ph)[12]. The small bite of the bidentate imine ligands produces the deviation of the angles around the palladium atoms from the ideal square disposition, 84.2(6) and 79.3(8)° in M1, and 77.8(7) and 83.1(6)° in M2. The angle between the two palladium-imine moieties is small, 16.5(2)° in M1 and 9.1(2)° in M2. The non-bonding Pd−Pd distances within each molecule are 3.443 Å in M1 and 3.437 Å in M2. Due to the tetrahedral coordination of the sulfur atom the first methylene of the thiolate group lies out of the mean Pd−S−Pd plane. The CH_2−S bond makes an angle with this Pd−S−Pd plane of 106° in M1 and 105.2° in M2. However, in both molecules the thiolato chains align themselves in the direction of the long molecular axis.

Figure 4a shows the crystal packing viewed perpendicular to the long molecular axis. A layer structure can be easily recognized where the molecular long axis is tilted respect to the layer plane, reminiscent of the S_C packing. The molecular arrangement within the layers is better seen in Figure 4b, which shows a view approximately along the molecular axis. It consists in arrays of pairs of molecules in alternate (zig-zag) directions. The minimun Pd−Pd distance between the antiparallel molecules making a pair is Pd(2)−Pd(4) = 4.024 Å. Some other non-bonding distances between the palladium atom and the carbon atoms of the other antiparallel molecule are quite short [e.g. Pd(2)−C(62) = 3.34 Å]. One of the rings linked to the nitrogen atom lies close to the empty space between the cyclopalladated moieties (Figure 4c), thus filling this space. The angles between the free-to-rotate phenyl ring linked to the nitrogen atom and the cyclometallated ring are quite different 38.7(4)° and 47.2(5)° in M1 and 21.5(4)° and 57.6(5)° in M2, indicating poor conjugation along the imine ligands.

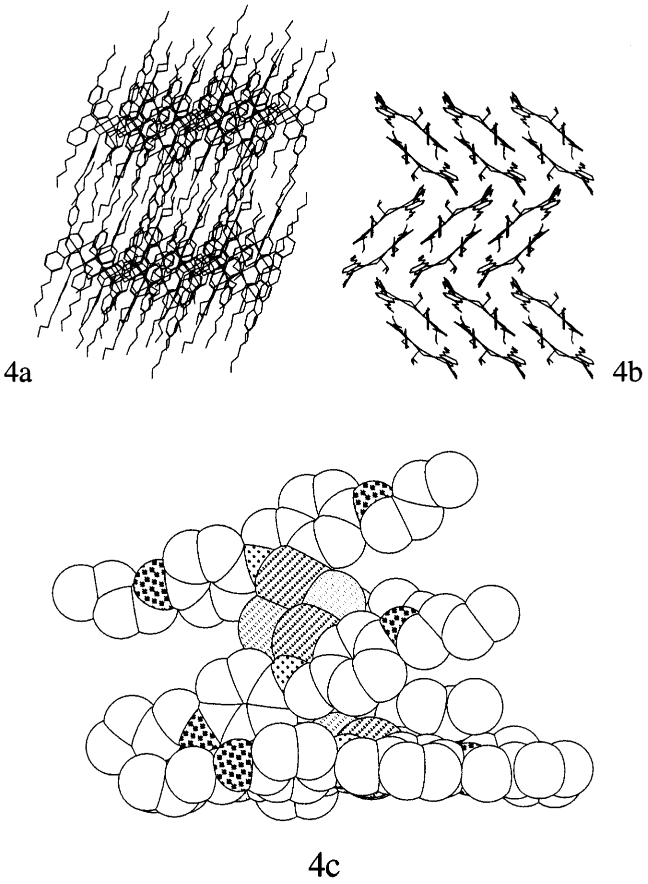


Figure 4. Crystal packing viewed (a) perpendicular to, and (b) approximately along the major molecular axis, (c) Chem3D view of the closest perpendicular molecules; hydrogen atoms are omitted for clarity

Characterization of Complexes 4

As for **3**, there is only one set of signals in the aromatic region of the ^{1}H-NMR spectra of complexes **4**, indicating the presence of only one isomer. It is assigned the structure *cis*-II (Figure 2) for the same reasons discussed for complexes **3**, and for the previously reported mixed-bridged thiolate-chiral carboxylate derivatives[13]. Both the signal of the first methylene group of the thiolate (δ = 2.47) and the methyl group of the acetato bridge (δ = 1.60) appear upfield with respect to their parent complexes **3** and **1**, respectively. The proposed disposition of the ligands is in agreement with the X-ray structures of similar orthopalladated complexes [Pd$_2$(μ-OAc)(μ-SR)(imine)$_2$][14] or [Pd$_2$(μ-CF$_3$CO$_2$)(μ-*t*BuS)(C-N)$_2$][15], (C-N = cyclopalladated 8-methylquinoline). According to these structures complexes **4** are not planar in the solid state, showing a folded structure with an average angle of 98° between the two moieties of the molecule in the acetate-thiolate complex above mentioned. In solution the NMR spectra observed are those expected for a planar complex, due to a fast inversion at the sulfur atom[17]. Furthermore, the different size of the two bridges leads to a non-parallel arrangement of the long axes of the imine ligands.

Mesogenic Behavior

All the complexes display liquid-crystal behavior. Their mesophases, nematic (N) and smectic A (S$_A$), and/or smectic C (S$_C$) have been identified by their characteristic textures, noticeably more viscous than in organic mesogens[18]. The transition temperatures, as well as the corresponding enthalpies were determined by differential scanning calorimetry and are given in Tables 3 and 4 (in a few cases the transitions could not be detected by DSC and microscope data are given). Figure 5 shows this mesogenic behavior compared to that of the parent dinuclear complexes **2** (for complexes **3**) or **1** (for complexes **4**).

Table 3. Optical, thermal, and thermodynamic data for the complexes **3**[a]

n/*m*	transition	*T* [°C]	ΔH [kJ mol^{-1}]
6/6	C-S$_C$	129.0	8.0
	S$_C$-S$_A$[b]	164.0	–
	S$_A$-I	210.1[c]	7.3
6/8	C-S$_C$	126.6	26.8
	S$_C$-S$_A$[b]	136.0	–
	S$_A$-I	189.4[c]	3.2
6/10	C-S$_C$	102.9	24.3
	S$_C$-S$_A$[b]	132.0	–
	S$_A$-I	196.5[c]	1.5
6/18	C-S$_C$	103.5	32.0
	S$_C$-S$_A$[b]	108.0	–
	S$_A$-I	192.7[c]	6.1
8/6	C-S$_C$	115.7	17.7
	S$_C$-S$_A$[b]	129.0	–
	S$_A$-I	193.1[c]	1.9
8/8	C-S$_C$	101.9	8.9
	S$_C$-S$_A$[b]	126.2	–
	S$_A$-I	192.4[c]	4.9
8/10	C-C′	66.5	−12.7
	C′-S$_C$	94.5	2.9
	S$_C$-S$_A$[b]	129.0	
	S$_A$-I	192.4[c]	4.2
8/18	C-S$_A$	111.8	35.5
	S$_A$-I	187.2[c]	6.2
10/6	C-S$_A$	115.8	18.7
	S$_A$-I	196.2[c]	7.0
10/8	C-S$_A$	118.4	19.9
	S$_A$-I	179.8[c]	8.8
10/10	C-S$_C$	108.2	20.5
	S$_C$-S$_A$[b]	112.0	–
	S$_A$-I	184.2[c]	8.6
10/18	C-S$_C$	114.7	39.8
	S$_C$-S$_A$[b]	117.0	
	S$_A$-I	181.8[c]	

[a] C, C′ = crystal; N = nematic; S$_A$ = smectic A; S$_C$ = smectic C. – [b] Optical microscopy data. – [c] Decomposition.

Complexes **3** show lower melting and clearing temperatures than the chloro complexes **2**. In all cases there is some decomposition at the clearing point. In complexes **4** the improvement of the mesogenic properties is clear, since the acetato complexes **1** are not mesogenic. Furthermore, compared to **1** these complexes display nematic phases for short

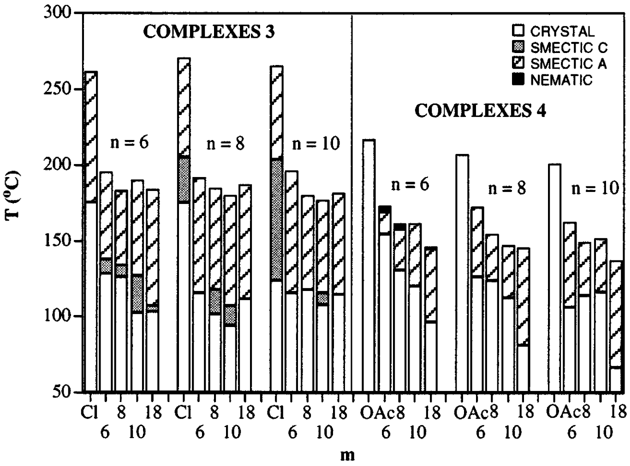
Table 4. Optical, thermal, and thermodynamic data for the complexes **4**[a]

n/*m*	transition	T [°C]	ΔH [kJ mol^{-1}]
6/6	C-S_A	154.4	13.7
	S_A-N	168.9	2.5[b]
	N-I	173.2	
6/8	C-S_A	130.8	16.5
	S_A-N	158.0	2.8[b]
	N-I	161.8	
6/10	C-S_A	120.0	19.5
	S_A-I	161.3	3.2
6/18	C-S_A	96.7	13.8
	S_A-N	144.6	2.8[b]
	N-I	146.4	
8/6	C-S_A	126.4	11.4
	S_A-I	172.1	3.8
8/8	C-S_A	124.0	28.5
	S_A-I	156.9	3.3
8/10	C-S_A	112.7	23.5
	S_A-I	146.9	3.0
8/18	C-S_A	81.0	6.4
	S_A-I	145.6	3.6
10/6	C-S_A	106.9	21.4
	S_A-I	163.4	4.2
10/8	C-S_A	114.1	28.2
	S_A-I	149.2	3.6
10/10	C-S_A	116.3	33.7
	S_A-I	141.7	3.5
10/18	C-S_A	67.0	19.1
	S_A-I	136.9	3.7

[a] C = crystal; N = nematic; S_A = smectic A. − [b] Combined enthalpies.

chains in the imines and the thiolate. This phase is not usual in dinuclear cyclopalladated imine mesogens. It is also remarkable that complexes **4** are able to display lyotropic behavior on mixing with linear alkanes or chiral solvents. The derivatives with $n = m = 6$ display broad ranges of nematic (or chiral nematic) lyomesophases, which are maintained until room temperature[16].

Figure 5. Thermotropic behavior of complexes **3** and **4**; *n* and *m* represent the number of carbon atoms in the imine and thiolate, respectively; the left bar on each group corresponds to the chloro-brigded derivative in complexes **3**, and to the acetato-brigded derivative in complexes **4**



Comparing the properties of compounds **3** and **4**, the influence of the structure on the liquid crystal behavior appears clearly. Planar complexes **3** display quite high transition temperatures as a consequence of the strong intermolecular interactions as well as a good packing of molecules leading to ordered smectic mesophases (S_A, S_C). Changing to the folded structure in complexes **4**, a less efficient packing of molecules leads to lower molecular interactions, less ordered mesophases (appearance of nematic phases), and lower transition temperatures. The stronger molecular interactions in complexes **3** can be also verified looking at the enthalpy figures of the same transition in both families: The crystal to smectic A mesophase gives a value of 21.4 and 18.7 kJ mol^{-1} for the complexes **3** and **4** (n = 10, m = 6), respectively.

Conclusions

i) Isomerically pure dinuclear complexes with mixed bridges leading to a *cis* structure can be easily prepared. ii) These complexes improve the mesogenic properties of the starting materials, either by decreasing the transition temperatures or by generating new mesophases . iii) The mesogenic properties of this kind of compounds can be doubly tuned, either by varying the nature of the thiolato bridge, or by replacing the second bridge with other bridging groups.

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Experimental Section

General Procedures and Measurements:. ^{1}H-NMR spectra: Bruker AC-80 or AC-300 MHz spectrometers using $CDCl_3$. − Elemental analyses: Perkin-Elmer 2400 microanalyzer. − IR spectra: Perkin-Elmer 843 spectrophotometer using KBr pellets, unless otherwise noted. − 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°C min^{-1} on heating, using aluminium crucibles and N_2 as inert gas. The apparatus was calibrated with indium (156.6°C, 28.5 J g^{-1}) as standard.

Materials: CH_2Cl_2 was distilled from CaH_2. Literature procedures were used to synthesize the silver thiolates (AgSRm)[19], $[Pd(\mu\text{-OAc})Ln]_2$ (**1**) and $[Pd(\mu\text{-Cl})Ln]_2$ (**2**)[3]. AgOAc and aliphatic thiols (HSRm) were obtained from commercial sources and were used without further purification.

Preparation of $[Pd_2(\mu\text{-}Cl)(\mu\text{-}SRm)Ln_2]$ (**3**): A solution of **2** (0.2 mmol) in 25 ml of CH_2Cl_2 was treated with a slight excess of the correspondig silver thiolate (Pd/AgSRm = 1:1.1), and the mixture was stirred in the dark for 5 h. The AgCl formed, as well as the excess thiolate, were filtered off and ethanol was added to the solution. Evaporation of the CH_2Cl_2 gave complexes **3** as yellow crystalline solids, which were filtered, washed with ethanol and air-dried. Yields were in the range 75−92%. − IR (KBr): $\tilde{\nu}$ = 1603 s (C=N), 1247 s 1028 m (C−O−C), 1574 s 829 m (Ar) cm^{-1}. − Analysis (%) for each *n*/*m* compound: **6/6**: calcd. C, 59.70; H, 7.24; N, 2.49; found C, 59.64; H, 7.10; N, 2.53. **6/8**: calcd. C, 60.33; H, 7.42; N, 2.43; found: C 60.07, H 7.28, N 2.64. **6/10**: calcd. C 60.93, H 7.58, N 2.37; found C 61.34, H 7.50, N 2.38. **6/18**: calcd. C 63.07, H 8.17, N 2.16; found C 63.13, H 8.11, N 2.09. **8/6**: calcd. C 62.05, H 7.89, N 2.26; found C 62.44, H 7.71, N 2.30. **8/8**: calcd. C 62.57, H 8.03, N 2.21; found C 62.35, H 7.55, N 2.41. **8/10**: calcd. C 63.07, H 8.17, N 2.16; found C 62.86, H 8.11, N 2.12. **8/18**: calcd. C 64.87, H 8.66, N 1.99; found C 64.66, H 8.37, N 1.92. **10/6**: calcd. C 64.01, H 8.43, N 2.07; found: C 64.11, H 8.19, N 2.09. **10/8**: calcd. C 64.41, H 8.55, N 2.03; found C 64.58, H 8.35, N 1.92. **10/10**: calcd. C 64.87, H 8.66, N 1.99; found C 64.89, H 8.53, N 1.79. **10/18**: calcd. C 66.40, H 9.08, N 1.84; found C 65.97, H 8.79, N 1.94.

Preparation of $[Pd_2(\mu\text{-}OAc)(\mu\text{-}SRm)Ln_2]$ (**4**). − *Method A:* AgOAc (0.1 mmol) was added to a solution of **3** (0.1 mmol) in 25 ml of CH_2Cl_2 (Pd/AgOAc = 2:1), and the mixture was stirred in the dark for 1 h. After removal of the AgCl formed, ethanol was added to the solution and the CH_2Cl_2 was removed in vacuo, yielding complexes **4** as yellow crystalline solids, which were filtered, washed with ethanol and air-dried. − *Method B:* To a red solution of **1** (0.1mmol) in 25 ml of CH_2Cl_2 was added the corresponding amount of thiol (0.1 mmol, Pd/HSRm = 2:1). The solution became orange-yellow, and was stirred for 2 h. After addition of ethanol, the solution was worked up as in method A. − Yields were in the range 65−86%. − IR (KBr): $\tilde{\nu}$ = 1605 s (C=N), 1245 s 1028 m (C−O−C), 1574 s 829 m (Ar) cm^{-1}. − Analysis (%) for each *n*/*m* compound: **6/6**: calcd. C 60.57, H 7.36, N 2.43; found C 60.51, H 7.22, N 2.48. **6/8**: calcd. C 61.16, H 7.52, N 2.37; found C 60.99, H 7.22, N 2.06. **6/10**: calcd. C 61.73, H 7.68, N 2.32; found C 61.66, H 7.53, N 2.25. **6/18**: calcd. C 63.76, H 8.25, N 2.12; found C 63.70, H 8.00, N 2.05. **8/6**: calcd. C 62.79, H 7.98, N 2.22; found C 62.73, H 7.83, N 2.63. **8/8**: calcd. C 63.29, H 8.12, N 2.17; found C 63.25, H 7.91, N 2.25. **8/10**: calcd. C 63.76, H 8.25, N 2.12; found C 63.07, H 8.00, N 1.91. **8/18**: calcd. C 65.48, H 8.73, N 1.95; found C 65.71, H 8.54, N 1.81. **10/6**: calcd. C 64.66, H 8.50, N 2.09; found C 64.61, H 8.01, N 2.37. **10/8**: calcd. C 65.08, H 8.62, N 2.00; found C 65.32, H 8.50, N 1.85. **10/10**: calcd. C 65.48, H 8.73, N 1.96; found C 65.53, H 8.55, N 1.61. **10/18**: calcd. C 66.95, H 9.14, N 1.81; found C 67.04, H 8.94, N 1.55.

Crystal-Structure Determination of **3** ($n = m = 4$)[20]: Details of the crystal and refinement data for the structure are given in Table 5.

Suitable yellow single crystals were grown by slow diffusion of a $CHCl_3$ solution of the complex into ethanol at room temperature. All diffraction measurements were made with an Enraf-Nonius CAD-4 single-crystal diffractometer. The unit-cell dimensions were determined from the angular settings of 25 reflections in the range $15° < \theta < 22°$. The intensity data of 8915 reflections were measured, using the ω-2θ scan technique and a variable scan rate with a maximum scan time of 60 s per reflection. The intensity of the primary beam was checked throughout the data collection by monitoring three standard reflections every 60 min. The final drift correction factors were between 0.96 and 1.09. On all reflections profile analysis was performed[21][22]. 8230 reflections were "observed" with $I > 2\sigma(I)$. Lorentz and polarization corrections were applied and the data were reduced to F_o values. The structure was solved by Patterson methods using the program DIRDIF[23]. After isotropic least-squares refinement, using SHELXL93[24], an empirical absorption correction was applied using DIFABS[25]. The maximum and minimum absorption correction factors were 0.48 and 0.41, respectively. During the final stages of the refinement on F^2, the positional parameters and the anisotropic thermal parameters of the non-H atoms were refined, except the carbon atoms of the *n*-butoxy groups, which were refined isotropically as a rigid group with a common thermal parameter for each group. Hydrogen atoms were isotropically refined riding on their parent atoms with a common thermal parameter. The final conventional agreement factors were $R = 0.042$ and $wR^2 = 0.115$ for the 8230 "observed" reflections and 775 variables. The function minimized was $\Sigma w(F_o - F_c)^2$, $w = 1/[\sigma^2(F_o^2) + 0.0868\cdot P)^2]$ with $\sigma(F_o)$ from counting statistics and $P = [\max(F_o^2,0) + 2\cdot F_c^2]/3$. The maximum shift/e.s.d. ratio in the last full-matrix least-squares cycle was 0.019. Atomic scattering factors were taken from International Tables for X-ray Crystallography[26]. Geometrical calculations were made with PARST[27]. The figure showing the coordination and the atomic numbering scheme was drawn by EUCLID package[28]. All calculations were made with VAX computers at the Scientific Computer Center of the University of Oviedo.

Table 5. Crystal data and structure refinement for complex **3** ($n = m = 4$)

crystal data	
formula	$C_{46}H_{61}ClN_2O_4Pd_2S$
mol weight	986.28
crystal system	monoclinic
space group	P21
a [Å]	10.275(5)
b [Å]	23.713(7)
c [Å]	18.780(13)
β [°]	93.52(5)
V [Å]^3	4566(4)
Z	4
$D_{calcd.}$ [g cm^{-3}]	1.435
F(000)	2032
μ [$^{-1}$]	0.934
crystal size [mm]	0.36 × 0.25 × 0.20
data collection and refinement	
T [K]	293
θ_{max} [°]	25
radiation, λ [Å]	Mo-K_α ⊥ft parenthesis-graphite), 0.71073
scan type	ω-2θ
data set	*h* −12:12, *k* −28:0, *l* −22:0
total no. of data	8915
obsd. data [$I > 2\sigma(I)$]	8230
no. of refined parameters	775
weighting scheme	$w = 1/[\sigma^2 (F_o^2) + (0.0868\cdot P)^2]$
final *R*, *wR2*	0.042, 0.115
min and max residual density [e $Å^{-3}$]	−0.57, 0.71

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