

The effect of polyether terminal chains in the liquid crystalline behavior of *ortho*-palladated complexes

M.J. Baena^a, J. Buey^b, P. Espinet^{b,*}, C.E. García-Prieto^b

^a *Química Inorgánica, E. T. S. de Ingenieros Industriales, Universidad de Valladolid, 47011 Valladolid, Spain*

^b *Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain*

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Abstract

A series of benzylideneanilines bearing terminal polyether chains, HL (HL = R-C₆H₄-CH=N-C₆H₄-R': R = OC₈H₁₇, R' = O(CH₂CH₂O)₂C₂H₅; R = O(CH₂CH₂O)₂C₂H₅, R' = OC₈H₁₇; R = R' = O(CH₂CH₂O)₂C₂H₅; R = OC₁₂H₂₅, R' = O(CH₂CH₂O)₃C₂H₅; R = O(CH₂CH₂O)₃C₂H₅, R' = OC₁₂H₂₅; R = R' = O(CH₂CH₂O)₃C₂H₅) have been prepared. Their dinuclear, [Pd(μ-X)L]₂ (X = OAc, Cl, Br, SC₈), [Pd₂(μ-SCn)(μ-X)L₂] (X = OAc, Cl; n = 8, 2) and mononuclear orthopalladated derivatives, Pd(acac)L, Pd(Ala)L, are reported and their mesogenic properties are compared with those of the analogous compounds with alkoxy chains. In general a great lowering in the melting points is produced for all the products. The free ligands and the alanine complexes are not liquid crystals. The chloro-bridged complexes bearing alkoxy and short polyether chains (O(CH₂CH₂O)₂C₂H₅) show the larger improvement of mesogenic properties. Longer polyether chains (O(CH₂CH₂O)₃C₂H₅) result usually in a destabilization of the mesophases. If only polyether chains are present, the destabilization is important regardless of the chain length. The ability of these molecules as ionic extractants and transporters was qualitatively evaluated for the more propitious *cis*-dinuclear complexes, which in fact showed some extracting ability, modest but improved compared to the free ligands.

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1. Introduction

Metallomesogens (metal-containing liquid crystals) is an area of research with a fast development in the last two decades. A great variety of such compounds have been synthesized, and some reviews have appeared [1]. Since the first report by Ghedini et al. [2] of orthopalladated mesogens other groups have developed these interesting systems, as they form thermally stable complexes, give rise to calamitic, discotic and lyotropic mesophases, and offer different possibilities for tuning the mesogenic properties. Our group has reported in the last years a variety of cyclometallated (Pd^{II}, Pt^{II}) imine com-

plexes and studied the structure-mesogenic activity relationships in these different molecular types [3], where we have found the first cholesteric metallomesogens [4], as well as properties of non-linear optics [5], ferroelectricity [6] or lyotropism [7]. A few of these studies have been carried out on orthopalladated azines [8].

Important issues for the potential application of metallomesogens in liquid crystal displays are the reduction of transition temperatures, the expansion of mesogenic ranges, the increase of thermal stability, and the improvement of miscibility with other ingredients (such as polar solvents) in mixtures. It is known that polyether or polyethyleneglycol ligands can enhance the solubility of the complexes in organic solvents and in water due to the polarity introduced by the oxygen atoms [9]. It is also likely that the introduction of polyether chains

* Corresponding author. Tel.: +34983423231; fax: +34983423013.
E-mail address: espinet@qi.uva.es (P. Espinet).

may be beneficial for the mesogenic properties of orthopalladated derivatives [10]. The higher flexibility and the preferred gauche conformation of the $(\text{OCH}_2\text{CH}_2)_n$ units makes that these chains can adopt more easily a helical conformation and occupy a significantly larger mean lateral area per chain than comparable aliphatic chains of the same length. Thus, it is expected that they might lower the melting points and produce a significant perturbation in the range of smectic mesophases. Depending on the amphiphilicity of the molecule and its ability to induce microsegregation, these mesophases can result stabilized or destabilized [11].

Polyether chains have been utilized before in mesogenic materials. For example, rod shaped organic esters with a polyether terminal group show tilted and orthogonal smectic phases [12]. On the other hand, the addition of alkaline triflate to lamellar phases of mesogenic polyethers induces the formation of columnar phases [13]. By combining the ionophore activity of polyethers with the peculiarities of the mesomorphic state (i.e., sensitivity to small external influences and anisotropy) these systems could play the function of a membrane. The main advantages are the availability of low dimensional ionic conductivities and an easy processability. In fact, the investigation on liquid crystalline based membranes is an area of growing interest [14]. Usually, organic LC amphiphilic systems are used for this purpose and, to our knowledge, no metallomesogens have been tested. The cases of metal containing liquid crystals bearing polyethers are very few. For example, orthopalladated phenylpyrimidines [d,15] linked by oxyethylene units to form macrocyclic molecular structures displaying smectic and columnar mesophases have been reported. Phthalocyanine metallomesogens derivatives have been proposed as materials for the transport of either photons or electrons due to their stacking order, and they are considered also suitable for ion transport. 15-crown-5 ether copper phthalocyanine has been reported to form mesophases in which channels are defined along the columnar axis, but no data about their transport properties are available [16]. A third example is an anne-

lide complex of cobalt (III) with a hydrophobic octadecyl chain and two hydrophylic fragments, the cationic cobalt centre and two oxyethylene chains. This compound behaves as lyotropic liquid crystal [17].

In this paper, we report the preparation and mesogenic properties of orthopalladated complexes containing polyether chains. In spite of the non-macrocyclic nature of the polyether moieties in the complexes, some of the compounds reported were checked towards extraction of potassium ion.

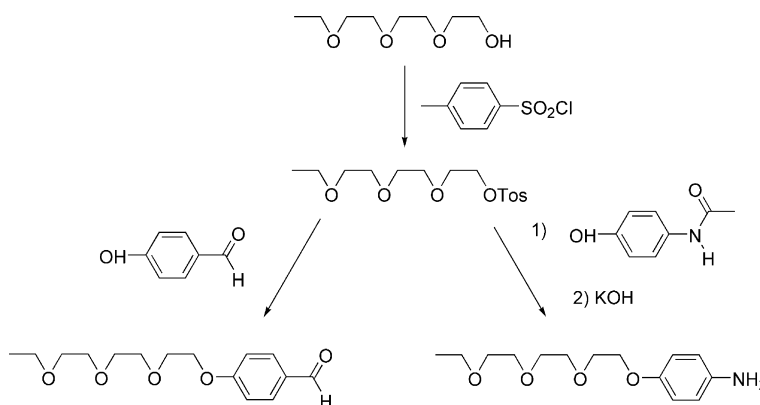
2. Results and discussion

In the text and Schemes to follow the chains $\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{C}_2\text{H}_5$ are abbreviated as $\text{O}_3\text{C}_6\text{H}_{13}\text{O}_2$, while $\text{O}_4\text{C}_8\text{H}_{17}$ stands for $\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{C}_2\text{H}_5$.

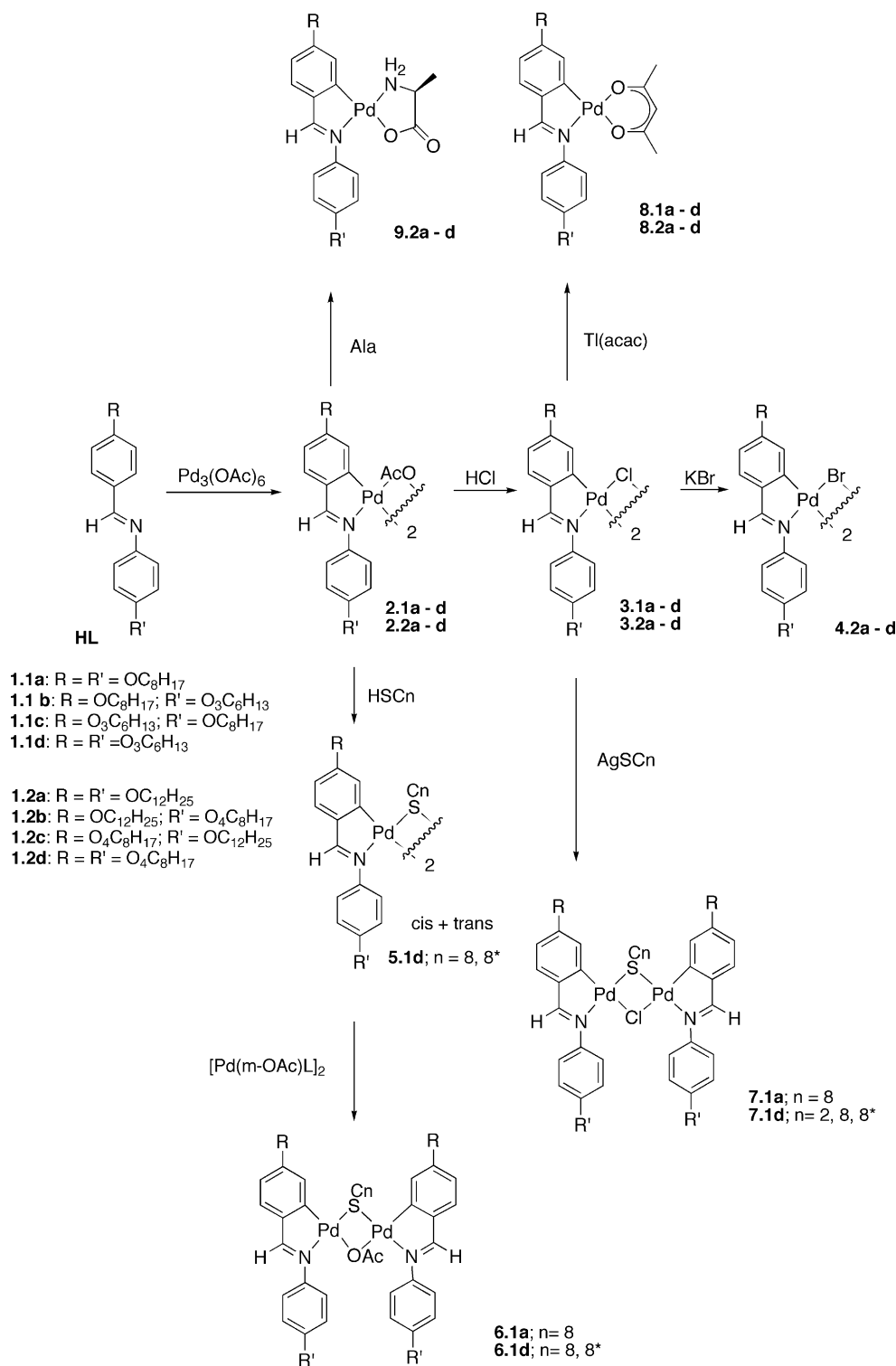
2.1. Synthesis and structures

The imines **1.1** and **1.2** were readily prepared in good yields by condensation of the corresponding aldehydes and anilines. Imine **1.1a** was already reported [3e]. The method followed to introduce the polyether chains on the *p*-hydroxybenzaldehyde or on the *p*-hydroxyacetanilide is depicted in Scheme 1. As expected, the solubility of the ligands depends on the nature and number of the substituents. Ligands with two alkoxy chains precipitate in ethanol, whereas ligands with a polyether chain are more soluble. The double-chained derivative is completely soluble.

The cyclopalladated complexes were synthesized as depicted in Scheme 2. The orthometallation of the imine ligands was carried out as described elsewhere [3f], but derivatives **2.2b** and **2.2c** could not be obtained sufficiently pure. In these cases, the crude acetate-complexes were treated with HCl, the chloro-complexes were purified by column chromatography and then reacted with sodium acetate in order to get the pure acetate bridged complexes. The trend of the solubility of the complexes is the same as for the free ligands. Chloro bridged



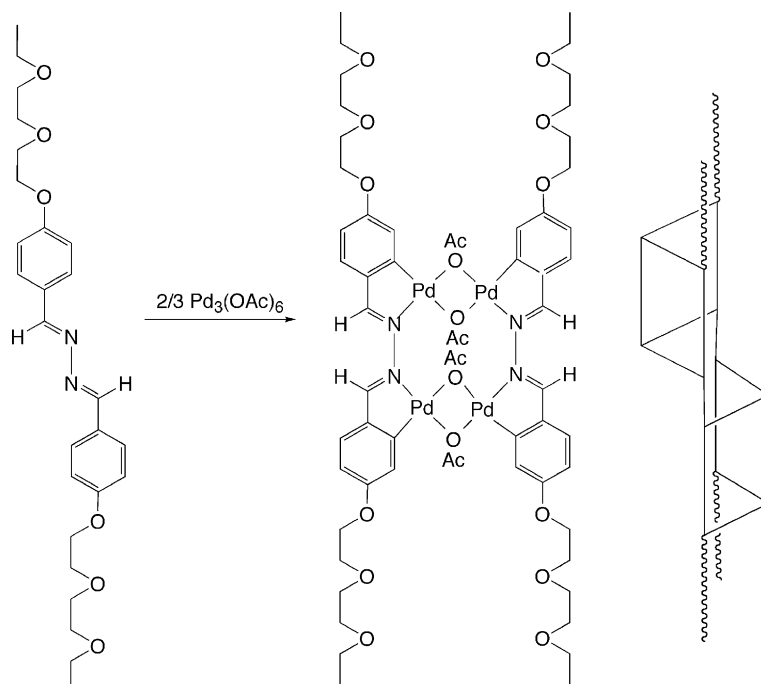
Scheme 1.



Scheme 2.

complexes **3.1** and **3.2** were obtained by treatment of the acetate bridged complexes with HCl; these complexes were precursors of the following complexes: (i) bromo bridged derivatives **4.2** by reaction with KBr, (ii) chloro- and thiolate-mixed bridged derivatives **6.1** and **7.1** by reaction with one equivalent of the appropriate silver

thiolate, (iii) mononuclear derivatives **8.1** and **8.2** by reaction with thallium acetylacetonate. Complexes **5.1** have two thiolate bridges and this is the first time that this molecular type is reported as mesogen. Reaction of **2.1** with two equivalents of alkylthiol affords these new complexes. Mononuclear derivatives **9.2** were ob-



Scheme 3.

tained by reaction of the acetate bridged complex with two equivalents of alanine.

Some syntheses were carried out with a *p*-polyether disubstituted azine. A tetranuclear orthopalladated complex **10** was obtained by reaction of the azine with two equivalents of palladium acetate (Scheme 3).

All the compounds gave satisfactory CHN analyses, IR and ^1H NMR spectra. Except for the new double-thiolate bridged complexes **5**, the main structural features for complexes **2–4** and **6–9** have been reported in detail in previous papers dealing with their analogs with alkyl chains [3e–3g]. The acetate-bridged complexes **2** are butterfly-shaped and are obtained mainly as a *cis:trans* mixture 1:24. The chloro- and bromo-bridged complexes **3** and **4** are planar and only the *trans* isomer is formed. Mixed-bridged compounds **6** and **7** are *cis* isomers with the thiolate bridge *cis* to the orthometallated carbons. The thiolate–acetate bridged complexes are non-planar in the solid state [18], but their NMR spectra in solution indicate that a fast inversion at the sulfur atom occurs [19]. The different size of the two bridges leads to a non-parallel arrangement of the imine ligands, which converge towards the thiolate moiety. Thiolate–chloro bridged complexes are planar with the long axes of the imines parallel to each other and the thiolate chain pointing backwards the Pd–Pd plane. Only one isomer is possible for the acac complexes **8**. For the alanine derivatives **9** the reaction affords only the isomer with the two nitrogen atoms mutually *trans* [20]. For complexes **5**, *cis* and *trans* isomers are seen in their ^1H NMR spectra, which show two signals for the iminic proton. The *cis:trans* ratios of these isomers are 1:6 for

$n = 8$ and 1:1.3 for $n = 8^*$. An exchange between isomers was observed in solution for the last one, producing a small excess of the *cis* form in two days. For complex **10** only one isomer was found in the resonance spectrum which is assigned to the structure depicted in Scheme 3, consistent with the spectral features observed.

2.2. Mesogenic properties

Optical, thermal and thermodynamic data of the complexes studied are collected in Tables 1–8 and compared in Figs. 1–3. When mesogenic behavior appeared, the mesophases were identified by their characteristic textures [21].

2.2.1. Imines

Out of the eight ligands prepared, six are non-mesogenic and only the two with two alkoxy chains exhibit a short range of mesophase (Table 1). In general, the melting points of the compounds with polyether chains are about 30 °C lower than the analogous derivatives with alkoxy chains, and the more polyether chains, the lower the melting point.

2.2.2. Dinuclear complexes

$[\text{Pd}(\mu\text{-OAc})\text{L}]_2$. Due to its unfavorable molecular geometry, the acetate bridged complexes do not show liquid crystal behavior (Table 2). Nevertheless, the presence of polyether chains causes the melting points to decrease over 80 °C in compounds **2.1b–d** and 100 °C in compounds **2.2b–d** compared to their homologous with alkoxy chains **2.1a** and **2.2a**. For the same chain

Table 1
Optical, thermal and thermodynamic data for the imine ligands, **HL** (**1.1f** and **1.2**)

Ligand	Transition ^a	<i>T</i> (°C)	ΔH (kJ mol ⁻¹)
1.1a	C–S _C [3e]	100.6	36.8
	S _C –N	109.7	8.0 ^b
	N–I	112.5	
1.1b	C–I	71.8	41.1
1.1c	C–I	76.3	43.1
1.1d	C–I	74.7	43.1
1.2a	C–S _C	101.1	80.4 ^b
	S _C –I	106.7	
1.2b	C–I	78.5	58.8
1.2c	C–I	75.2	58.8
1.2d	C–I	68.4	76.3

^a C = crystal; S_C = smectic C; I = isotropic liquid.

^b Combined enthalpies.

length, a decrease in the melting point is observed when more polyether chains are involved.

[Pd(μ-Cl)L]₂. All the new chloro-bridged complexes synthesized are liquid crystals (Table 3), exhibiting S_C and S_A mesophases as expected for species with long chain substituents. Fig. 1 displays graphically their thermal behavior. Again large differences in melting point are observed between the complexes with four alkoxy groups and those with four polyether groups: $\Delta T = 60$ °C (**3.1a** versus **3.1d**) and $\Delta T = 140$ °C (**3.2a** versus **3.2d**). In addition, the ranges of mesophase are 20–50 °C broader for the polyether derivatives. The range of mesophase in **3.2d** is much smaller than in **3.1d** (35 °C versus 110 °C). Again this suggests that the more disordered conformation of the longer chains for the polyether prevents efficient intermolecular interactions and facilitates a lower clearing temperature. The compounds with two polyether chains and two alkoxy chains (**3.1b**, **3.1c** and **3.2b**, **3.2c**) have more or less intermediate prop-

Table 2
Optical, thermal and thermodynamic data for the complexes **2.1** and **2.2**

Complex	Transition ^a	<i>T</i> (°C)	ΔH (kJ mol ⁻¹)
2.1a	C–I ^b	206.6	57.7
2.1b	C–C'	80.2	3.3
	C'–I	150.4	32.9
2.1c	C–C'	46.6	10.8
	C'–I	161.5	36.4
2.1d	C–I	127.7	29.9
2.2a	C–I ^b	185.0	
2.2b	C–I	127.7	33.2
2.2c	C–I	139.4	39.5
2.2d	C–C'	48.4	4.7
	C'–C''	58.7	0.5
	C''–I	88.6	21.6

^a C, C', C'' = crystal; I = isotropic liquid.

^b Decomposition.

Table 3
Optical, thermal and thermodynamic data for complexes **3.1** and **3.2**

Complex	Transition ^a	<i>T</i> (°C)	ΔH (kJ mol ⁻¹)
3.1a	C–S _C	175.3	15.4
	S _C –S _A ^b	205.0	
	S _A –I	270.0 ^c	–
3.1b	C–S _C	108.9	4.8
	S _C –S _A ^b	170.0	
	S _A –I	260.0 ^c	–
3.1c	C–S _C	122.5	17.5
	S _C –S _A ^b	160.0	
	S _A –I	260.0 ^c	–
3.1d	C–S _C	111.7	13.7
	S _C –S _A ^b	120.0	
	S _A –I	220.0 ^c	–
3.2a	C–S _C	120.2	59.1
	S _C –S _A ^b	213.0	
	S _A –I	254.8 ^c	11.0
3.2b	C–C'	86.0	17.0
	C'–S _C	95.8	6.7
	S _C –S _A ^b	138.0	
	S _A –I	215.0 ^c	6.5
3.2c	C–S _C	96.0	13.6
	S _C –S _A ^b	137.4	
	S _A –I	220.5	8.6
3.2d	C–S _C	79.6	15.9
	S _C –S _A ^b	105.0	
	S _A –I	115.1	1.0

^a C = crystal; S_C = smectic C; S_A = smectic A; I = isotropic liquid.

^b Optical microscopy data.

^c Decomposition.

Table 4
Optical, thermal and thermodynamic data for the complexes **4.2**

Complex	Transition ^a	<i>T</i> (°C)	ΔH (kJ mol ⁻¹)
4.2a	C–C'	94.3	27.6
	C'–S _C	160.8	30.6
	S _C –S _A ^b	194.7	–
	S _A –I	248.5 ^c	9.5
4.2b	C–S _A	118.7	19.5
	S _A –I	203.7	7.6
	I–S _A	187.7	–1.0
	S _A –S _C ^b	116.0	–
	S _C –C	87.8	–10.7
4.2c	C–S _A	105.2	22.8
	S _A –I	203.5	8.51
	I–S _A	200.7	–8.9
	S _A –S _C ^b	100.8	–
4.2d	S _C –C	75.7	–9.3
	C–S _C	58.7	68.6
	S _C –S _A ^b	82.7	–
	S _A –I	84.9	2.3

^a C, C' = crystal; S_C = smectic C; S_A = smectic A; I = isotropic liquid.

^b Optical microscopy data.

^c Decomposition.

Table 5
Optical, thermal and thermodynamic data for the complexes **5.1d**

Complex	Transition ^a	<i>T</i> (°C)	ΔH (kJ mol ⁻¹)
5.1d (<i>n</i> = 8)	C–I	58.9	35.0 ^b
	C'–I	73.9	
5.1d (<i>n</i> = 8*)	C–I	69.2	7.4
	C'–I	83.5	5.9
	I–S _C [*]	64.1	–1.7

^a C, C' = crystal; S_C^{*} = chiral smectic C; I = isotropic liquid.

^b Combined enthalpies.

erties. A handicap of these compounds is that, even when the transition temperatures decrease by introduction of polyether substituents, nearly all of them undergo some decomposition at the clearing point, which prevents their use in repeated heating-cooling cycles.

[Pd(μ-Br)L]₂. Bromo-bridged derivatives were synthesized in order to evaluate the influence of a small structural change on the mesogenic properties. The long chain series **4.2** was chosen for this study. All of them are liquid crystals with the same kind of mesophases (S_C and S_A) as their chloro-bridged parents (Table 4 and Fig. 1). Changing four alkoxy chains by four polyether chains results in a dramatic decrease of the melting ($\Delta T = 100$ °C) and clearing temperatures ($\Delta T = 160$ °C). At the same time the range of mesophase is severely reduced. The location of the polyether chain (either in the orthometallated or in the anilinic ring) seems not to affect largely the mesogenic properties, neither for the bromo- nor for the chloro-complexes. The change of halogen atom often causes a stabilization of the less ordered mesophases [3f]. In the present study the range of smectic A mesophase for **4.2** broadens respect to com-

Table 6
Optical, thermal and thermodynamic data for complexes **6.1** and **7.1**

Complex	(μ-X)	Transition ^a	<i>T</i> (°C)	ΔH (kJ mol ⁻¹)
6.1a (<i>n</i> = 8)	(μ-OAc)	C–S _A [3g]	124.0	28.5
		S _A –I	156.9	3.3
6.1d (<i>n</i> = 8)	(μ-OAc)	C–I	51.9	56.2
		C'–I	76.1	19.9
		I–S _C ^b	47.0	–4.3
6.1d (<i>n</i> = 8*)	(μ-OAc)	C–I	70.5	25.6
7.1a (<i>n</i> = 8)	(μ-Cl)	C–S _C [3g]	101.9	8.9
		S _C –S _A	126.2	–
		S _A –I	192.4	4.9
7.1d (<i>n</i> = 8)	(μ-Cl)	C–I	106.7	22.9
		I–S _C	101.5	–2.8
7.1d (<i>n</i> = 8*)	(μ-Cl)	C–S _C [*] –I	81.4	21.0
		S _C [*] –I ^b	64.6	1.8
7.1d (<i>n</i> = 2)	(μ-Cl)	C–S _A	91.7	11.4
		S _A –I	142.8	4.5

^a C, C' = crystal; S_A = smectic A; S_C = smectic C; S_C^{*} = chiral smectic C; I = isotropic liquid.

^b Data from the second heating.

Table 7
Optical, thermal and thermodynamic data for the complexes **8.1** and **8.2**

Complex	Transition ^a	<i>T</i> (°C)	ΔH (kJ mol ⁻¹)
8.1a	C–S _A	63.2	35.8
	C'–S _A	84.6	1.9
	S _A –N	123.7	3.7 ^b
	N–I	124.6	
8.1b	C–S _A –N	78.3	47.7
	N–I	84.9	0.6
	S _A –N ^c	76.0	1.2
8.1c	C–S _A	73.0	36.9
	S _A –N	78.0	0.5
	N–I	81.5	1.5
8.1d	C–I	52.9	20.2
	I–N	21.4	–0.5
8.2a	C–C'–S _A	91.7	34.1
	S _A –I	124.4	7.2
8.2b	C–S _A	58.5	27.6
	S _A –I	65.6	2.9
8.2c	S _A –I	66.0	3.6
8.2d	I	–	–

^a C, C' = Crystal; S_A = smectic A; N = nematic; I = isotropic liquid.

^b Combined enthalpies.

^c Second heating.

plexes **3.2**, except for complex **4.2d**. Comparing **3.2d** and **4.2d** the transition temperatures are lower for the latter and the mesophase range is shorter. Derivatives **4.2b** and **4.2c** display higher melting points than the chloro-complexes analogous, and the smectic C mesophase is monotropic.

[Pd(μ-SCn)L]₂. It is known that thiolates form very stable and planar Pd^{II}- or Pt^{II}-bridged complexes [22,19]. If this bridging ligands bears long alkyl chains, the empty space between the iminic chains in the dimer could be filled and this should produce an important effect on the thermal properties. Double long chain thiolate-bridged complexes, not described so far, looked promising but the results reported here show that they do not fulfill the expectations. As we can see from Table 5, compound **5.1d** (*n* = 8) is not mesogenic, while **5.1d** (*n* = 8*) only develops a monotropic chiral smectic C phase. The compounds were obtained as a mixture of *cis*- and *trans*-isomers. Thus, the two melting points observed can be attributed to the different melting point of

Table 8
Optical, thermal and thermodynamic data for the complexes **9.2**

Complex	Transition ^a	<i>T</i> (°C)	ΔH (kJ mol ⁻¹)
9.2a	C–C'	47.3	9.3
		175.3	15.7
9.2b	C–I	155.9	17.7
9.2c	C–I	149.9	19.3
9.2d	C–I	124.0	14.8

^a C = crystal, I = isotropic liquid.

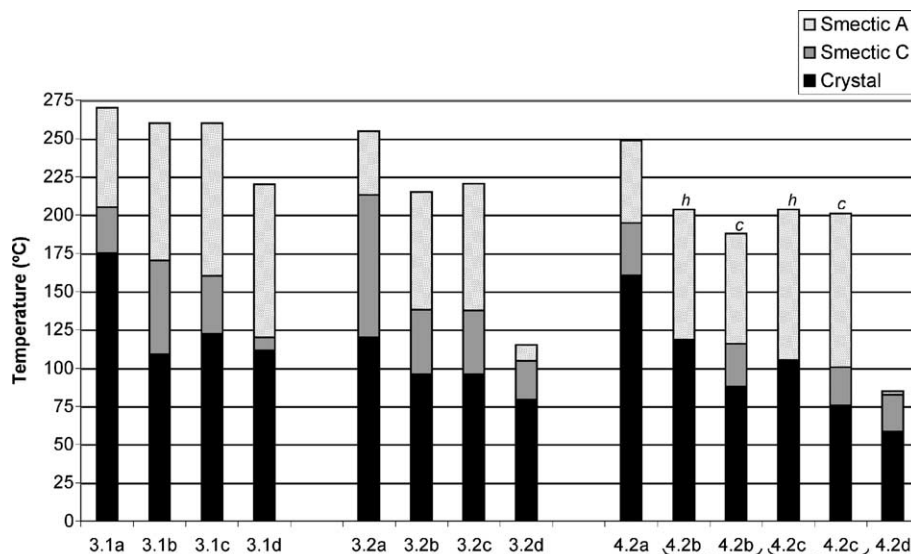


Fig. 1. Thermal behavior of compounds **3.1**, **3.2** and **4.2** (*h*: phases present on heating; *c*: phases present on cooling).

each isomer. The introduction of a chiral centre in the alkyl thiolate chain is deemed responsible for the mesogenic behavior of **5.1d** ($n = 8^*$), as it carries also a small dipolar moment which increases the intermolecular forces.

Dinuclear complexes with mixed bridges. In general, the complexes were not isolated as microcrystalline solids, but as plastic-like materials. Most of them do not crystallize on cooling and the mesophase (sometimes fairly fluid) is maintained at room temperature. Only one, **7.1d** ($n = 8$) devitrifies on heating and its analogue **7.1d** ($n = 8^*$) apparently shows a glass transition (T_g). Table 6 and Fig. 2 gather the mesogenic properties observed. As expected, the polyether derivatives have lower transition temperatures than the alkoxy derivatives, but the thermal stability of the mesophases also de-

creases. With polyether chains the thiolate-acetate complex **6.1d** ($n = 8$) shows a monotropic S_C mesophase. Its chiral analog **6.1d** ($n = 8^*$) is not liquid crystal in this case.

The chloro-thiolate complexes are liquid crystals, displaying enantiotropic smectic C and smectic A phases for the alkoxy derivatives, but only smectic A and monotropic smectic C for the complexes with polyether. The introduction of a chiral center affords a chiral mesophase (**7.1d**, $n = 8^*$).

2.2.3. Mononuclear derivatives

A usual strategy to improve the mesogenic properties from dinuclear complexes is to reduce the symmetry of the molecular shape by converting them into mononuclear acetylacetonato derivatives [3e]. The

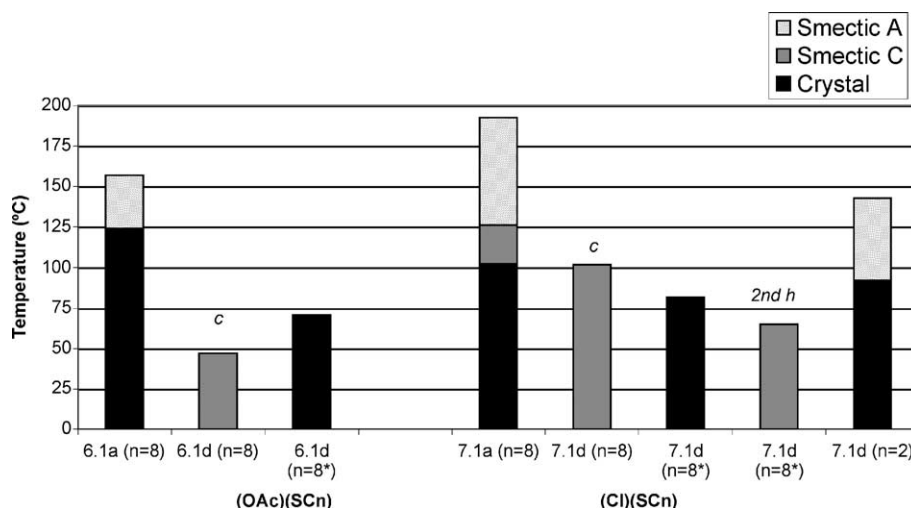


Fig. 2. Thermal behavior of compounds **6.1** and **7.1** (*c*: mesophase observed on cooling; 2nd *h*: mesophase observed on the 2nd heating).

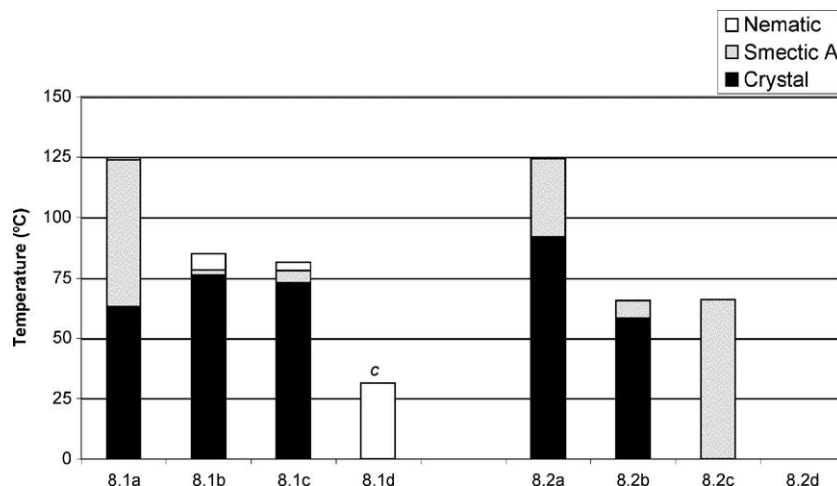


Fig. 3. Thermal behavior of compounds **8.1** and **8.2**. (c: mesophase observed on cooling).

new polyether complexes studied here might combine the reduction in symmetry with the presence of more disordered chains to give rise to complexes with very low transition temperatures. Acetylacetonato **8.1** and **8.2** and alanine **9.2** orthopalladated imines were synthesized with this aim.

Pd(acac)L. Both series of acetylacetonate complexes have lower melting and clearing points than the halo-bridged complexes and exhibit more disordered mesophases. Table 7 and Fig. 3 show the behavior of these compounds. S_A and N for **8.1b** and **8.1c**, only S_A for **8.2b** and **8.2c**. This last complex is liquid crystal at room temperature. Also complex **8.1d** is a monotropic nematic liquid crystal at room temperature, while **8.2d** is obtained as an isotropic liquid, which shows no mesophases at lower temperature.

The ranges of mesophase are very narrow and almost all the acetylacetonate complexes with polyether chains retain the mesophase texture on cooling. For derivatives **8.1b** and **8.2b** the enthalpy of the melting point is larger than for **8.1c** and **8.2c**. This is in agreement with the previously observed feature [3f] that when the more disordered chains (polyether chains) are on the free ring, the packing is less efficient leading to lower melting points and transition enthalpies.

[Pd(Ala)L]. The alanine derivatives **9.2** were synthesized with aiming at producing chiral mesophases, since the amino acid bears a chiral centre. This strategy failed due to the high melting points exhibited by the compounds (Table 8). Despite this, a cholesteric mesophase could be observed at rapid cooling rates (faster than 10 °C/min).

2.2.4. Tetranuclear derivative **10**

In spite of the beneficial effects of polyether chains on the melting points, neither the azine ligand nor the acetate-bridged complex are liquid crystals (see Scheme 3).

2.3. Experiments of ionic extraction and transport

Representative complexes were chosen for extraction experiments. These included the dinuclear mixed bridged complexes because the *cis*-disposition of the terminal chains is a good preconditioning and might decrease the unfavorable entropic effect in a cooperative complexation of cations by two chains of the dimer, compared to complexation of two chains of different molecules in other molecular types [23]. The acetate–thiolate complexes were chosen because the convergence in the space of the chains could be a further structural factor to enhance the ion capture. Extraction and transport experiments were as well carried out with the tetranuclear specie **10** which, due to its folded structure, brings the chains closer than the chloro-bridged compounds. The experiments were carried out as described in the Experimental Section.

Qualitative results for transport experiments show that the complexes are only modest transporters. The acetate–thiolate bridges are better than the chloro–thiolate or the tetranuclear complex but none of them can be considered useful as ionic transporter.

More accurate measurements were carried out on extraction efficiency, comparing the complexes with the free ligands. (Table 9). For all the cases, the extraction, although poor, improved significantly with the complexes compared to the ligands. Again the mixed acetate–thiolate bridge combined with a long alkyl chain at the thiolate produced the highest complexation of K⁺.

3. Conclusions

In summary, the substitution of alkoxy terminal chains by polyether chains in complexes derived of orthopalladated imines leads to a marked lowering of the melting points. The presence of four polyether

Table 9
Efficiency as extractant (ϵ) [24] of representative complexes and ligands (npc = number of polyether chains)

Compound	mol L ⁻¹	npc	mmol KPic extracted	ϵ
10	2×10^{-3}	4	1.91×10^{-4}	0.96
6.1d ($n = 8^*$)	2×10^{-3}	4	4.61×10^{-4}	2.3
[Pd ₂ (μ -OAc)(μ -SC ₂)(L) ₂], L = Im O ₄ C ₈ /OC ₄	2×10^{-3}	2	2.68×10^{-4}	1.3
7.1d ($n = 2$)	2×10^{-3}	4	3.05×10^{-4}	1.5
[Pd ₂ (μ -Cl)(μ -SC ₂)(L) ₂], L = Im O ₄ C ₈ /OC ₁₂	1.8×10^{-3}	2	2.19×10^{-4}	1.2
H ₂ Az, O ₃ C ₆ /O ₃ C ₆	2×10^{-3}	2	0.0	0.0
1.1d	4×10^{-3}	2	2×10^{-5}	0.03

chains affords the lowest transition temperatures, but the change from O₃C₆ to O₄C₈ produces the disappearing of mesogenic stability for all types of complexes.

The complexes with *cis* conformation of the polyether chains in orthometallated-imine dimeric complexes are very modest ionic transporters. The best transporters are the acetate–thiolate bridged complexes.

4. Experimental

4.1. General procedures

¹H NMR spectra were recorded in Bruker AC-300 or ARX-300 MHz spectrometers, in CDCl₃. Elemental analyses were made in a Perkin–Elmer 2400 microanalyzer. IR spectra were recorded with a FT 1720X Perkin–Elmer spectrophotometer (4000–400 cm⁻¹) using KBr pellets, or a Perkin–Elmer 883 spectrophotometer (4000–200 cm⁻¹) using a Nujol emulsion supported between two polyethylene films. The textures of the mesophases were studied with a Leica polarizing microscope mod. DMRB, equipped with a Mettler FP-82HT hot stage and a temperature controller Mettler FP-90. Transition temperatures and enthalpies were measured by differential scanning calorimetry, with a Perkin–Elmer DSC-7, using aluminum crucibles. The apparatus was calibrated with indium (156.6 °C, 28.45 J g⁻¹) as standard. Concentrations of KPic were determined colorimetrically with a Shimadzu UV–visible spectrophotometer UV-1603.

Solvents were dried and distilled before use. Stationary phase used for column chromatography was silica-gel (230–400 mesh ASTM). Literature procedures were used to synthesize the silver thiolates (AgSC_nH_{2n+1}) [25], and the compounds **1.1a** [3e], **2.1a** [3e], **3.1a** [3e], **8.1a** [3e], **6.1a** [3g], and **7.1a** [3g]. The compounds 4-hydroxybenzaldehyde, 4-hydroxyacetanilide, polyethyleneglycols O₃C₆H₁₄ and O₄C₈H₁₈, *p*-toluenesulfonyl chloride (TosCl), AgOAc, and aliphatic thiols were obtained from commercial sources and used without further purification. KPic was obtained by reaction of picric acid with sodium carbonate and recrystallized.

Milli-Q quality water was used for the extraction and transport experiments.

4-Dodecyloxianiline [26] and 4-dodecyloxibenzaldehyde [27] were synthesized by conventional methods. Similar methods were used to attach the polyether chains, but using tosylate precursors instead of bromides.

Note. Since it is known that polyethers tend to interact with water, the complexes were checked and confirmed to be water free prior to any thermal studies. Watering on purpose, followed by air drying, showed considerable uptake of water by the samples, although the influence on the LC behavior and the transition temperatures was very small (variations of about 3 °C were observed in the cases tested).

4.2. O₃C₆H₁₃Tos and O₄C₈H₁₇Tos

100 mL of triethylamine and 25 mL (143.07 mmol) of the corresponding polyethyleneglycol were mixed and introduced in an ice bath. 30 g (157.38 mmol) of TosCl (10% of excess) were added and the mixture was stirred for 6 h. Then, 150 mL of HCl and 200 g of ice were added and the product was extracted with diethylether, washed with water to neutral pH, and dried over MgSO₄. Further filtration and solvent evaporation gave the product as a viscous liquid.

4.3. *p*-(1,4,7-Trioxanonanyl)aniline and *p*-(1,4,7,10-tetra-oxadodecanyl)aniline

The tosylate (35.32 mmol) was added over an ethanolic solution (50 mL) of 4-hydroxyacetanilide (2.9 g, 32.11 mmol) and KOH (2.2 g, 40.14 mmol) dissolved in the minimum amount of water. The mixture was refluxed for 4 h. Then, water was added, ethanol was evaporated and the product was extracted with chloroform. The organic phase was separated and dried over MgSO₄. After filtration, the solvent was removed and the compound was vacuum-dried. A viscous liquid was obtained which corresponds to the polyether substituted acetanilide. To a solution of the described acetanilide (10 g, 32.11 mmol) in 40 mL of ethanol, a solution of KOH (11.19 g, 199.43 mmol) in 10 mL of water was added. The red solution was refluxed for

5 h. Then, ethanol was evaporated and the product was extracted in chloroform. The organic layers were collected, dried over MgSO_4 and, after vacuum evaporation of the solvent, the amine was obtained as a dark red liquid.

4.4. *p*-(1,4,7-Trioxanonanyl)benzaldehyde and *p*-(1,4,7,10-tetraoxadodecanyl) benzaldehyde

To a solution of 4-hydroxybenzaldehyde (35.42 mmol) in 100 mL of acetone, was added 38.96 mmol of the corresponding tosylate, and 70.8 mmol of K_2CO_3 . The mixture was then refluxed for 48 h. and the yellow suspension was filtered to remove the excess of K_2CO_3 and KCl formed. The filtrate was taken to dryness and the residue was chromatographed on a silica column using a mixture of *n*-hexane/ethyl acetate 2:3 as eluent.

4.5. Imines (HL) (1.1b–d, 1.2a–d)

All the imines were synthesized by condensation of their respective aldehydes and anilines in absolute ethanol with acetic acid as catalyst [28]. Yields were in the range 60–70%. IR (KBr): **1.2a**: 1623 s (C=N), 1253 vs, 1025 s (C–O–C), 1680 s, 842 m (Ar) cm^{-1} ; **1.1b–d**, **1.2b–d**: 1623 s $\nu(\text{C}=\text{N})$, 1254 vs, 1025 m, 1141 s $\nu(\text{C}–\text{O}–\text{C})$, 1609 s, 842 m $\nu(\text{Ar})$ cm^{-1} . Analysis (%): **1.1b**: calc.: C, 67.39; H, 7.92; N, 3.14; found: C, 67.50; H, 7.74; N, 3.06. **1.1c**: calc.: C, 73.43; H, 8.90; N, 3.17; found: C, 73.23; H, 8.68; N, 3.47; **1.1d**: calc.: C, 73.43; H, 8.40; N, 3.17; found: C, 73.33; H, 8.66; N, 3.66; **1.2a**: calc.: C, 80.82; H, 10.82; N, 2.55; found: C, 81.15; H, 11.11; N, 2.57; **1.2b**: calc.: C, 73.16; H, 9.50; N, 2.58; found: C, 73.01; H, 9.49; N, 2.34; **1.2c**: calc.: C, 73.16; H, 9.50; N, 2.58; found: C, 73.36; H, 9.69; N, 2.68; **1.2d**: calc.: C, 65.27; H, 8.12; N, 2.64; found: C, 65.59; H, 8.35; N, 2.33.

4.6. $[\text{Pd}(\mu\text{-OAc})\text{L}]_2$ derivatives (2.1b–d, 2.2a–d)

A mixture of 1.29 mmol of palladium acetate [29] and the stoichiometric amount of the corresponding imine (3.86 mmol) in 15 mL of glacial acetic acid was stirred at 50 °C for 14 h. The compounds were isolated in different ways depending on their nature. **2.2a** was filtered off from the resulting suspension, washed with cold acetone and dried in vacuum, obtaining a yellow solid (yield: 91%). To obtain **2.1d** and **2.2d**, the acetic acid was evaporated, the reddish solid was dissolved in CH_2Cl_2 and then filtered through a pad of Kieselgur. *n*-hexane was added and CH_2Cl_2 was evaporated to obtain a yellow solid which was filtered off, washed with cold *n*-hexane, and vacuum dried. Yields: 85–99%. Complexes **2.1b**, **2.1c**, **2.2b** and **2.2c** were not obtained pure in this way. Purification was

carried out transforming into their chloro-bridge derivatives as reported below. From these, pure acetate complexes were recovered as follows: sodium acetate ($\text{Pd}:\text{OAc} = 1:2$) was added to 30 mL of an acetone-dichloromethane solution of 0.07 mmol of $[\text{Pd}(\mu\text{-Cl})\text{L}]_2$ and was stirred for 14 h. The resulting suspension was evaporated to dryness and the complex was extracted in CH_2Cl_2 and filtered through a pad of Kieselgur. By addition of *n*-hexane and further evaporation of the CH_2Cl_2 , a yellow solid was obtained which was filtered off, washed with cold *n*-hexane and dried in vacuum (yields: 85–90%). All these compounds, except **2.2a**, acquire pasty textures. IR (KBr): **2.2a**: 1610 s (C=N), 1252 vs, 1029 s (C–O–C), 1542 s, 836 m (Ar), 1573 vs (C=O); **2.1b–d**, **2.2b–d**: 1608 s $\nu(\text{C}=\text{N})$, 1251 vs, 1062 m, 1119 s $\nu(\text{C}–\text{O}–\text{C})$, 1543 s, 834 m $\nu(\text{Ar})$, 1573 vs $\nu(\text{C}=\text{O})$. Analysis (%): **2.1b**: calc.: C, 53.16; H, 6.11; N, 2.30; found: C, 54.94; H, 5.95; N, 2.30; **2.1c**: calc.: C, 57.47; H, 6.82; N, 2.31; found: C, 57.12; H, 6.62; N, 2.72; **2.1d**: calc.: C, 57.47; H, 6.82; N, 2.31; found: C, 57.07; H, 6.58; N, 2.88; **2.2a**: calc.: C, 65.57; H, 8.70; N, 1.96; found: C, 65.68; H, 8.78; N, 1.99; **2.2b**: calc.: C, 59.52; H, 7.56; N, 1.98; found: C, 59.51; H, 7.37; N, 1.98; **2.2c**: calc.: C, 59.52; H, 7.56; N, 1.98; found: C, 59.50; H, 7.41; N, 1.88; **2.2d**: calc.: C, 53.33; H, 6.49; N, 2.00; found: C, 53.02; H, 6.20; N, 2.24.

4.7. $[\text{Pd}(\mu\text{-Cl})\text{L}]_2$ derivatives (3.1b–d, 3.2a–d)

To a stirred solution of $[\text{Pd}(\mu\text{-OAc})\text{L}]_2$ (1.75 mmol) in 20 mL of dichloromethane was added dropwise the stoichiometric amount of a solution of HCl in methanol ($\text{Pd}:\text{HCl} = 1:1$). After 1 h stirring the solvent was evaporated and the product was chromatographed through a silica column using different eluents: CH_2Cl_2 for **3.2a**; a 98.5:1.5 CH_2Cl_2 /methanol mixture for **3.1d** and **3.2d**, and a 99.9:0.1 CH_2Cl_2 /methanol mixture for **3.1b**, **3.1c**, **3.2b** and **3.2c**. The solutions obtained were taken to dryness and dissolved in dichloromethane. **3.2a** precipitates by adding acetone. The other complexes precipitate by adding *n*-hexane. The solids were filtered off, washed with the appropriate solvent and vacuum dried. All of them are yellow solids with different grades of pasty texture. Yields: 60–95%. IR (KBr): **3.2a**: 1610 s (C=N), 1250 vs, 1029 s (C–O–C), 1582 s, 832 m (Ar), 250 Pd–Cl (Nujol) cm^{-1} ; **3.1b–d**, **3.2b–d**: 1607 s (C=N), 1251 vs, 1031 m, 1114 s (C–O–C), 1580 vs, 831 m (Ar), 248 Pd–Cl (Nujol); Analysis (%): **3.1b**: calc.: C, 51.20; H, 5.84; N, 2.39; found: C, 50.88; H, 5.59; N, 2.30; **3.1c**: calc.: C, 55.68; H, 6.57; N, 2.40; found: C, 55.32; H, 6.44; N, 2.66; **3.1d**: calc.: C, 55.68; H, 6.57; N, 2.40; found: C, 55.41; H, 6.36; N, 2.42; **3.2a**: calc.: C, 64.33; H, 8.46; N, 2.02; found: C, 64.13; H, 8.09; N, 2.05; **3.2b**: calc.: C, 58.06; H, 7.38; N, 2.06; found: C, 57.34; H, 6.95; N, 2.05; **3.2c**: calc.: C, 58.06; H, 7.38; N, 2.06;

found: C, 57.78; H, 7.17; N, 2.08; **3.2d**: calc.: C, 51.64; H, 6.27; N, 2.07; found: C, 51.11; H, 6.05; N, 2.14.

4.8. $[Pd(\mu-Br)L]_2$ derivatives (**4.2a–d**)

To a suspension of 0.068 mmol of $[Pd(\mu-Cl)L]_2$ in 40 mL chloroform/acetone (2:1) was added an excess of KBr (2.08 mmol; Pd:Br 1:15), and the solution was refluxed for 5 h. After this time, the reaction was evaporated to dryness, dissolved in dichloromethane and filtered through Kieselgur in order to eliminate the potassium salts formed. EtOH was poured on the solution in **4.2a** and *n*-hexane was added in the other cases. After that, dichloromethane was evaporated. The solids obtained were filtered, washed with the adequate cold solvent and dried in vacuum. Yields: 73–95%. IR (KBr): **4.2a**: 1609 s (C=N), 1250 vs, 1028 s (C–O–C), 1580 s, 831 m (Ar) cm^{-1} ; **4.2b–d**: 1607 s (C=N), 1250 vs, 1029 m, 1114 s (C–O–C), 1580 s, 832 m (Ar). Analysis (%): **4.2a**: calc.: C, 60.45; H, 7.95; N, 1.90; found: C, 60.46; H, 7.68; N, 1.92; **4.2b**: calc.: C, 54.51; H, 6.93; N, 1.93; found: C, 55.2; H, 6.84; N, 2.14; **4.2c**: calc.: C, 54.51; H, 6.93; N, 1.93; found: C, 54.58; H, 6.64; N, 2.10; **4.2d**: calc.: C, 48.45; H, 5.89; N, 1.95; found: C, 48.69; H, 5.73; N, 2.07.

4.9. $[Pd(\mu-SC_n)L]_2$ derivatives (**5.1d** ($n = 8, 8^*$)))

The *n*-alkyl-thiol ($n = 8, 8^*$) (26.2 μ L, 0.15 mmol) was added to the yellow solution of **2.1d** (87.6 mg, 0.072 mmol) in 20 mL of CH_2Cl_2 . Immediately the color got lighter. After 1 h the solvent was evaporated and the product was crystallized in cold CH_2Cl_2 /EtOH. The yellow solid was filtered off and washed with cold EtOH. Yields: 53, 75%. IR (KBr): One isomer: 1604 s (C=N), 1263 s, 1062 m, 1109 s (C–O–C), 1539 s, 829 m (Ar). The other isomer: 1576 s (C=N), 1247 s, (C–O–C), 1504 s, 829 m (Ar) (cm^{-1}). Analysis (%): **5.1d** ($n = 8$): calc.: C, 56.93; H, 7.38; N, 2.01; found: C, 56.51; H, 7.13; N, 1.71; **5.1d** ($n = 8^*$): calc.: C, 56.93; H, 7.38; N, 2.01; found: C, 52.49; H, 6.28; N, 2.31.

4.10. $[Pd(\mu-SC_n)(\mu-OAc)L]_2$ derivatives (**6.1d** ($n = 8, 8^*$)))

A solution of **2.1d** (0.038 mmol) and **5.1d** ($n = 8, 8^*$) (0.038 mmol) in 20 mL of CH_2Cl_2 was stirred for 2 h. After removal of the solvent, the residue was treated with *n*-hexane, filtered off and washed with cold *n*-hexane. The yellow solid obtained had a pasty texture. Yields: 80, 85%. IR (KBr): 1607 m, 1580 vs (C=N), 1251 vs, 1056 m, 1113 vs (C–O–C), 1556, 1541 vs, 833 m ν (Ar) (cm^{-1}). Analysis (%): **6.1d** ($n = 8$): calc.: C, 55.17; H, 6.79; N, 2.14; found: C, 54.98; H, 6.48; N, 2.15; **6.1d** ($n = 8^*$): calc.: C, 55.17; H, 6.79; N, 2.14; found: C, 54.79; H, 6.26; N, 2.14.

4.11. $[Pd(\mu-SC_n)(\mu-Cl)L]_2$ derivatives (**7.1d** ($n = 2, 8, 8^*$)))

Complex **3.1d** (0.827 mmol) was dissolved in 20 mL of CH_2Cl_2 . To this solution was added the respective $AgSC_nH_{2n+1}$ (0.827 mmol) and the mixture was stirred for 2 h protected from the light. After filtration through a pad of Kieselgur, the solution was evaporated to dryness. The residue was treated with acetone and a gelatinous solid was obtained, filtered off, washed with acetone and vacuum dried. Yields: 75–95%. IR (KBr): 1607 s (C=N), 1265 s, 1061 m, 1117 vs (C–O–C), 1577 s, 831 m (Ar) (cm^{-1}). Analysis (%): **7.1d** ($n = 2$): calc.: C, 52.11; H, 5.89; N, 2.34; found: C, 51.65; H, 5.93; N, 2.34; **7.1d** ($n = 8$): calc.: C, 54.31; H, 6.68; N, 2.18; found: C, 54.21; H, 6.16; N, 2.24; **7.1d** ($n = 8^*$): calc.: C, 54.31; H, 6.68; N, 2.18; found: C, 54.01; H, 6.35; N, 1.98.

4.12. $Pd(acac)L$ derivatives (**8.1b–d, 8.2a–d**)

To a stirred solution of $[Pd(\mu-Cl)L]_2$ (0.07 mmol) in 20 mL of CH_2Cl_2 was added 0.14 mmol of thallium(I) acetylacetonate (Pd:acac = 1:1). The solution was protected from the light and stirred for half an hour. Then it was filtered through a pad of Kieselgur in order to remove the TlCl. *n*-Hexane was added to the filtrate and the dichloromethane was evaporated. The solid formed was filtered off, washed with *n*-hexane, and dried in vacuum, except the derivative **8.2d** which was obtained as a liquid at room temperature. Yields: 60–90%. IR (KBr): **8.2a**: 1609 s (C=N), 1253 vs, 1039 s (C–O–C), 1535 s, 833 m (Ar), 1573 vs (C=O) cm^{-1} . **8.1b–d, 8.2b–d**: 1609 s (C=N), 1252 vs, 1034 m, 1115 s (C–O–C), 1536 s, 829 m (Ar), 1578 vs (C=O). Analysis (%): **8.1b**: calc.: C, 5.93; H, 6.36; N, 2.15; found: C, 54.68; H, 5.93; N, 2.32; **8.1c**: calc.: C, 59.49; H, 7.02; N, 2.17; found: C, 59.36; H, 6.87; N, 2.49; **8.1d**: calc.: C, 59.49; H, 7.02; N, 2.17; found: C, 58.86; H, 6.71; N, 2.09; **8.2a**: calc.: C, 66.87; H, 8.68; N, 1.85; found: C, 66.56; H, 8.61; N, 1.64; **8.2b**: calc.: C, 61.16; H, 7.69; N, 1.87; found: C, 60.74; H, 7.54; N, 2.32; **8.2c**: calc.: C, 61.16; H, 7.69; N, 1.87; found: C, 60.96; H, 7.35; N, 1.87.

4.13. $Pd(Ala)L$ derivatives (**9.2a–d**)

To a stirred suspension of $[Pd(\mu-OAc)L]_2$ (0.068 mmol) in 20 mL of methanol was added the stoichiometric amount of alanine and the mixture was refluxed for 1 h. The solvent was evaporated to dryness and the product was extracted in CH_2Cl_2 and filtered through a pad of Kieselgur in order to eliminate the remaining alanine. The compounds were column chromatographed using dichloromethane–methanol (97:3) as eluent. The resultant solution was evaporated to dryness and dissolved in dichloromethane. **9.2a** was precipitated by

addition of EtOH; **9.2b–d** were precipitated with *n*-hexane. The solid was filtered off, washed with the appropriate cold solvent and dried by suction in vacuum. Yields: 50–80%. IR (KBr): **9.2a**: 1611 s (C=N), 1253 vs, 1051 s (C–O–C), 1579 s, 832 m ν (Ar), 3218 (NH₂) cm⁻¹. **9.2b–d**: 1609 s (C=N), (C=O), 1252 vs, 1061 m, 1115 s (C–O–C), 1500 s, 834 m (Ar), 3242 (NH₂). Analysis (%): **9.2a**: calc.: C, 64.63; H, 8.68; N, 3.77; found: C, 62.59; H, 8.41; N, 3.53; **9.2b**: calc.: C, 58.81; H, 7.68; N, 3.81; found: C, 58.37; H, 7.38; N, 3.88; **9.2c**: calc.: C, 58.81; H, 7.68; N, 3.81; found: C, 58.72; H, 7.10; N, 3.86; **9.2d**: calc.: C, 52.86; H, 6.65; N, 3.85; found: C, 52.64; H, 6.46; N, 3.77.

4.14. Azine ligand (H₂Az)

To a stirred solution of H₁₃C₆O₃–C₆H₄–CHO (2 g, 8.40 mmol) in absolute ethanol was added H₂N–NH₂·H₂O (0.210 g, 4.20 mmol) and a few drops of acetic acid. A yellowish solid was formed which was filtered and washed with cold ethanol. Yield: 82%. IR (KBr): 1630 m ν (C=N), 1251 s, 1065 m, 1103 vs ν (C–O–C), 1604 s, 841 m ν (Ar) cm⁻¹. Analysis (%): calc.: C, 66.08; H, 7.68; N, 5.93; found: C, 66.21; H, 7.73; N, 6.04.

4.15. [Pd₂(μ -OAc)Az]₂ (**10**)

Palladium acetate (1g, 1.48 mmol) and the azine (1.052g, 2.23 mmol) were mixed in 10 mL of acetic acid and heated at 50 °C for 36 h. The acetic acid was evaporated and the residue was treated with CH₂Cl₂ and filtered through a pad of Kiesseltur. Evaporation of the solvent gave an orange solid which was washed with cold EtOH. Yield: 89% IR (KBr): 1566vs (C=N), 1266 s, 1053 m, 1131 s (C–O–C), 1577 vs (Ar). Analysis (%): calc.: C, 44.96; H, 5.53; N, 3.50; found: C, 44.61; H, 4.89; N, 3.47.

4.16. Extraction experiments

In a 25 mL vial were placed 10 mL of a 2 × 10⁻³ M solution of the corresponding extracting complex in dichloromethane and 10 mL of an aqueous solution of potassium picrate (KPic) 10⁻⁴ M. Both phases were vigorously stirred for 3 h and let to completely separation for 1 h. A similar vial with 10 mL of dichloromethane and 10 mL of 10⁻⁴ M KPic was used as blank test. The final KPic concentration in the aqueous phase was determined by UV–Vis spectrophotometry (λ = 357 nm).

4.17. Ionic transport experiments

In a U tube was placed the liquid membrane made of 15 mL of a solution of the complex in dichloromethane.

The source phase was 10 mL of 10⁻² M KPic and the receiving phase was 10 mL of H₂O. A second identical U tube with 15 mL of dichloromethane as liquid membrane and equal source and receiving phases was used as reference. After moderate stirring for 77 h, [KPic] at the receiving phase was determined by UV–Vis spectrophotometry (λ = 357 nm).

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Appendix A. Supplementary material

Tables of relevant ¹H NMR data for compounds **1–10**. Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2004.11.010.

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