Binuclear cyclopalladated cyclophanes: towards a new family of metallomesogens

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Macrocyclic liquid crystals consisting of a biphenyl rigid core and a 2-phenylpyrimidine unit are fused by cyclopalladation giving a novel type of metallomesogens with nematic and smectic mesophases.

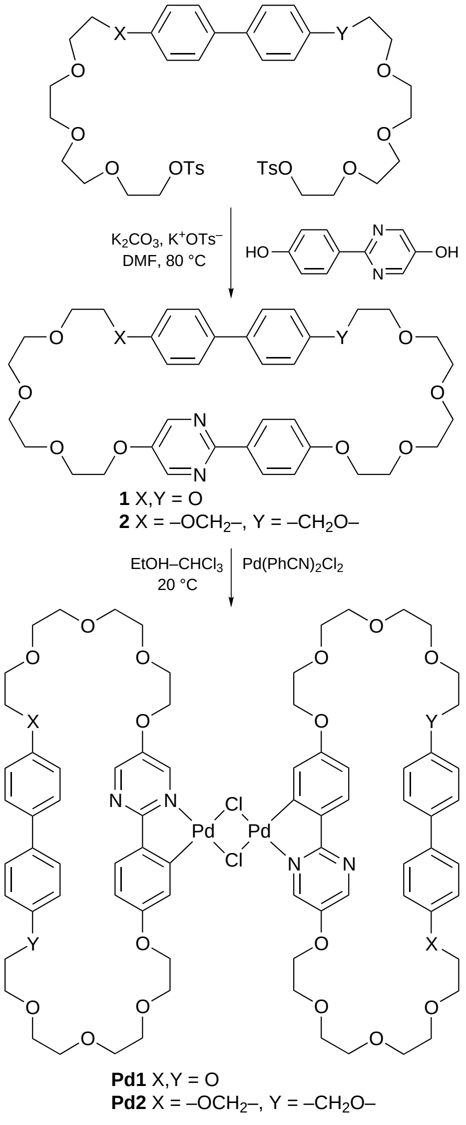
The continuing development of liquid-crystal-based technologies requires novel mesomorphic materials with special physical properties and much research has been carried out to prepare new types of liquid crystalline materials. In recent years metal containing liquid crystals have been developed and intensively investigated.[1] These metallomesogens allow the creation of quite unusual molecular geometries, which are difficult to achieve with purely organic materials. Additionally, interesting electronic and magnetic properties have been reported. Recently, another type of unconventional liquid crystals has been described. These are macrocyclic compounds incorporating conformationally flexible[2] or rigid[3] rod-like groups connected by appropriate flexible spacer units. It was found that they exhibit mesophases that are more stable than those of the corresponding low and high molecular mass open chain liquid crystals. Based on this observation we decided to synthesise macrocycles incorporating two different units. One of them is mainly responsible for the liquid crystalline properties whereas the other one should introduce a certain functionality, such as electron acceptor/donor properties,[4] photosensitivity or molecular recognition ability. Using the macrocycle approach these functional units can be connected with the mesogenic groups in a side specific manner, which should allow the tailoring of specific properties hopefully without losing the liquid crystalline properties.

Here, we describe the synthesis and the liquid crystalline behaviour of novel macrocyclic compounds which combine a 4,4′-substituted biphenyl core with a 2-phenylpyrimidine unit connected by polyether chains. The 2-phenylpyrimidine units can serve as ligands for the formation of liquid crystalline organometallics by orthopalladation.[5,6] In this way it should be possible to fuse two macrocyclic liquid crystals side by side. This novel molecular architecture combines a flat metallomesogenic heart with two additional calamitic mesogens.

The synthesis of the macrocycles **1** and **2** was carried out as outlined in Scheme 1 by cyclisation of 4,4′-bis[13-(toluenesulfonyloxy)-2,5,8,11-tetraoxatridecyl]biphenyl[7] or 4,4′-bis[12-(toluenesulfonyloxy)-4,7,10-trioxadodecyloxy]biphenyl† with 2-(hydroxyphenyl)-5-hydroxypyrimidine under high dilution conditions in the presence of potassium toluene-*p*-sulfonate (K^+OTs^-) as a template resulting in a yield of 21 and 35%, respectively. Correct spectral data which support the cyclic structure were obtained for both compounds.‡ The $[M + H]^+$, $[M + Na]^+$ and $[M + K]^+$ peaks in the electrospray MS§ correspond to the cyclic structures. No additional peaks could be detected in the scanned range up to $m/z = 2000$. Therefore other macrocycles with larger sizes should be absent.

The phase behaviour of the macrocycles was investigated by polarising microscopy. Compound **1** shows a monotropic nematic phase with a clearing temperature at 142 °C. The isotropic melt of compound **2** in which the polyether chains are connected *via* flexible methylene units with the biphenyl core can easily be supercooled to room temp. without transition to a liquid crystalline phase.

The orthopalladation reaction was carried out by reaction of the macrocyclic ligands **1** and **2** with $Pd(PhCN)_2Cl_2$[8] which leads in moderate yields (63 and 42%, respectively) to the corresponding metallomesogens **Pd1** and **Pd2** (Scheme 1). The ^1H NMR spectra of the complexes show a substitution pattern expected for palladium attack at C-2′ and one of the nitrogen atom of the phenylpyrimidine core. In negative ionization ESMS several peaks with typical isotopic pattern corresponding



1 X,Y = O
2 X = –OCH_2–, Y = –CH_2O–

Pd1 X,Y = O
Pd2 X = –OCH_2–, Y = –CH_2O–

Scheme 1

Table 1 Phase transition temperatures (T/°C)

Compound	X	Y	cr		S_A		N		is
1	O	O	●	172	—	—	(●	142)	●
Pd1	O	O	●	168	●	208	●	226[a]	●
2	OCH_2	CH_2O	●	87	—	—	—	—	●
Pd2	OCH_2	CH_2O	●	118	—	—	(●	91)	●

[a] Decomposition.

to $[Pd_2(Cl)_2L_2 + Cl]^-$ occur.¶ From these results and from the structures of related 2-phenylpyrimidine-Pd^{II} complexes[5] we assume the complexes contain a dimetallic core in which each Pd^{II} atom is in a square geometry.

The phase transition temperatures of **Pd1** and **Pd2** are shown and compared with the free ligands in Table 1. Compound **Pd1** exhibits an enantiotropic nematic phase indicated by the typical *schlieren* texture and marbelled textures observable between crossed polarizers. The clearing temperature of the nematic phase is significantly enhanced in comparison to the parent macrocycle **1**. On cooling below 208 °C the transition to another enantiotropic phase takes place which is indicated by the occurrence of a focal conic fan texture. This can easily be homeotropically aligned and thus clearly indicates a smectic A phase.

The metallomesogen **Pd2** obtained from the non-mesomorphic cyclophane **2** shows exclusively a monotropic nematic phase with a clearing temperature at 91 °C.

The higher clearing temperatures of the complexes in comparison with the ligands, the formation of an S_A layer structure in the phase sequence of compound **Pd1**, and the induction of a liquid crystalline nematic phase in the metallomesogen **Pd2** indicate a significant mesophase stabilisation caused by the orthopalladation with formation of a fused macrocyclic ring system. The amount of mesophase stabilisation corresponds to that observed for the orthopalladation of conventional 2-phenylpyrimidines[5] and should result from the better intermolecular interaction due to the $Pd(\mu\text{-}X)_2Pd$ core as well as from their rigid molecular structure.

The unusual molecular shape of compounds **Pd1** and **Pd2** imposes the question concerning the type of the observed nematic phases. One can assume that they represent uniaxial nematic phases made up by the individual rod-shaped rigid building blocks. On the other hand the molecules as a whole can probably adapt a disc- or a board-like shape. Thus, the nematic phases could also be made up by disc-shaped molecules. However, the occurrence of a smectic layer structure as a low temperature mesophase in the phase sequence of compound **Pd1** and the complete miscibility of the nematic phases of **Pd1** and **Pd2** with those of calamitic compounds are in line with a nematic phase made up of rod like molecules.

Interestingly, a biaxial nematic phase was recently proposed for a macrocyclic liquid crystal.[9] However, no hint of the presence of a biaxial nematic phase‖ has been found for the macrocyclic metallomesogens **Pd1** and **Pd2**.

In summary, the macrocyclic 2-phenylpyrimidine derivatives **1** and **2** are able to form dinuclear metallomesogens. The orthopalladated compounds **Pd1** and **Pd2** represent a novel type of metallomesogens and form more stable liquid crystalline phases than the parent macrocyclic ligands.

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Footnotes and References

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† Synthesised from 4,4′-bis[2-(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)ethoxy]biphenyl].[7]

‡ *E.g.* **1**: ^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$) 3.70–3.76 (m, 16 H, OCH_2), 3.86–3.93 (m, 8 H, OCH_2), 4.01 (t, ^3J 4.7 Hz, 2 H, OCH_2), 4.07–4.11 (m, 6 H, OCH_2), 6.77 (d, ^3J 8.8 Hz, 2 H, H-3′, 5′ Ph), 6.84 (d, ^3J 8.6 Hz, 2 H, H-3, 5 Ph), 6.89 (d, ^3J 9.0 Hz, 2 H, H-3, 5 *Ph*py), 7.25 (d, ^3J 8.8 Hz, 2 H, H-2′, 6′ Ph), 7.30 (d, ^3J 8.6 Hz, 2 H, H-2, 6 Ph), 8.17 (d, ^3J 9.0 Hz, 2 H, H-2, 6 *Ph*py) 8.32 (s, 2 H, H-4, 6 py); ESMS: *m/z* 691 $[M + H]^+$ (100), 713 $[M + Na]^+$ (35), 729 $[M + K]^+$ (8).

§ A solution of the compound in $CHCl_3$–MeOH–H_2O with a concentration of *ca.* 10 μg ml^{-1} was used for the ESMS investigations with a Finnigan MAT LCQ spectrometer.

¶ *E.g.*: **Pd1**: ^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$) 3.70–3.73 (m, 32 H, OCH_2), 3.81–3.94 (m, 16 H, OCH_2), 4.08–4.12 (m, 16 H, OCH_2), 6.58 (d, ^3J 8.4 Hz, 2 H, H-5′ *Ph*py), 6.75 (d, ^3J 8.4 Hz, 4 H, H-3′, 5′ Ph), 6.84 (d, ^3J 8.4 Hz, 4 H, H-3, 5 Ph), 6.92 (s, 2 H, H-3′ *Ph*py), 7.26 (d, ^3J 8.4 Hz, 4 H, H-2′, 6′ Ph)), 7.32 (d, ^3J 8.4 Hz, 2 H, H-6′ *Ph*py) 7.36 (d, ^3J 8.4 Hz, 4 H, H-2, 6 Ph) 8.24 (s, br, 2 H, H-4 py) 8.32 (s, br, 2 H, H-6 py). ESMS (negative ionisation), *m/z* (relative intensity): 1704 (30), 1703 (49), 1702 (52), 1701 (78),1700 (98), 1699 (90), 1698 (100), 1697 (80), 1696 (60), 1695 (46), 1694 (34), 1693 (21) $[Pd_2(Cl)_2L_2 + Cl]^-$, 1727 (28), 1726 (33), 1725 (35), 1724 (47), 1723 (40), 1722 (54), 1721 (52), 1720 (51), 1719 (43), 1718 (35), 1717 (25) $[Pd_2(Cl)_2L_2 + AcO]^-$; ESMS/MS (parent ion 1662 ± 5, 29%) daughter ion *m/z*: 1628, 1627, 1626, 1625 $[Pd_2ClL_2 + H]^+$; ESIMS^n $n = 3$ (parent ion 1626 ± 5, 31%) daughter ion *m/z*: 799, 798, 797, 796, 795, 794, 793 ($[PdL + H]^+$).

‖ The absence of four-brush disclinations in the nematic *schlieren* textures was suggested as a hint on the biaxiality of nematic phases.[10] However, not only two-brush but also four-brush disclinations were found in the textures of the nematic phases of **Pd1** and **Pd2**.

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