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MULTI-NUCLEAR PALLADIUM ORGANYLS– NOVEL STRUCTURES AND PROPERTIES OF DISC-LIKE METALLOMESOGENS[1]

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Abstract The first non-calamitic/disc-shaped metal organyl series **3** and **6** containing two or even four palladium atoms and eight or twelve flexible side chains presented here have been synthesized via the novel roof-shaped/bent dimers **2** or (the thermomesomorphic) **5**, respectively. In addition, from the chemical point of view the dodecaethers **5** and **6a-c** are the first derivatives of four novel, uniquely structured tetrapallado-macroheterocycles. Whereas the type of mesophase of **5** is still not distinctly clear yet those ones of **6a-c** are enantiotropic *discotic hexagonal columnar* (D_h) over a wide range of temperature. On the other hand, the dinuclear palladocompounds **3a-d** represent the first (monotropic) cases of metallomesogens exhibiting the *nematic-discotic* (N_D) phase. This thermotropic nematic type of phase clearly gets stabilized by doping **3c**, **d** with a strong electron acceptor; under such circumstances mesophase conversions/inductions ($N_D \rightarrow D_h$) are observed in the cases of **3a-c**. Finally, it is important to emphasize that the very large, thermotropically D_h phase displaying macroheterocycles **6a-c** are also *lyotropic* in various organic solvents exhibiting now a *nematic* phase.

I. INTRODUCTION

Although research on metal-containing liquid crystals has a long history[2-5] and world-wide enjoys strongly increasing interest during the last decade,[6] the study on metallomesogens still is in its infancy.

Most of these mesogens seem to have metal heteroatom bonds whereas examples with at least one metal carbon bond, so called metal organyls, are less

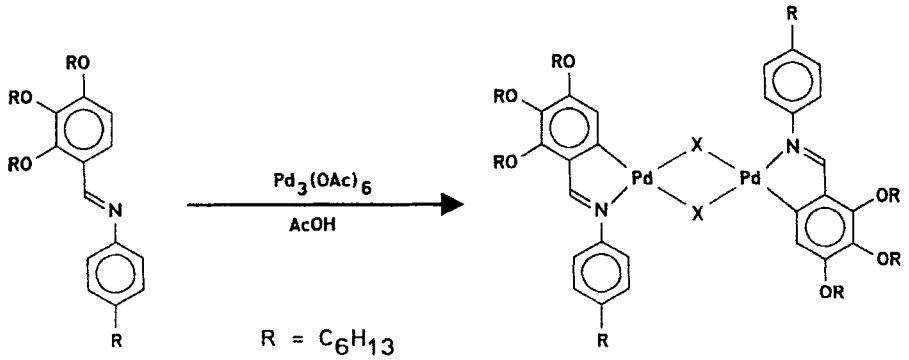
known.[6] However, there is a growing group of cyclometallated mesogens,[7,8] still characterized by palladium only, which contain both types of bonds in dinuclear, centrally fused *siamese twin-like* molecules. In contrast to classical calamitic liquid crystals[9] these metallocompounds are *parallel-rod-shaped* in structure and also form thermotropic nematic and smectic phases.[7,8]

In particular, this latter branch is most likely to be a promising one for future work. New shapes, easily generated for example by applying differently substituted ligands,[10] and hence novel mesophases should then be possible. Two such new cases are presented here, examples in plate-shape exhibiting the first *nematic-discotic* phases observed so far.

II. RESULTS AND DISCUSSION

1. Disc-shaped dinuclear palladium mesogens

The imine ligand **1** (prepared as usual by p-toluenesulfonic acid catalyzed condensation of the commercially available 4-hexylaniline and the 2,3,4-tri(hexyloxy)benzaldehyde[10] in toluene) reacted in glacial acetic acid as expected with palladium acetate $Pd_3(OAc)_6$ under formation of the acetato-bridged dinuclear palladium compound **2**.



1

2 : X = acetyloxy

3a : X = Cl
b : X = Br
c : X = I
d : X = SCN

SCHEME 1

The preparations of this new chloro-bridged palladium organyl **3a** from **2** and

of **3b**, **c**, and **d** from **3a**, respectively, were carried out by exchange reactions following published procedures [7, 8] for preparations of similar metallomesogens having only half the number of side arms than in **2** and **3a-d**.

As shown in their formulas of scheme 1 the arrangement of the two ligands **1** in **2** and **3a-d** is anti-parallel which can be derived from their NMR spectra.

Whereas the acetato-bridged palladium compound **2** possesses an *open-book* [8] or a *roof-like* shape and, therefore, may exist as an enantiomeric mixture [8] (a kind of atropisomerism), the four analogs **3a-d** in analogy to related systems with similar core structures [8] are assumed to be more or less planar giving NMR spectra easily to interpret, see experimental.

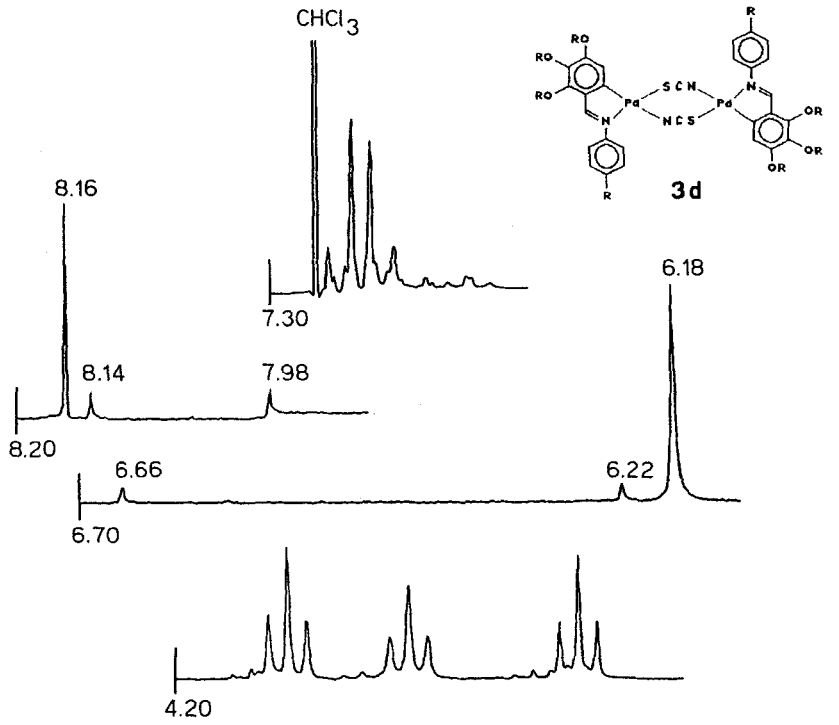


FIGURE 1. Part of the ^{1}H-NMR spectrum of the palladium organyl **3d**. The resonances at $\delta = 6.66$, 6.22, and 6.18 ppm belong to the protons of the aromatic rings substituted by palladium whereas those at $\delta = 8.16$, 8.14, and 7.98 ppm are caused by the olefinic proton of the imino groups. The three multiplets below $\delta = 4.20$ ppm show the methyleneoxy groups; the other aliphatic proton resonances are skipped here.

However, a certain complication in the NMR of **3d** stems from the fact that the two thiocyanato bridging groups of this dipalladomesogen are built-in in two ways, parallel or anti-parallel to each other,[8] leading to two structural isomers. Consequently, the number of magnetic resonances of the olefinic protons as well as of those aromatic ones at the palladium substituted phenyl rings in **3d** is each tripled, see figure 1. The ratio of these two isomers calculated from their proton signals is 87 (anti-parallel) to 13 (parallel).

It should also be mentioned that in the proton NMR of the halogeno-bridged palladium organyls **3a-c** some of the aromatic and O-CH_2 signals are very broad, see experimental, an observation also made on ortho-palladated azines.[7]

Investigations of the new series of palladium organyls by polarizing microscopy and differential scanning calorimetry (DSC) have shown that the halogeno- and thiocyanato-bridged members **3a-d** are monotropic *nematic-discotic* whereas the non-planar acetato-bridged one (**2**) is not liquid-crystalline as expected. The phase transition data of these five new heterocyclic compounds are summarized in table 1.

TABLE 1. Phase transition temperatures (°C)[a] and enthalpies (kJ/mol)[a] of the binuclear palladium organyls **2** and **3**; Cr: crystalline, N_D: nematic-discotic, I: isotropic.

Pd organyl	X	Cr		N_D		I
2	OAc	●	55.8 (84.2)	—		●
3a	Cl	●	79.2 (35.3)	{●	43.5 (0.1)}	●
3b	Br	●	72.6 (39.4)	{●	27.9 (0.1)}[b]	●
3c	I	●	97.4 (39.4)	{●	27.2 (0.1)}[c]	●
3d	SCN	●	96.1 (39.2)	{●	≈ 50 (—)}[d]	●

[a] Mettler TA 3000/DSC-30 S; on heating with 5 K/min (**2**, **3b-d**) or 10 K/min (**3a**), respectively. The phase transition enthalpies are put in parentheses. The values of monotropic transitions are given in {....}.

[b] This monotropic transition was found by DSC only on heating with 10 K/min.

[c] This monotropic phase transition could be determined by DSC only on cooling with 20 K/min because of rapid crystallization.

[d] This monotropic phase transition could be detected by hot stage polarizing microscopy only (heating rate 5 K/min).

The halogeno- or thiocyanato-bridged palladium organyls **3a-d** exhibit monotropic nematic mesophases with Schlieren texture and typical thermal fluctuations on cooling from the isotropic phase. Based on miscibility studies (contact method) with 1,2,3,5,6,7-hexakis(4-nonylphenylethynyl)naphthalene[11] the nematic phase observed in case of the chloro-bridged palladium nematogen **3a** was identified as *nematic-discotic* (N_D). Contact preparations of **3a** with each the bromo-, iodo-, and thiocyanato-bridged analogs **3b-d** confirm the *nematic-discotic* type of phase for all of these new palladium mesogens, the first examples of *disc-shaped* metallorganyls.

Also these *nematic-discotic* (N_D) metallomesogens **3a-c** show very small clearing enthalpies $\triangle H_{N_D \rightarrow I}$ of approximately 0.1 kJ/mol, see table 1, like other disc-shaped, but metal-free nematogens, a charakteristic for nematogens with planar geometry.[10-14]

In comparison with the halogeno-bridged compounds **3a-c** and other nematogens showing $N_D \rightarrow I$ transitions, the thiocyanato-bridged one (**3d**) displays an unusual clearing behaviour. The clearing temperature of **3d** is not sharp as expected for such transitions. On the contrary, the clearing process of **3d** occurs over a biphasic temperature range of about 5 K, see table 1, most probably caused by the composition of this nematogen, being a mixture of two structural isomers as already described above.

The significance of geometry and *number* of flexible lateral chains for the kind of exhibited mesogenity can be seen convincingly by comparing the *nematic-discotic* (N_D) chloro-, bromo-, and thiocyanato-bridged palladium organyls **3a-d**, with structurally related calamitic palladomesogens,[8] e.g., containing 4-decylbenzene(4-decyloxybenzal)imine as ligands and identical bridging groups, but exhibiting *smectic* mesophases, see introduction. The presence of two additional alkoxy chains in the positions 2 and 3 of the ligand yields **1**, making possible the synthesis of the new mesogens **3a-d** with a more *disc-like/elliptical* molecular shape which enables them to exhibit the *nematic-discotic* type of mesophase.

It is of great interest to note that mesophase stabilizations and/or inductions by charge transfer (CT) interactions found recently in various cases[15-19] are also observed in mixtures of each of the halogeno- and thiocyanato-bridged dinuclear palladium nematogens of type **3** with strong electron acceptors, eg., with 2,4,7-trinitrofluorenone (TNF).

TABLE 2. Thermomesomorphic properties[a] of charge transfer complexes generated by mixing the dinulear palladium organyls **2** and **3** with 2,4,7-trinitrofluorenone (TNF). The maxima of the clearing temperatures are put in parentheses; D_h: hexagonal columnar, N_D: nematic-discotic.

TNF complex of	X	mesophase
2	OAc	no mesophase
3a	Cl	D_h (180°C)
3b	Br	D_h (142°C)
3c	I	D_h (102°C) N_D (73°C)
3d	SCN	N_D (112°C)

[a] Results based on contact preparations and on mixtures with specific acceptor contents.

The types of mesophases induced here were found to be strongly influenced by the bridging group X, as can be seen in table 2.

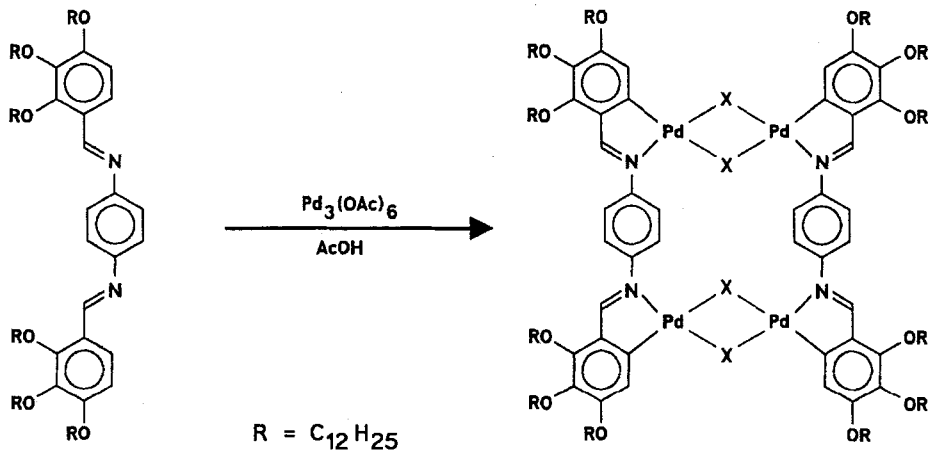
1) Each of the mixtures of the chloro- or bromo-bridged nematodiscogens **3a** or **b**, respectively, with TNF exhibit an induced hexagonal columnar (D_h) phase, an observation also made with other binary systems composed of disc-shaped electron donors and strong electron acceptors.[15-19]
2) In mixtures consisting of TNF and the thiocyanato-bridged compound **3d** the monotropic N_D phase of pure **3d**, see table 1, gets stabilized and becomes enantiotropic.
3) The situation in case of the iodo-bridged mesogen **3c**, doped with TNF, is more complex; this particular binary system now exhibits even *two* mesophases, i.e., an induced D_h phase appears along with an additional *nematic-discotic* (N_D) one at higher TNF concentrations.

Detailed results of these ongoing studies[20] will be published elsewhere in due course.

2. Disc-shaped tetranuclear palladium mesogens

The application of the ortho-palladation reaction on the new bisimine **4** led to the *tetranuclear* palladium organyl **5** (scheme 2); this seems to be the first example of a *fourfold ortho-palladation.*

The preparations of the halogeno- and thiocyanato-bridged dodeca-ethers **6a-c** were carried out by exchange reactions following the procedures briefly described for the dinuclear palladium compounds **3a**, **b**, and **d**, see experimental.



4

5 : X = acetyloxy

6a : X = Cl
b : X = Br
c : X = SCN

SCHEME 2

The postulated structures for this novel series of cyclometallated compounds (**5** and **6a-c**), each containing four metallacyclic rings and twelve long flexible side chains, are in agreement with results of IR and NMR measurements. First mass spectrometric studies on chloro-bridged dodeca-ethers with shorter alkyloxy chains (butyloxy and hexyloxy) confirm the presence of four palladium atoms in each of these molecules. Furthermore, preliminary osmometric molecular weight determinations seem to prove the non-oligomeric character of these thermomesomorphic palladium organyls **6a-c** which most probably are "the heaviest low molecular weight liquid crystals" known so far. They contain

three unique types of macroheterocyclic cores of rectangular shapes with diagonal diameters from oxygen to oxygen up to approximately 21 (X = Cl) to 24 Å (X = SCN), as taken from Dreiding models.

From their NMR data we assume an isomeric composition of the acetato- and thiocyanato-bridged palladium organyls **5** and **6c**, see experimental. The stereochemical situation of the core structures in this new family of tetranuclear palladium organyls **5** and **6** is not yet fully clear. Their NMR data (in part broad proton resonances, cf. **3a-c**) and thermomesomorphic properties seem to indicate that the halogeno- and thiocyanato-bridged members **6a-c** are planar or nearly planar.

First investigations of these palladium organyls **5** and **6a-c** by polarizing microscopy and differential scanning calorimetry (DSC) have shown that they are mesogenic and exhibit enantiotropic mesophases, see table 3.

TABLE 3. Phase transition temperatures[a] (°C) and enthalpies[a] (kJ/mol) of the tetranuclear palladium organyls **5** and **6**; Cr: crystalline, D_h: discotic hexagonal columnar, M: a highly viscous phase of not yet known type, I: isotropic.

Pd organyl	X	Cr	D_h	M	I
5	OAc	○ 71.0 (127.8)	—	◎ 114.4 (1.1)	◎
6a	Cl	○ 71.1 (86.7)	◎ 301 (45.7)	—	◎
6b	Br	○ 69.1 (111.5)	● 279 (28.3)	—	●
6c	SCN	○ 50.6 (128.7)	● 290 (---)[b]	—	●

[a] Mettler TA 3000/DSC-30 S; on heating with 1 K/min (**5**) or 5 K/min (**6a-c**), respectively, for the melting and 20 K/min for the clearing processes. Strong **decompositions** take place in the isotropic phases of **6a-c**.
The phase transition enthalpies are put in parentheses.

[b] Because of strong **decomposition** this transition temperature could only be estimated (polarizing microscopy, heating rate 20 K/min).

On heating these palladium mesogens above their melting points a highly viscous and birefringing mesophase can be seen (polarizing microscopy of covered samples). The liquid-crystalline phases of the halogeno- and thiocyanato-bridged dodeca-ethers **6a-c** show very high clearing temperatures close to 300°C with unusually high clearing enthalpies, see table 3.

In the isotropic phases strong decompositions take place, therefore, only on rapid cooling of samples of the halogeno-bridged palladomesogens **6a** and **b** from the isotropic liquid fan-shaped domains of hexagonal symmetry are developed typical for formations of a hexagonal columnar type (D_h) of phase. This mesophase specification based on polarizing microscopy is confirmed by first X-ray measurements[20] at least for the bromo-bridged tetranuclear palladium organyl **6b**. The extremely strong decomposition of the thiocyanato-bridged compound **6c** in the isotropic phase prohibited successful DSC measurements and texture studies. Miscibility tests (contact method) seem to confirm the identity of the liquid-crystalline phases within this series of disc-shaped palladium organyls **6**.

A somewhat unusual behaviour is found for the acetato-bridged tetranuclear palladium compound **5**. After melting a highly viscous, most likely liquid-crystalline "M" phase is observed up to about 114°C. Contact preparations - problems emerge from high viscosity and decompositions of the compounds in the isotropic phase - seem to indicate that this "M" phase is miscible with the D_h phase of the three halogeno- and thiocyanato-bridged palladomesogens **6a-c**. But, further studies are necessary; until a final decision is made we assign this phase with the symbol "M".

On further heating above 114°C **5** forms an isotropic or pseudoisotropic phase, at 250°C it decomposes. The viscosity of this latter phase is comparable to those of highly ordered mesophases. On pressing such a sample (between glass plates) with a steel needle some birefringence is induced which remains for a few minutes and during subsequent cooling to room temperature leading to a glassy material; no phase transition back into the "M" phase is detectable. From these observations we cannot exclude that this high temperature phase is a liquid-crystalline one.

Finally, it is also interesting to note that the halogeno- and thiocyanato-bridged metallomesogens **6a-c** form *lyotropic nematic* phases in lipophilic organic solvents, e.g., dissolved in chloroform or pentadecane. In other words, they represent a type of disc-shaped compounds that form *both* thermotropic *and* lyotropic mesophases, a phenomenon discussed already some time ago[21] as a function of the design of mesogens.

In this connection we should point out that a few years ago a disc-shaped derivative of benzenehexamine[22] was described[23] which also exhibit a *lyotropic*

nematic phase and a mesophase with *hexagonal* structure in various lipophilic organic solvents in dependence of the concentration.

IV. CONCLUDING REMARKS

Also these first results on new, easily and in good yields accessible compounds presented here support the growing opinion that the liquid-crystalline properties of metallomesogens are dominantly controlled by the structure of the ligands. In particular and not unexpected, the number and positions of their side chains are very important. These two features of suitable ligands in known[7,8] as well as in our new metallomesogens determine the type of mesophase, e.g., after palladation, rod-shaped ligands can deliver either nematic or smectic liquid crystals[7,8] or, as shown in this study, even nematic-discotic or discotic hexagonal columnar ones. The differently bridged pairs of palladium atoms between such ligands essentially act as a kind of "internal fastener" holding the two identical ligands coplanar and tightly together.

The fact that our new compounds of both series (**3** and **6**) exhibit interesting and in part new properties on heating and on dissolving the tetranuclear compounds of type **6** in lipophilic organic solvents make them promising for future work of various kinds. The same is true for their capability to form charge transfer complexes on doping with electron acceptor molecules leading to mesophase stabilizations, conversions, and/or inductions.

V. EXPERIMENTAL

A. Equipment applied for structural elucidations and phase transition studies

The characterizations of the numerous new compounds presented here are based on correct elementary analyses and on various spectroscopic data, e.g., ^{1}H-NMR (Bruker WH 400, $CDCl_3$), ^{13}C-NMR (Bruker AM 270, $CDCl_3$), IR (Beckmann 9, CCl_4), and MS (Varian MAT 711 or AMD Intectra at Varian MAT 311 A - basis). Structurally relevant data are given only, see below.

The phase transitions were studied by DSC (Mettler TA 3000/DSC-30 S with TA 72 software) and by polarizing microscopy (Leitz Laborlux 12 Pol with a hot stage Mettler FP 82).

B. Synthetic descriptions of all new compounds

1) The new *2,3,4-tri(dodecyloxy)benzaldehyde*, $C_{43}H_{78}O_4$ (659.1), colourless crystals, m.p. 37°C, was obtained in two steps by etherification of pyrogallol with dodecylbromide (K_2CO_3, acetone) and subsequent Vilsmeyer formylation, overall yield 75%. ^{1}H-NMR: δ = 10.26 (s; CHO), 7.57, 6.71 (2 d, J ≈ 9 Hz; the 2 aromatic hydogens), 4.17, 4.03, 3.97 (3 t, J ≈ 6.5 Hz each; 3 OCH_2 groups). ^{13}C-NMR: δ = 189.09 (d; CHO), 159.24, 156.67, 141.00, 123.43 (4 s; aromatic carbons), 123.68, 108.02 (2 d; 2 aromatic CH situations), 75.30, 73.72, 68.87 (3 t; 3 OCH_2 groups). MS: m/z (%) = 658 [65; M^+].

2) The ligands **1** and **4**:

a) *4-hexylbenzene[2,3,4-tri(hexyloxy)benzal]imine* (**1**) $C_{37}H_{59}NO_3$ (565.9). This imine was prepared in the usual way by a p-toluenesulfonic acid (40 mg) catalyzed condensation of 10 mmol 2,3,4-tri(hexyloxy)benzaldehyde[10] with 15 mmol 4-hexylaniline (commercially available) in 50 ml toluene and purified by column chromatography on alkaline aluminium oxide (eluent petroleum ether (b.p. 30-70°C)/ethyl acetate 10:1). Yield 92%, yellow-orange oil. ^{1}H-NMR: δ = 8.77 (s; HC=N), 7.84, 7.19, 7.13, 6.74 (4 d, J ≈ 8.5 Hz each; 1, 2, 2, and 1 aromatic hydrogen, respectively), 4.10, 4.03, 3.99, 2.61 (4 t, J ≈ 7.5 Hz each; 4 α-CH_2 groups). ^{13}C-NMR: δ = 156.14, 154.07, 150.33, 141.67, 140.24, 123.06 (6 s; aromatic carbons), 155.52 (d; CH=N), 128.91, 122.15, 120.79, 108.47 (4 d; 6 aromatic CH situations), 74.77, 73.59, 68.67, 35.41 (4 t; 4 α-CH_2 groups); MS: m/z (%) = 565 [7; M^+], 390 [100; $M^+ - C_{12}H_{19}N$].

b) *1,4-benzene-bis[2,3,4-tri(dodecyloxy)benzal]imine* (**4**) $C_{92}H_{160}O_6N_2$ (1390.3). The p-toluenesulfonic acid (40 mg) catalyzed condensation of 10 mmol of the new 2,3,4-tri(dodecyloxy)benzaldehyde with 1,4-benzenediamine (5 mmol) in toluene gave after recrystallization from ethanol the yellow crystalline **4**. Yield 79%, m.p. 62.9°C. ^{1}H-NMR: δ = 8.80 (s; 2 hydrogens, HC=N), 7.86, 6.75, (2 d, J ≈ 8.5 Hz each; 2 aromatic hydrogens each), 7.25 (s; 4 aromatic hydrogens), 4.11, 4.03, 3.99, (3 t, J ≈ 6.5 Hz each; 6 α-CH_2 groups). ^{13}C-NMR: δ = 156.32, 154.22, 150.34, 141.22, 123.07 (5 s; 10 aromatic carbons), 155.48 (d; 2 CH=N), 122.29, 121.82, 108.52 (3 d; 2, 4, and 2 aromatic CH situations, respectively), 74.88, 73.68, 68.73, (3 t; 6 α-CH_2 groups).

A monotropic nematic phase was observed for this bisimine **4**; attempts to determine its transition data failed because of rapid crystallization.

3) The **ortho-palladated organyls 2**, **3**, **5**, and **6** with the ligands ^{1}L ≡ *4-hexylbenzene[2,3,4-tri(hexyloxy)benzal]imine* (**1**) or ^{2}L ≡ *1,4-benzene-bis-[2,3,4-tri(dodecyloxy)benzal]imine* (**4**), respectively.

a) The acetato-bridged di- and tetranuclear palladium compounds **2** and **5**. The ortho-palladation was carried out by refluxing 2 mmol of the ligand compounds **1** or **4** with 2 or 4 mmol palladium acetate $Pd_3(OAc)_6$, respectively, in glacial acetic acid (**1**: in 90 ml, 10 min; **4**: in 130 ml, 35 min) under argon. The acid was evaporated completely. The crude products were dissolved in dichloromethane, filtered, and after removal of the solvent at 30°C under reduced pressure the palladium compounds were crystallized from acetone/ethanol (**2**) or from dichloromethane/ethanol (**5**) avoiding heating above 30°C. The acetato-bridged palladium organyls **2** and **5** were obtained as isomeric mixtures.

$Pd_2{}^1L_2(\mu\text{-}OAc)_2$ (**2**), $C_{78}H_{122}N_2O_{10}Pd_2$ (1460.6), yield 73%, brownish crystals, m.p. 55.8°C. ^{1}H-NMR: δ = 7.70 (s; 2 HC=N), 6.96, 6.75 (2 d, J = 8.5 Hz each; 4 aromatic hydrogens each), 5.83 (s; 2 aromatic hydrogens), 4.14 - 4.07, 4.04 - 3.93, 3.76 - 3.69 (3 m; 6 OCH_2 groups), 2.56 (t, J = 8 Hz; aryl-CH_2 groups), 1.78 (s; 6 hydrogens, 2 bridging acetato groups). ^{13}C-NMR: δ = 180.04 (s; 2 bridging CH_3-$\underline{C}O_2$), 168.35 (d; 2 CH=N), 154.91, 151.89, 151.64, 145.72, 141.32, 137.16, 131.43 (7 s; 14 aromatic carbons) 127.53, 122.95, 111.48 (3 d; 4, 4, and 2 aromatic CH situations), 73.97, 73.69, 68.24, 35.56 (4 t; 8 α-CH_2 groups).

$Pd_4{}^2L_2(\mu\text{-}OAc)_4$ (**5**), $C_{192}H_{328}N_4O_{20}Pd_4$ (3438.3), yield 76%, orange solid, m.p. 71.0°C. ^{1}H-NMR: δ = 8.01, 7.97 (2 s; ratio 1:0.16, HC=N), 7.00, 6.96 (2 s; ratio 1:0.16, aromatic hydrogens of the p-di-N–substituted benzene rings), 6.05 (s; 4 aromatic hydrogens), 4.14 - 3.89, 3.80 - 3.68 (2 m; 12 OCH_2 groups), 2.26, 1.71 (2 s; isomeric acetato-bridges). ^{13}C-NMR: δ = 182.01, 179.21 (2 s; 4 bridging CH_3-$\underline{C}O_2$), 168.79 (d; 4 CH=N), 155.15, 151.69, 151.39, 147.22, 137.22, 131.60 (6 s; 24 aromatic carbons), 122.75, 111.73 (2 d; 8 and 4 aromatic CH situations), 74.64, 73.49, 68.62 (3 t; 12 α-CH_2 groups).

b) The chloro-bridged di- and tetranuclear palladium compounds **3a** and **6a**. Treatment of these acetato-bridged palladium compounds **2** (1.34 mmol) and **5** (0.174 mmol), respectively, dissolved in dichloromethane, with 0.1 M isopropanolic hydrochloric acid at room temperature under argon (**2**: in 150 ml CH_2Cl_2, 2.95 mmol HCl, 4 h; **5**: in 50 ml CH_2Cl_2, 0.80 mmol HCl, 16 h) furnished the chloro-bridged palladium mesogens **3a** and **6a**, respectively, which were purified by crystallization from acetone/ethanol (**3a**) or from acetone/CH_2Cl_2 (**6a**).

$Pd_2{}^1L_2(\mu\text{-}Cl)_2$ (**3a**), $C_{74}H_{116}N_2O_6Pd_2Cl_2$ (1413.5), yield 74%, yellow crystals, m.p. 79.2°C. ^{1}H-NMR: δ = 8.03 (s; 2 HC=N), 7.29 - 7.20, 7.18 - 7.08 (2 m; 4 aromatic hydrogens each), 6.57 (s, broad; 2 aromatic hydrogens), 4.11, 3.85 (2 t, J = 6.5 Hz each; 4 OCH_2 groups), 3.95 (s, broad; 2 OCH_2 groups), 2.63 - 2.54 (t, broad; 2 aryl-CH_2 groups). ^{13}C-NMR: δ = 170.60

(d; 2 CH=N), 155.14, 151.91, 149.80, 146.94, 142.09, 137.61, 132.11 (7 s; 14 aromatic carbons) 128.30, 123.24, 112.83 (3 d; 4, 4, and 2 aromatic CH situations), 74.59, 73.61, 68.62, 35.59 (4 t; 8 α-CH_2 groups). MS: m/z (%) = 1412 [M^+].

$Pd_4{}^2L_2(\mu\text{-}Cl)_4$ (**6a**), $C_{184}H_{316}N_4O_{12}Pd_4Cl_4$ (3344.0), yield 89%, yellow-green crystals, m.p. 71.1°C. ^{1}H-NMR: δ = 8.01 (s; 4 HC=N), 7.19, 6.78 (2 s; 8 and 4 aromatic hydrogens, respectively), 4.12, 4.07, 3.86 ((3 t, J≈ 6.5 Hz each; 4 OCH_2 groups each). ^{13}C-NMR: δ = 171.06 (d; 4 CH=N), 155.59, 152.26, 150.76, 147.21, 137.60, 132.11 (6 s; 24 aromatic carbons), 123.81, 112.48 (2 d; 8 and 4 aromatic CH situations), 74.60, 73.69, 68.71 (3 t; 12 OCH_2 groups).

c) The bromo-, iodo-, and thiocyanato-bridged Pd-organyls **3b-d** and **6b, c**. The bromo- and thiocyanato-bridged palladium organyls **3b**, **d** and **6b**, **c** as well as the iodo-bridged **3c** were prepared from the analogous chloro-bridged compounds **3a** or **6a**, respectively, by simple exchange reactions with potassium bromide, potassium thiocyanate and lithium iodide, respectively, in dichloromethane/acetone in an argon atmosphere at room temperature (dinuclear palladium compounds **3b**: 0.5 mmol **3a**, 15 mmol KBr, 60 h; **3c**: 0.5 mmol **3a**, 40 mmol LiI, 95 h; **3d**: 0.5 mmol **3a**, 30 mmol KSCN, 60 h, in 150 ml CH_2Cl_2/75 ml acetone; tetranuclear compounds **6b**: 0.34 mmol **6a**, 33 mmol KBr, 90 h; 150 ml CH_2Cl_2/100 ml acetone; **6c**: 0.29 mmol **6a**, 10 mmol KSCN, 150 ml CH_2Cl_2/75 ml acetone, 90 h). The crude products were purified by recrystallization from acetone/ethanol (**3b** and **c**) or acetone (**3d**) in case of the dinuclear compounds and from dichloromethane/acetone (**6b**) or dichloromethane/ethanol (**6c**) for the tetranuclear palladium organyls.

$Pd_2{}^1L_2(\mu\text{-}Br)_2$ (**3b**), $C_{74}H_{116}N_2O_6Pd_2Br_2$ (1502.4), yield 52%, yellow-orange crystals, m.p. 72.6°C. ^{1}H-NMR: δ = 8.06 (s; 2 HC=N), 7.27-7.05 (m; 8 aromatic hydrogens), 6.75 (s, broad; 2 aromatic hydrogens), 4.10, 3.85 (2 t, J≈ 6.5 Hz each; 4 OCH_2 groups), 3.95 (s, broad; 2 OCH_2 groups), 2.60 (t, broad; 2 aryl-CH_2 groups). ^{13}C-NMR: δ = 171.00 (d; 2 CH=N), 155.37, 151.98, 141.93, 137.45, 123.34 (5 s; 14 aromatic carbons), 128.35, 123.27, 114.54 (3 d; 4, 4, and 2 aromatic CH situations), 74.54, 73.53, 68.58, 35.49 (4 t; 8 α-CH_2 groups).

$Pd_4{}^2L_2(\mu\text{-}Br)_4$ (**6b**), $C_{184}H_{316}N_4O_{12}Pd_4Br_4$ (3521.9), yield 70%, yellow crystals, m.p. 69.1°C. ^{1}H-NMR: δ = 8.04 (s; 4 HC=N), 7.17, 6.84 (2 s; 8 and 4 aromatic hydrogens, respectively), 4.12, 4.08, 3.87 (3 t, J≈7, 7, and 6.5 Hz; 4 OCH_2 groups each). ^{13}C-NMR: δ = 171.40 (d; 4 CH=N), 155.82, 152.34 ,151.96, 151.57, 137.48, 132.37 (6 s; 24 aromatic carbons), 123.85, 114.10 (2 d; 8 and 4 aromatic CH situations), 74.52, 73.58, 68.70 (3 t; 12 OCH_2 groups).

$Pd_2\,{}^1L_2(\mu\text{-}I)_2$ (**3c**), $C_{74}H_{116}N_2O_6Pd_2I_2$ (1596.4), yield 50%, orange crystals, m.p. 97.4°C. ^{1}H-NMR: δ = 8.14 (s; 2 HC=N), 7.24–7.04 (m; 10 aromatic hydrogens), 4.09 (t, J ≈ 6.5 Hz; 2 OCH_2 groups), 3.96, 3.84 (2 t, broadened, J ≈ 6.5 Hz each; 4 OCH_2 groups). ^{13}C-NMR: δ = 171.89 (d; 2 CH=N), 156.35, 154.20, 152.52, 148.68, 141.86, 137.41, 133.20 (7 s; 14 aromatic carbons), 128.39, 123.56, 123.46, 118.06, 118.03 (5 d; 10 aromatic CH situations), 74.67, 73.59, 68.74, 35.49 (4 t; 8 α-CH_2 groups).

$Pd_2\,{}^1L_2(\mu\text{-}SCN)_2$ (**3d**), $C_{76}H_{116}N_2O_6Pd_2S_2$ (1458.7), yield 95%, yellow crystals, m.p. 96.1°C. ^{1}H-NMR: δ = 8.16, 8.14, 7.98 (3 s; ratio 1:0.075:0.075, HC=N, two isomers), 7.26–6.97 (m; aromatic hydrogens), 6.66, 6.22, 6.18 (3 s; ratio 0.075:0.075:1, aromatic hydrogens), 4.10, 3.90, 3.74 (3 t, J ≈ 7 Hz each; 6 OCH_2 groups), 2.65, 2.58 (2 t, broad, ratio 1:0.2; aryl-CH_2 groups). ^{13}C-NMR: δ = 171.84 (d; 2 CH=N), 155.69, 152.77, 149.79, 147.86, 142.27, 137.83, 133.65, 125.96 (8 s; 14 aromatic carbons and 2 SCN), 128.57, 122.68, 111.89 (3 d; 10 aromatic CH situations), 74.65, 73.61, 68.71, 35.55 (4 t; 8 α-CH_2 groups). IR (CCl_4) $\tilde{\nu}_{SCN}$ = 2160 cm^{-1}.

$Pd_4\,{}^2L_2(\mu\text{-}SCN)_4$ (**6c**), $C_{188}H_{316}N_8O_{12}Pd_4S_4$ (3434.6), yield 34%, yellow solid, m.p. 50.6°C. ^{1}H-NMR: δ = 8.13, 8.02 (2 s; ratio 1:1, 4 HC=N), 7.26, 7.13 (2 d, J ≈ 8 Hz each; 8 aromatic hydrogens), 6.69, 6.21 (2 s; ratio 1:1, 4 aromatic hydrogens), 4.19–3.98, 3.92–3.81 (2 m; 12 OCH_2 groups). ^{13}C-NMR: δ = 173.66, 173.64, 171.13 (3 d; CH=N), 157.31, 156.20, 155.79, 153.09, 152.53, 150.51, 148.62, 148.08, 137.76, 137.72, 136.96, 133.61, 131.55, 127.98, 126.98 (15 s; 24 aromatic carbons and 4 SCN), 123.69, 123.23, 114.14, 111.96 (4 d; 12 aromatic CH situations), 74.63, 73.71, 73.67, 69.00, 68.77 (5 t; 12 OCH_2 groups). IR (CCl_4) $\tilde{\nu}_{SCN}$ = 2170–2150 cm^{-1}.

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