Disc-Like Chiral Palladium and Platinum Complexes: Synthesis and Mesomorphic Properties

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Dedicated to Professor Dr. R. Miethchen on the occasion of his 60th birthday

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ortho-Palladated and -platinated benzalimines are a widely studied novel type of liquid-crystals. These sheet-shaped materials contain two or even four metal atoms and carry eight and twelve flexible side-chains, respectively. Here we present the preparation and mesomorphic properties of dinuclear chiral homologues of such sheet-like compounds. On their own, the chiral members of the dinuclear cyclopalladated series exhibit no liquid-crystalline properties, but show mesophase inductions ($\mathrm{Col_h}$-phase) in mixtures with an electron-acceptor, e.g., 2,4,7-trinitrofluorenone (**TNF**). A diplatinated chiral analogue, however, monotropically exhibits the cholesteric nematic discotic ($\mathrm{N_D^*}$) type of mesophase. Mixtures of this platinum nematogen with **TNF** also show the induction of a columnar mesophase ($\mathrm{Col_h}$) due to charge-transfer interactions.

Introduction

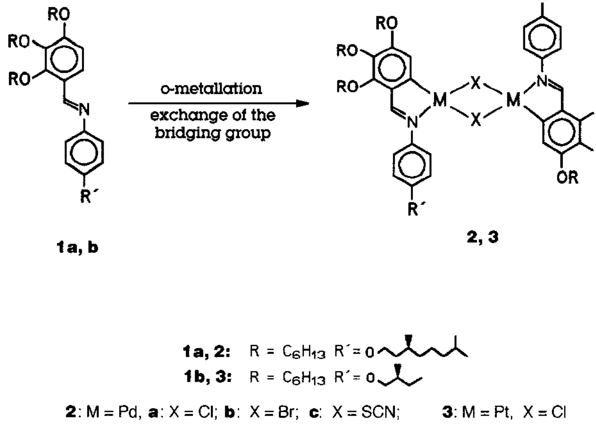
Cyclometallated complexes containing platinum group metals are of considerable academic and commercial interest and have grown to be a significant subject in current liquid-crystal research.[1,2] Within this field *ortho*-palladated metal organyls − organometallic compounds with metal-carbon bonds − originally attracted interest because of their promising combinations of properties attributed to transition-metal complexes and to the self-organization in liquid-crystalline phases.[1,2] Most cyclopalladated mesogens found so far are calamitic in nature, and they are either rod-shaped in the case of mononuclear complexes or can be viewed as twin-mesogens made up by two rod-shaped moieties fused by means of bridging groups. Consequently, usually typical nematic and/or smectic phases consistent with their rod-like structures are observed.

However, by changing the number and position of the peripheral alkyl chains of such *ortho*-metallated mesogens more sheet-like or ellipsoid shapes can be obtained, leading to the formation of the nematic discotic ($\mathrm{N_D}$) type of mesophase.[2,3] We have studied structure-property relations for such sheet-like *ortho*-metallated complexes by varying both their core section (bridging ligands and the metal atom) as well as their aliphatic periphery.[3−7]

Chiral mesophases formed by chiral mesogens are of special interest with respect to their electro-optical properties and possible applications resulting from these properties. The number of sheet- or disc-like chiral mesogens in general and particularly of those exhibiting the cholesteric-nematic discotic ($\mathrm{N_D^*}$) type of mesophase found so far is quite limited.[8,9] Here, we report the synthesis and liquid-crystalline properties of the first chiral members of flat, sheet-like dinuclear palladium and platinum organyls.

Result and Discussion

Chirality can be introduced into sheet-like dinuclear palladium or platinum organometallic compounds of the type



Scheme 1

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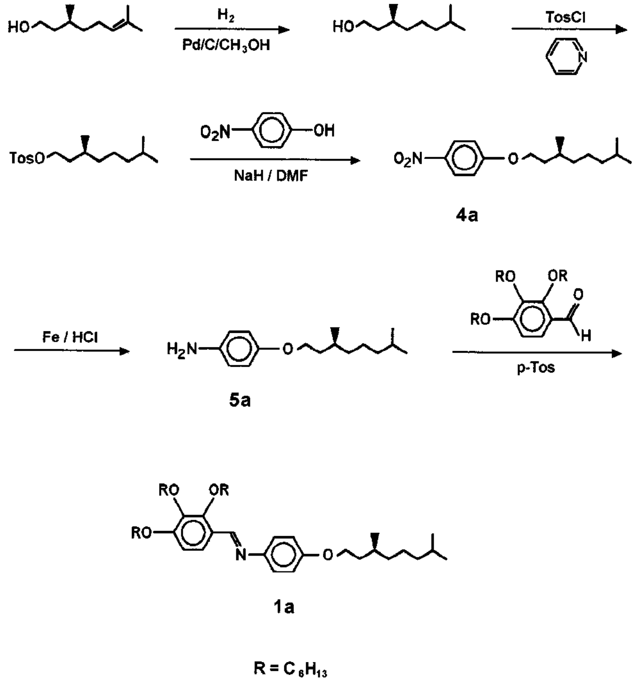
studied here (see Scheme 1) through their peripheral aliphatic chains, either in the aniline- or in the benzaldehyde-derived[10] parts of the ligands.

Dinuclear palladium organyls in general can be obtained from imines, for example **1a** in Scheme 1, by *ortho*-palladation of the ligands with palladium acetate in glacial acetic acid. Exchange of the acetato-bridges with hydrochloric acid leads to chloro-bridged dinuclear palladium complexes (**2a**) from which the bromo- and thiocyanato-bridged homologues **2b** and **c** are accessible by simple exchange reactions with KBr and KSCN, respectively. The dinuclear chloro-bridged platinum complexe **3** (cf. Scheme 1) on the other hand, was obtained by direct *ortho*-platination of the respective imine ligand **1b** with (di-μ-chloro-bis(η^3-2-methylallylplatinum).

The chiral ligands **1a** and **b** were synthesized from 4-nitrophenol, by the usual etherification with the corresponding alkyl tosylates. These tosylates[9] are easily prepared from the hydrogenation product of (*S*)-β-*citronellol* and from (*S*)-*2-methylbutyl alcohol*, respectively, and the citronellol derivative is given as an example in Scheme 2. Reduction of the 4-nitrophenol ethers with Fe/HCl followed by acid-catalyzed condensation with 2,3,4-tri(hexyloxy)-benzaldehyde[11] gave the new chiral imines **1a** and **b**.



Scheme 2

The new ligands **1a** and **b** as well as their metal complexes **2a−c** and **3** were characterized by ^{1}H and ^{13}C NMR spectroscopy and gave correct elemental analysis (see Experimental Section). Furthermore, ^{1}H and ^{13}C NMR spectroscopic data for the dipalladium organyls **2a−c** and the diplatinum organyl **3** are very similar to those of non-chiral analogs with planar structures and antiparallel orientations of their ligands, as shown by X-ray analysis.[6]

No mesophase formation could be observed for the chloro-, bromo- and thiocyanato-bridged chiral dinuclear palladium organometallic compounds **2a**, **b** or **c**, respectively, in contrast to their achiral analogs,[4] which all exhibit the nematic-discotic ($\mathbf{N_D}$) type of mesophase monotropically. These palladium and platinum organometallic compounds with eight peripheral chains all show a tendency for significant supercooling and slow crystallization. However, when using hot-stage polarizing microscopy even with cooling rates as high as 100 K/min, no formation of a mesophase could be observed by cooling **2a−c** from their isotropic phases.

The new diplatinum organyl **3**, on the other hand, carrying two short chiral side-chains exhibits a monotropic cholesteric nematic-discotic mesophase (N_D^*).

The thermal transition data of these four new chiral metallocyclic compounds are summarized in Table 1.

Table 1. Phase transition temperatures *T* (°C) and enthalpies (kJ mol^{-1}) of **2a−c** and **3**:
Cr: crystalline, N_D*: cholesteric nematic discotic and Iso: isotropic

Organometallic compound	M	X	Cr	$T^{[a]}$	N_D^*	Iso
2a	Pd	Cl	•	65.3 (38.6)	–	•
2b	Pd	Br	•	67.2 (58.4)	–	•
2c	Pd	SCN	•	98.7 (53.8)	–	•
3	Pt	Cl	•	90.1 (39.1)	{• 72.2 (0.3) }	•

[a] Mettler TA 3000/DSC-30 S with TA 72.5 software. Heating rates 5 K min^{-1} for the melting process, the entalpies are given in parentheses. To prevent crystallization the clearing process of **3** was measured with 10 K min^{-1}.

The properties of the sheet-like[3−7] and calamitic[12] dinuclear palladium and platinum organyls found so far allow for the conclusion that the number and kind of side-chains play a determining role in the formation of the liquid-crystalline phase. The type of metal (Pd or Pt), on the other hand, has only very little or no influence on the type and stability of the mesophase formed. In general, for sheet-like members a more or less coplanar arrangement of the ligands is a further requirement for the formation of nematic discotic phases. A comparison of the phase transition data of the chiral dinuclear palladium organyls **2a−c** with their achiral analogs[4] shows that the two bulkier and chiral 3,7-dimethyloctyloxy chains in **2a−c** led to lower melting temperatures and prevented the formation of a mesophase, at least in the observable temperature range. We attribute this to the steric hindrance to a nematic packing due to the methyl groups and not to an effect of the chirality per se.

It should be emphasized here that the two chiral lateral chains in the ligands of the dinuclear platinum organyl **3** differ from those present in the series of di-palladium complexes **2**. In the diplatino mesogen **3**, the chiral center is nearer to the molecular core and, most probably more important, these two chains are significantly shorter and lack the terminal branching. Therefore, a very fluid cholesteric nematic discotic (N_D^*) mesophase with "strain" or fingerprint texture and strong thermal fluctuations is observed on cooling **3** from the isotropic melt. The phase transition from the N_D^* phase to the isotropic liquid is very sharp; the clearing enthalpy of 0.3 kJ/mol is within the range of 0.1−0.4 kJ/mol, common for nematic discotic mesophases.[4,6,11,13]

Nematic discotic phases are usually observed in systems composed of flat, sheet-like molecules lacking significant intermolecular interactions perpendicular to their molecular plane. For such systems, even minor changes in the packing of the peripheral aliphatic chains can favor or prevent the self-organization in a mesophase.

In systems composed of electron-rich flat molecules, strong attractive interactions between these molecules can often be introduced by charge-transfer interactions with a suitable electron-acceptor, for example 2,4,7-trinitrofluorenone (**TNF**). In these systems, the mixed interactions perpendicular to the molecular planes are significantly stronger than those between molecules of the same kind, leading to the formation of columnar mesophases with an alternating stacking of electron-donor and -acceptor molecules.[13−15]

The new chiral sheet-like dinuclear palladium organometallic compounds **2a−c**, not liquid-crystalline in their pure state, all formed charge-transfer complexes with 2,4,7-trinitrofluorenone (**TNF**) as indicated by a change of color to brown-red. As expected, an induced mesophase was formed in mixtures of the chiral sheet-like dinuclear chloro- and bromo-bridged compounds **2a** and **b**, respectively. In contact preparations with **TNF**, each showed the formation of induced hexagonal columnar (Col_h) mesophases, a behavior already observed for their achiral dipalladium and diplatinum analogs.[4,6,13] On cooling from the isotropic phase, droplets with linear defects as well as star-shaped domains with homeotropic orientation and hexagonal symmetry were formed, developing into a mosaic texture similar to that observed for the Col_h phase of **TNF** complexes of the achiral dinuclear palladium and platinum analogs.[4,6,13]

Contact mixtures of the thiocyanato-bridged derivative **2c** with **TNF**, on the other hand, show the stabilization of the nematic cholesteric phase in the contact zone, as was observed for its achiral thiocyanato-bridged palladium and platinum analogs.[4,6,13] So far, dinuclear palladium and platinum organyls with eight peripheral chains and a thiocyanato- and (in one case) a iodo-bridge are the only examples[13] showing the stabilization of the nematic discotic type of mesophase by charge-transfer interactions with a strong electron acceptor, for example **TNF**, rather then the induction of a nematic columnar one.[15−17]

The maximum clearing temperatures of the charge-transfer complexes of the dipalladium organometallic compounds **2a−c** and the diplatinum mesogen **3** with **TNF** in contact preparations are summarized in Table 2, as determined by polarizing microscopy.

It is interesting to note that in contact mixtures of the palladium organyl **2c** and **TNF,** on cooling from the isotropic phase, textures typical for cholesteric nematic phases are only formed in regions with low **TNF** concentrations; in the areas of higher **TNF** contents, Schlieren textures characteristic of achiral nematic phases are observed.

Table 2. Thermomesomorphic properties of charge-transfer complexes generated by mixing the chiral dinuclear palladium organyls **2a−c** and platinum organyl **3**, respectively, with 2,4,7-trinitrofluorenone (**TNF**). The maxima of the clearing temperatures are put in parentheses; Col_h: hexagonal columnar, N: nematic

TNF complex of	M	X	mesophase[a]
2a	Pd	Cl	Col_h (145 °C)
2b	Pd	Br	Col_h (86 °C)
2c	Pd	SCN	N* and N (79 °C)
3	Pt	Cl	Col_h (189 °C)

[a] Results based on contact preparations. The phase transition temperatures have been determined by hot stage polarizing microscopy (heating rate 5 K min^{-1}).

As expected, an induced mesophase is also formed in mixtures of the chiral sheet-like dinuclear platinum organometallic compound **3** with **TNF**. Contact preparations of **3** with **TNF** exhibit a highly viscous induced mesophase up to 189 °C. On cooling from the isotropic liquid, droplets with linear defects as well as star-shaped domains with homeotropic orientation and hexagonal symmetry are formed, developing into a mosaic texture similar to that observed for the Col_h phases of **TNF** complexes of dinuclear palladium and platinum analogs.[4,6,13]

Conclusion

The series of dinuclear palladium organometallic compounds **2a−c** with two chiral peripheral chains each are not liquid-crystalline, most probably because of the space requirements of these citronellol-derived side-chains. The shorter chiral (*S*)-2-methylbutyloxy chains present in the diplatinum complex **3**, on the other hand, allow for the formation of a monotropic cholesteric nematic discotic mesophase. All of the dipalladium organyls **2a−c** and the diplatinum complex **3** form charge-transfer complexes with strong electron acceptors such as 2,4,7-trinitrofluorenone (**TNF**). These charge-transfer complexes exhibit enantiotropic columnar hexagonal (Col_h) induced mesophases or in the case of the thiocyanato-bridged di-palladium complex **2c**, a stabilized cholesteric nematic discotic phase. Dinuclear chiral *ortho*-metallated compounds of the type studied here seem to be incapable of forming enantiotropic cholesteric nematic mesophases, similar to their achiral analogs, which also only form monotropic nematic-discotic phases. However, the charge-transfer induced hexagonal columnar mesophases of mixtures of **TNF** with **2a**, **b** and **3** and the stabilized cholesteric nematic phase in the binary system **TNF/2c** make these dinuclear metal organometallic compounds suitable for studying the relationship between molecular chirality and mesophase chirality in the nematic as well as in higher-ordered hexagonal columnar phases. Besides charge-transfer complexes with achiral electron-acceptors such as **TNF**, those with the enantiomers of 2-(2,4,5,7-tetranitrofluorenyliden aminooxy propionic acid (**TAPA**) should allow for a detailed study of the influence of molecular chirality on mesophase properties.

Experimental Section

The characterizations of the compounds **1−5** presented here are based on correct elemental analyses (Perkin−Elmer Series II CHNS/O Analyzer 2400) and on various spectroscopic data, e.g., ^{1}H, ^{13}C NMR (Bruker WH-400 or AM-270 spectrometers, respectively, $CDCl_3$ solutions), IR (Beckmann 9, CCl_4 solutions) and MS (Varian MAT 711). Only structurally relevant resonances are given below.

Phase transition data were determined by differential scanning calorimetry (Mettler TA 3000/DSC-30 S with TA 72.5 software) and by polarizing microscopy (Leitz Laborlux 12 Pol with a hotstage Mettler FP 82 with heating rates of 5 or 10 K min^{-1} in both methods. To obtain cooling rates of up to 100 K/min a Linkam hotstage THMS 600 system with a TMS 91/C 9196 controller combination was employed).

Synthesis of the 4-Nitrophenol Ethers 4a and b: A solution of 4-nitrophenol (13.91 g, 100 mmol) {**4b**: (8.35 g, 60 mmol)} in dry DMF (80 mL) {**4b**: 50 mL} was added dropwise at ambient temperature under argon and with stirring to a suspension of sodium hydride (60 wt.% suspension in paraffin oil, 4.40 g, 110 mmol) {**4b**: (2.64 g, 66 mmol)} in dry DMF (30 mL) {**4b**: 20 ml}. After stirring this mixture for 2h at room temperature, a solution of (*S*)-3,7-dimethyloctyl tosylate[9] (31.25 g, 100 mmol, prepared by hydrogenation of commercially available citronellol followed by routine tosylation, Scheme 2) in dry DMF (50 mL) or (*S*)-2-methylbutyl tosylate[9] (14.54 g, 60 mmol) in dry DMF (30 mL), respectively, was added. The reaction mixtures were stirred at 80 °C for 12 h or 4 h, respectively, and, after cooling, poured into ice water. After extraction with diethyl ether and usual workup procedures, the crude products were purified by flash-column chromatography on silica gel with petroleum ether/ethyl acetate mixtures (20:1 and 10:1) as eluents.

(*S*)-4-(3,7-Dimethyloctyloxy)nitrobenzene (4a): Yield: 24.30 g (87%) yellow oil. − ^{1}H NMR: δ = 8.18, 6.93 (2d, $J \approx 9$ Hz each; 2 arom. H), 4.14−4.03 (m; OCH_2). − ^{13}C NMR: δ =164.19, 141.27 (2s, 2 arom. C), 125.85, 114.36 (2d, 2 arom. CH each), 67.21 (t, OCH_2). − GC/MS; *m*/*z* (%): 279 (6) [M^+], 140 (7) [$C_{10}H_{20}$], 57 (100). − $C_{16}H_{25}NO_3$ (279.4): MS (HR); *m*/*z*: 279.1834 [M^+]; calcd.: 279.1834.

(*S*)-4-(2-Methylbutyloxy)nitrobenzene[18] (4b): Yield: 10.53 g (84%) yellow oil. − ^{1}H NMR: δ = 8.19, 6.94 (2d, $J \approx 9$ Hz each; 2 arom. H), 3.91, 3.83 (2 dd, $J \approx 6.5$ Hz and 9 Hz, respectively, OCH_2). − ^{13}C NMR: δ =164.37, 141.26 (2s, 2 arom. C), 125.85, 114.36 (2d, 2 arom. CH each), 73.58 (t, OCH_2). − GC/MS; *m*/*z* (%): 209 (12) [M^+], 139 (28) [$M^+ - C_5H_{10}$], 70 (100) [C_5H_{10}]. − $C_{11}H_{15}NO_3$ (209.2): MS (HR); *m*/*z*: 209.1052 [M^+]; calcd. 209.1052.

Synthesis of the Chiral Aniline Compounds 5a and b: A mixture of (*S*)-4-(3,7-dimethyloctyloxy)nitrobenzene (**4a**, 5.59 g, 20 mmol) or (*S*)-4-(2-methylbutyloxy)nitrobenzene (**4b**, 4.18 g, 20 mmol),[18] respectively, with a suspension of iron powder (6.14 g, 110 mmol) in ethanol/water (50 mL:10 mL) and HCl (20%, 0.6 mL) was heated at reflux for 4 h or 2 h. After the addition of $NaHCO_3$ powder (1.93 g, 23 mmol) to the boiling reaction mixture, the mixture was heated at reflux for 1 h and filtered hot. The crude products were extracted from the residues with hot ethanol and, after removal of the solvent, purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate (5:1) as eluent.

(*S*)-4-(3,7-Dimethyloctyloxy)aniline (5a): Yield: 3.90 g (78%) orange oil. − ^{1}H NMR: δ = 6.75, 6.64 (2d, $J \approx 9$ Hz each; 2 arom. H), 3.96−3.86 (m, OCH_2), 3.41 (s, broad, NH_2). − ^{13}C NMR: δ = 152.25, 139.76 (2s, 2 arom. C), 116.34, 115.58 (2d, 2 arom. CH each), 66.92 (t, OCH_2). − GC/MS; *m*/*z* (%): 249 (2.7) [M^+], 109 (100) [$M^+ - C_{10}H_{20}$]. − IR (CCl_4): $\tilde{\nu}$ = 3460 and 3383 cm^{-1} (NH_2). − $C_{16}H_{27}NO$ (249.4): MS (HR); *m*/*z*: 249.2093 [M^+]; calcd.: 249.2093.

(*S*)-4-(2-Methylbutyloxy)aniline[18] (5b): Yield: 3.10 g (86%) yellow oil. − ^{1}H NMR: δ = 6.75, 6.64 (2d, $J \approx 9$ Hz each; 2 arom. H), 3.75, 3.65 (2 dd; $J \approx 6.5$ Hz and 9 Hz, respectively, OCH_2), 3.41 (s, broad, NH_2). − ^{13}C NMR: δ =152.46, 139.69 (2s, 2 arom. C), 116.32, 115.58 (2d, 2 arom. CH each), 73.58 (t, OCH_2). − GC/MS; *m*/*z* (%): 179 (13) [M^+], 109 (100) [$M^+ - C_5H_{10}$]. − IR (CCl_4): $\tilde{\nu}$ = 3460 and 3383 cm^{-1} (NH_2). − $C_{11}H_{17}NO$ (179.3): MS (HR); *m*/*z*: 179.1310 [M^+]; calcd.: 179.1310.

Synthesis of the Imine Ligands 1a and b: The imines **1a** and **b** were prepared in the usual way[4] by a *p*-toluenesulfonic acid (40 mg) catalyzed condensation of 2,3,4-tri(hexyloxy)benzaldehyde[11] (4.07 g, 10 mmol) with **5a** (3.74 g, 15 mmol) or with **5b** (2.69 g, 15 mmol) in toluene (50 mL) and purified by column chromatography on basic aluminum oxide using petroleum ether/ethyl acetate (20:1 to 5:1) as eluent.

(*S*)-*N*-[4-(3,7-Dimethyloctyloxy)phenyl]-2,3,4-tris(hexyloxy)-benzalimine (1a): Yield: 5.79 g (91%) orange oil. − ^{1}H NMR: δ = 8.77 (s, HC=N), 7.83, 6.73 (2 d, $J \approx 9$ Hz each; 2 arom. H of the benzyliden rings), 7.19, 6.91 (2 d, $J \approx 9$ Hz each; 4 arom. H of the N-substituted phenyl rings), 4.10 (t, $J \approx 6.5$ Hz; OCH_2), 4.06−3.94 (m, 3 OCH_2). − ^{13}C NMR: δ =157.46, 156.09, 154.03, 145.64, 141.29, 123.24 (6 s, 6 arom. C), 154.44 (d, HC=N), 122.11, 122.07, 114.92, 108.59 (4 d; 1, 2, 2 and 1 arom. CH), 74.84, 73.67, 68.76, 66.58 (4 t, 4 OCH_2). − MS; *m*/*z* (%): 637 (12) [M^+], 496 (2) [$M^+ - C_{10}H_{21}$], 389 (100) [$M^+ - C_{16}H_{26}NO$]. − $C_{41}H_{67}NO_4$ (637.9): MS (HR); *m*/*z*: 637.5070 [M^+]; calcd.: 637.5070.

(*S*)-*N*-[4-(2-Methylbutyloxy)phenyl]-2,3,4-tris(hexyloxy)benzalimine (1b): Yield: 4.80 g (85%) orange oil. − ^{1}H NMR: δ = 8.77 (s, HC=N), 7.84, 6.74 (2 d, $J \approx 9$ Hz each; 2 arom. H of the benzyliden rings), 7.19, 6.92 (2 d, $J \approx 9$ Hz each; 4 arom. H of the N-substituted phenyl rings), 4.11 (t, $J \approx 6.5$ Hz; OCH_2), 4.07−3.92 (m, 2 OCH_2), 3.84, 3.75 (2 dd, $J \approx 6.5$ Hz and 9 Hz, respectively; OCH_2 of the chiral alkyl chain). − ^{13}C NMR: δ =157.67, 156.09, 154.03, 145.62, 141.29, 123.25 (6 s, 6 arom. C), 154.43 (d, HC=N), 122.09, 122.07, 114.93, 108.59 (4 d; 1, 2, 2 and 1 arom. CH), 74.85, 73.68, 73.16, 68.76 (4 t, 4 OCH_2). − MS; *m*/*z* (%): 567 (6.5) [M^+], 496 (6.2) [$M^+ - C_5H_{11}$], 389 (100) [$M^+ - C_{11}H_{16}NO$]. − $C_{36}H_{57}NO_4$ (567.8): MS (HR); *m*/*z*: 567.4288 [M^+]; calcd.: 567.4288.

Synthesis of the Dinuclear Chloro-Bridged Palladium Organyl 2a: The palladium organometallic compound **2a** was prepared in two steps from the chiral imine ligand **1a** first by reacting 1**a** (5 mmol) with palladium acetate $Pd_3(OAc)_6$ (5 mmol) in glacial acetic acid followed by treatment of the red intermediate product (2 mmol) with a mixture of 2-propanolic hydrochloric acid (0.1 N) according to a description regarding the achiral analogs published elsewhere.[4,5] The desired palladium organometallic compound **2a** was purified by several recrystallizations from ethanol/acetone.

Di-μ-chlorobis[3,4,5-tris(hexyloxy)-2-{[[(*S*)-4-(3,7-dimethyloctyloxy)phenyl]imino]-methyl}phenyl-*C*,*N*]dipalladium(II) (2a): Yield: 2.30 g (74%) yellow crystals. − ^{1}H NMR: δ = 7.99 (s, 2 HC=N), 7.31−7.19, 6.88−6.79 (2 m, broad; 8 arom. H of the N-substituted phenyl rings), 6.57 (s, broad; 2 arom. H of the Pd-substituted phenyl rings), 4.11, 3.85 (2 t, $J \approx 6.5$ Hz each; 2 OCH_2

each), 4.03−3.92 (m, 4 OCH_2). − ^{13}C NMR: δ =170.16 (d, 2 HC=N), 158.63, 155.15, 152.01, 148.87, 140.92, 137.90, 131.68 (7 s, 14 arom. C), 124.00, 114.58, 111.33 (3 d; 4, 4 and 2 arom. CH), 74.64, 73.68, 68.98, 66.53 (4 t, 8 OCH_2). − $C_{82}H_{132}Cl_2N_2O_8Pd_2$ (1557.7): calcd. C 63.23, H 8.54, N 1.80; found C 62.94, H 8.59, N 2.12.

Synthesis of the Bromo- and Thiocyanato-Bridged Palladium Organyls 2b and c: The bromo- and thiocyanato-bridged palladium organometallic compounds **2b** and **2c** were prepared from the analogous chloro-bridged compound **2a** by simple exchange reactions with potassium bromide and potassium thiocyanate, respectively, in dichloromethane/acetone under argon at room temperature. The crude products were purified by recrystallization from methanol/acetone.

Di-μ-bromobis[3,4,5-tris(hexyloxy)-2-{[[(*S*)-4-(3,7-dimethyloctyloxy)phenyl]imino]-methyl}phenyl-*C*,*N*]dipalladium(II)(2b): The halogen-exchange reaction (Cl → Br) was carried out by stirring **2a** (0.31 g, 0.2 mmol) and KBr (0.71 g, 6 mmol) in a mixture of CH_2Cl_2 (60 mL) with acetone (30 mL) for 5 d. Yield: 280 mg (85%) yellow crystals. − ^1H NMR: δ = 8.03 (s, 2 HC=N), 7.28−7.21, 6.89−6.82 (2 d, broad; 8 arom. H of the *N*-substituted phenyl rings), 6.76 (s, broad; 2 arom. H of the Pd-substituted phenyl rings), 4.10, 3.85 (2 t, $J \approx 6.5$ Hz each; 2 OCH_2 each), 4.04−3.93 (m, 4 OCH_2). − ^{13}C NMR: δ =170.76 (d, 2 HC=N), 158.20, 155.35, 151.95, 150.80, 143.10, 137.55, 132.36 (7 s, 14 arom. C), 124.56, 114.61, 114.09 (3 d; 4, 2 and 4 arom. CH), 74.62, 73.60, 68.72, 66.52 (4 t, 8 OCH_2). − $C_{82}H_{132}Br_2N_2O_8Pd_2$ (1646.6): calcd. C 59.81, H 8.08, N 1.70; found C 59.16, H 8.13, N 1.82.

Bis[μ-(thiocyanato-*N*:*S*)]bis[3,4,5-tris(hexyloxy)-2-{[[(*S*)-4-(3,7-dimethyloctyloxy)phenyl]imino]methyl}phenyl-*C*,*N*]dipalladium(II) (2c):The halogen-exchange reaction (Cl → SCN) was carried out by stirring **2a** (0.31 g, 0.2 mmol) and KSCN (0.58 g, 6 mmol) in a mixture of CH_2Cl_2 (60 mL) with acetone (30 mL) for 5 d. Yield: 290 mg (90%) yellow green crystals. − ^1H NMR: δ = 8.12 (s, 2 HC=N), 7.26, 6.91 (2 d, $J \approx 9$ Hz each; 8 arom. H of the N-substituted phenyl rings), 6.18 (s, 2 arom. H of the Pd-substituted phenyl rings), 4.11, 3.85 (2 t, $J \approx 6.5$ Hz each; 2 OCH_2 each), 4.07−3.97 (m, 4 OCH_2). − ^{13}C NMR: δ =170.25 (d, 2 HC=N), 158.37, 155.56, 152.63, 149.69, 143.38, 137.81, 133.60, 126.02 (8 s, 14 arom. C and 2 SCN), 123.95, 114.30, 114.85 (3 d; 4, 4 and 2 arom. CH), 74.64, 73.61, 68.71, 66.65 (4 t, 8 OCH_2). − IR (CCl_4): $\tilde{\nu}$ = 2151 cm^{-1} (SCN). − $C_{84}H_{132}N_4O_8S_2Pd_2$ (1603.0): calcd. C 62.94, H 8.30, N 3.49; found C 62.75, H 8.48, N 3.47.

Synthesis of the Dinuclear Platinum Organyl 3: A solution of the chiral imine **1b** (1.16 g, 2.05 mmol) in dichloromethane (20 mL) was added under Ar to a suspension of di-μ-chloro-bis(η^3-2-methylallylplatinum)[19] (0.57 g, 1.0 mmol) in dry methanol (15 mL). After stirring the reaction mixture at room temperature for 25 d, an orange precipitate was filtered off. The chiral platinum organometallic compound **3** was purified by several crystallizations from methanol/acetone.

Based on the ^1H NMR spectroscopic data for **3** we assume this chiral platinum organometallic compound to be a mixture of two isomers, at least in solution, as reported in a previous paper for the achiral diplatinum analogue.[6] This is probably due to the different orientations of the two ligands i.e., parallel or antiparallel to each other.

Di-μ-chlorobis[3,4,5-tris(hexyloxy)-2-{[[(*S*)-4-(2-methylbutyloxy)phenyl]imino]-methyl}phenyl-*C*,*N*]diplatin(II) (3): Yield: 635 mg (40%) orange crystals. − ^1H NMR: δ = 8.12, 8.09 (2 s, ratio 1 (*anti*):0.2 (*syn*); HC=N), 7.30, 6.88 as well as 7.20, 6.80 (2 × 2 d, $J \approx 8.5$ Hz each; arom. H of the *N*-substituted phenyl rings), 6.64, 6.46 (2 s, ratio 0.2 (*syn*):1 (*anti*); arom. H of the Pt-substituted phenyl rings), 4.12, 3.98 (2 t, $J \approx 6.5$ Hz each; 2 OCH_2 each), 3.90−3.68 (m, 4 OCH_2). − ^{13}C NMR: δ =172.12 (d, 2 HC=N), 158.77, 157.15, 152.76, 142.19, 136.69, 134.75, 131.09 (7 s, 14 arom. C), 124.77, 114.23, 110.27 (3 d; 4, 4 and 2 arom. CH), 74.52, 73.45, 73.15, 68.64 (4 t, 8 OCH_2). − $C_{72}H_{112}Cl_2N_2O_8Pt_2$ (1594.8): calcd. C 54.23, H 7.08, N 1.76; found C 54.05, H 6.89, N 1.62.

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