Mesomorphic Cyclometalated (Cyclopentadienyl)palladium and -platinum Complexes

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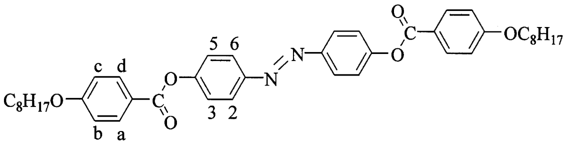
The mesogenic 4,4′-bis[4-(*n*-octyloxy)benzoyloxy]azobenzene (HL) ligand reacts with [$(PhCN)_2PdCl_2$] to give the dinuclear cyclometalated complex [(μ-Cl)(L)Pd]$_2$ (**1**), from which the mononuclear half-sandwich [(η^5-C_5H_5)(L)Pd] (**2**) species has been obtained by reaction with Tl(C_5H_5). The Pt^{II} analogue of **2**, [(η^5-C_5H_5)(L)Pt] (**4**), has been prepared in a similar manner starting from [(μ-Cl)(L)Pt]$_2$ (**3**). Both dinuclear complexes **1** and **3** display a smectic C phase (S_C) stable over 80°C. Whereas **4** is the first example of an 18-electron Pt^{II} mesogen, both mononuclear **2** and **4** are mesomorphic materials that exhibit a nematic phase spanning a wide temperature range.

Introduction

Cyclometalation of group-10 metals[1] still attracts a steady interest since the pioneering work of early sixties.[2] The interest has been considerably revived upon the discovery of thermotropic mesomorphism (i.e. liquid-crystal behaviour under temperature variation) in some halo-bridged dinuclear *ortho*-palladated complexes.[3] Since then, the area of transition-metal-based mesogens (*metallomesogens*)[4] has enlarged considerably, becoming rapidly a hot topic in materials science.[5][6] Although the variety of species has increased in recent years,[7][8] most molecular organometallic mesogens are of the cyclometalated type (and cyclopalladated for the most part) and their chemistry is predominantly that of planar 16-electron complexes.

Recently, we became involved in the design of high-coordination-number mesogenic complexes, a challenging task currently pursued by many different groups.[9] In a previous communication we described the first examples of liquid-crystalline cyclopalladated azobenzene complexes containing the η^5-C_5H_5 ligand.[10] Our aim was to see whether the (η^5-C_5H_5)Pd fragment could be incorporated into a thermotropic molecule without suppressing its mesomorphism. Following our communication, very recently, Lydon et al.[11] reported similar compounds derived from mesogenic Schiff bases. In particular, we proved that the use of symmetrically substituted nematogenic azobenzene ligands ($R = R' = C_6H_{13}$; $R = R' = OC_6H_{13}$) leads to the isolation of low-melting solids which do not exhibited liquid-crystal behaviour, whilst a more anisotropic ligand ($R = OC_6H_{13}$, $R' = OCOC_6H_4OC_8H_{17}$) gave a mesomorphic complex. However, although the latter ligand was able to compensate the reduction in structural anisotropy that originates from the lateral substitution of the organic molecule with a bulky (η^5-C_5H_5)Pd group, a second problem arose. Metalation of the unsymmetrical azobenzene is not stereospecific, and a pair of isomers was obtained as a result of reaction at either one of the phenyl rings which form the azobenzene core.[10]

In order to gain more reliable mesogenic materials (in terms of a reproducible thermal behaviour), it is preferable to avoid isomeric mixtures with uncontrolled composition. Therefore, we decided to go back to symmetrically substituted azobenzene ligands. Thus, taking advantage of the observed beneficial role that the $OCOC_6H_4OC_8H_{17}$ group exerts on the mesomorphism, we considered the 4,4′-bis[4-(*n*-octyloxy)benzoyloxy]azobenzene (HL) ligand.



HL

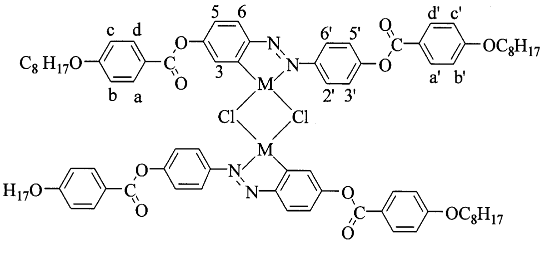
We report here the synthesis of HL and its cyclometalated (cyclopentadienyl)palladium(II) and -platinum(II) derivatives. The mesomorphic properties of both the ligand and complexes are also reported and discussed.

Results and Discussion

Synthesis

The synthesis of HL was carried out by esterification of 4-(*n*-octyloxy)benzoic acid and 4,4′-dihydroxyazobenzene in the presence of 1,3-dicyclohexylcarbodiimide and catalytic amounts of 4-pyrrolidinopyridine. HL is a red solid which was characterized by ^{1}H-NMR spectroscopy (see Experimental Section).

The cyclopalladation of HL with [$(PhCN)_2PdCl_2$] in benzene/methanol occurred with formation of the dinuclear species [(μ-Cl)(L)Pd]$_2$ (**1**) in good yield. Both the elemental analysis and ^{1}H-NMR spectrum of **1** account for the expected formula (Experimental Section).



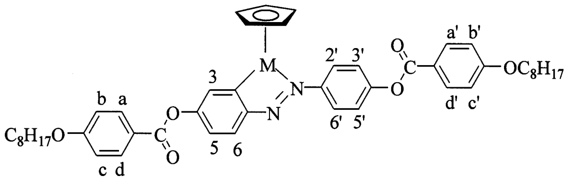
1 M = Pd
3 M = Pt

The subsequent bridge-splitting reaction with $Tl(C_5H_5)$[10][12] gives directly the monocyclopentadienyl complex $[(\eta^5-C_5H_5)(L)Pd]$ (**2**). Compound **2** is a very soluble, purple-blue (λ_{max} = 574 nm), air-stable solid. Beside the signals of the *o*-deprotonated L ligand, the ^{1}H-NMR spectrum of **2** shows a singlet at δ = 5.88 which corresponds to a cyclopentadienyl ring bound in an η^5 fashion.[12b][13][14] The X-ray structure of the homologous $[(\eta^5-C_5H_5)(pap)Pd]$ [pap = 2-(phenylazo)phenyl] has been previously reported. The C_5H_5 fragment was observed to assume an η^5 coordination with relevant asymmetry in the Pd−C bonds.[15]

Mesomorphic cycloplatinated complexes are still rare[16][17][18] compared to their palladium counterparts. Synthetic efforts were pushed forward when cycloplatination under mild conditions became affordable through the use of reagents such as $[(\mu-Cl)(\eta^3-C_4H_7)Pt]_2$.[19] Thus, we set out to prepare complex **4**, the platinum analogue of **2**. The best procedure involves the formation of the dinuclear precursor $[(\mu-Cl)(L)Pt]_2$ (**3**) through reaction of HL and $[(\mu-Cl)(\eta^3-C_4H_7)Pt]_2$ under reflux conditions. Complex **3** is a dark-red solid wherein *o*-platination is apparent from its ^{1}H-NMR spectrum (see Experimental Section). On further treatment of the dinuclear species with $Tl(C_5H_5)$ no reaction occurred. As earlier noted by Cross et al.[20] this same reaction did not take place for $[(\mu-Cl)(pap)Pt]_2$ whatever the excess of $Tl(C_5H_5)$. The reaction instead smoothly proceeds to the desired product if the addition of $Tl(C_5H_5)$ is preceded by bubbling CO through a solution of the chloro-bridged cycloplatinated dimer.[20] Starting from **3**, in situ formation of the orange complex [(CO)(Cl)(L)Pt] [$\tilde{\nu}_{CO}$ = 2102 cm^{-1} (KBr)] was followed by the chloride displacement reaction on addition of an excess of $Tl(C_5H_5)$. Complex $[(\eta^5-C_5H_5)(L)Pt]$ (**4**) was recovered as a dark-red (λ_{max} = 520 nm), air-stable solid upon purification by cromatography on silica gel. The ^{1}H-NMR spectrum of **4** shows in the region of aromatic protons the pattern typical for an *o*-metalated phenyl ring with no $^nJ(^1H^{195}Pt)$ coupling. A singlet at δ = 5.87, showing satellites due to ^{195}Pt coupling ($^3J_{PtH}$ = 13 Hz), can be safely assigned to an η^5-C_5H_5 ligand.[12b]

Mesomorphic Properties

The mesomorphic properties of the parent ligand HL and complexes **1**−**4** are reported in Table 1. The meso-



2 M = Pd
4 M = Pt

phases were assigned on the basis of their optical textures observed by thermal polarizing microscopy. Thermal and thermodynamic data were obtained through differential scanning calorimetry (DSC).

Table 1. Phase-transition data and assignments[a] for HL, $[(\mu-Cl)(L)M]_2$ [M = Pd (**1**); Pt (**3**)], $[(\eta^5-C_5H_5)(L)M]$ [M = Pd (**2**); Pt (**4**)]

Compound	Transition	T [°C]	ΔH [kJ mol^{-1}]
HL	C−S_C	140.0	26.5
	S_C−N	160.0	1.5
	N−I	314.1	3.2
1	C−C′	149.1	13.0
	C′−S_C	249.7	39.4
	S_C−I	330.7[b]	
2	C−N	142.8	37.5
	N−I	226.2	2.8
3	C−S_C	262.9	37.1
	S_C−I	342.0[b]	
4	C−N	160.4	40.8
	N−I	250.0[b]	

[a] C: crystal; S_C: smectic C; N: nematic; I: isotropic liquid. − [b] Decomposition.

HL exhibited enantiotropic smectic C (S_C) and nematic (N) phases, and both showed a marbled texture. Notwithstanding this, the S_C−N transition was clearly indicated by the appearance of characteristic transition bars.[21] The mesomorphism of HL is dominated by the nematic state which occurs over a wide range (some 150°C), whereas the fairly high clearing temperature is related to the high polarizability of the large rigid core of the molecule.

The dinuclear chloro-bridged complexes $[(\mu-Cl)(L)M]_2$ (**1**, **3**) are mesogens which display only a smectic C phase (schlieren texture) between 249 and 330°C for **1** and between 262 and 342°C for **3** and decompose at the clearing point. The metal complexation in both cases narrows the mesomorphic range of the ligand with transition temperatures for the platinum complex **3** higher than those of the palladium homologue.

The mononuclear palladium complex **2** melted to a nematic phase which exhibited a marbled texture on heating and a schlieren one on cooling from the melt. Thus, the mesomorphism of the mononuclear palladium derivative becomes dominated by the nematic phase. This is not surprising if one considers the presence of a large substituent (i.e. the organometallic fragment) in the middle of the molecule (which opposes lateral interactions)[9c][22] and of the two medium-sized alkyl chains (which are unable to stabilize smectic behaviour in this case). With respect to HL, the mononuclear compound **2** preserves a similar melting temperature although the stability of the nematic phase is much reduced. Both the presence of a single, nematic phase and the substantial lowering of the clearing point (some 90°C) are a likely consequence of the reduced anisotropy of molecular shape,[9d][9e][23][24] at least if no further effects (e.g. changes in the polarizability anisotropy and/or dipole moment variations following the lateral substitution) must be taken into account.

Changing palladium complex **2** for platinum complex **4** increases about 20°C both the melting and the clearing temperatures of the complex (Table 1), in line with the expected increase in polarizability by introduction of platinum. This trend has been seen at work in other Pd and Pt homologous series of calamitic mesogens.[15][18][25] However, more examples are needed to establish a general, less controversial behaviour since an opposite trend has occasionally been observed.[26] The increased stability of the nematic phase of **4** with respect to **2** is, however, thwarted by its lower thermal stability (toward decomposition) in the isotropic state.

Conclusions

Palladium(II) and platinum(II) mesogens are commonly available as planar, 16-electron species. In principle, the possibility to prepare metallomesogens with higher coordination numbers is restricted only by the loss of structural anisotropy as a consequence of extra coordination. However, from related studies on high-coordination-number calamitic mesogens we know that this disadvantage can be overcome by using ligands with high structural anisotropy.[22]

We have now demonstrated that the metalation of the highly anisotropic, mesogenic HL ligand through well-tested synthetic procedures allows the formation of 18-electron Pd^{II} and Pt^{II} species which are nematic liquid crystals. Interestingly, reporting the only other example of an 18-electron half-sandwich, isomerically pure palladium mesogen, the authors have pointed out the high tendency of this class of compounds to give preferentially nematic phases.[11][27] In conclusion, sterically demanding organometallic Pd^{II} and Pt^{II} mesogens can be conveniently prepared using the cyclopentadienyl group as a co-ligand. Whilst the only price to pay at this stage is a reduction in thermal stability of the mesogenic azobenzene precursor, this approach opens the way to further novel organometallic materials with interesting physical properties.

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Experimental Section

4-(*n*-Octyloxy)benzoic acid, 1,3-dicyclohexylcarbodiimide (DCC), 4-pyrrolidinopyridine (PPy), and thallium cyclopentadienide were available from Aldrich, and they were used as received. 4,4′-Dihydroxyazobenzene was prepared according to a published method.[28] − IR spectra were recorded as KBr pellets or nujol mulls with a Perkin Elmer System-2000 FT spectrophotometer. − ^1H-NMR spectra were obtained with a Bruker AC300 spectrometer with tetramethylsilane as an internal standard. − Elemental analyses were performed using a Perkin Elmer 2400 microanalyzer. − Absorption spectra were recorded with a Hitachi U-2000 spectrophotometer. − Phase transitions and optical textures were assigned by thermal optical microscopy by means of a Zeiss Axioskop polarizing microscope, equipped with a heating stage and a temperature-control unit. Transition temperatures and enthalpies were determined by differential scanning calorimetry (DSC) using a Perkin Elmer DSC-7 calorimeter operating at a scanning rate of 10°C min^{-1}.

4,4′-Bis[4-(n-octyloxy)benzoyloxy]azobenzene (HL): A mixture of 4,4′-dihydroxyazobenzene (0.40 g, 1.87 mmol), 4-(*n*-octyloxy)-benzoic acid (0.94 g, 3.74 mmol), DCC (0.85 g, 4.11 mmol), and PPy (0.055 g, 0.37 mmol) in dichloromethane (40 ml) was stirred at room temperature for 7 d. A grey solid was filtered off and the orange filtrate was washed with H_2O (2 × 30 ml), 5% CH_3COOH (2 × 25 ml), and H_2O (2 × 30 ml). The organic layer was dried with $NaSO_4$, then taken to dryness under reduced pressure. The yellow solid residue was recrystallized from dichloromethane/diethyl ether. Yield 0.69 g (54%). − ^1H NMR (300 MHz, $CDCl_3$): δ = 8.17 (d, J = 8.8 Hz, 2 H, $H^{a,d}$), 8.01 (d, J = 8.8 Hz, 2 H, $H^{2,6}$), 7.37 (d, J = 8.8 Hz, 2 H, $H^{3,5}$), 6.99 (d, J = 8.8 Hz, 2 H, $H^{b,c}$), 4.05 [t, J = 6.6 Hz, 2 H, $OCH_2(CH_2)_6CH_3$], 1.83 [m, 2 H, $OCH_2CH_2(CH_2)_5CH_3$], 1.50−1.29 [m, 10 H, $OCH_2CH_2(CH_2)_5CH_3$], 0.90 (t, J = 6.6 Hz, 3 H, CH_3). − IR (KBr): $\tilde{\nu}$ = 1740, 1730 cm^{-1} (COO). − $C_{42}H_{50}N_2O_6$ (678.9): calcd. C 74.31, H, 7.42, N, 4.13; found C 73.86, H, 7.45, N, 4.36.

Preparation of [(μ-Cl)(L)Pd]₂ (**1**): A suspension of the HL ligand (0.3 g, 0.44 mmol) in methanol (15 ml) was added to a stirred solution of an equimolar amount of $[(PhCN)_2PdCl_2]$ in benzene (15 ml) and the mixture was heated for 48 h at 100°C. The resulting orange solid was filtered off and recrystallized from hot methanol. Yield 0.29 g (80%). − ^1H NMR (300 MHz, $CDCl_3$): δ = 8.09 (d, 2 H, $H^{a,d}$), 8.07 (d, 2 H, $H^{a',d'}$), 7.92 (d, 2 H, $H^{2',6'}$), 7.89 (d, 1 H, H^6), 7.34 (d, 2 H, $H^{3',5'}$), 7.18 (d, 1 H, H^3), 7.13 (dd, 1 H, H^5), 6.92 (d, 2 H, $H^{b,c}$), 6.89 (d, 2 H, $H^{b',c'}$), 4.03 [t, 2 H, $OCH_2(CH_2)_6CH_3$], 3.97 [t, 2 H, $OCH_2(CH_2)_6CH_3$]. − $C_{84}H_{98}Cl_2N_4O_{12}Pd_2$ (1639.4): calcd. C 61.54, H 6.02, N 3.42; found C 61.35, H 6.11, N 3.07.

Preparation of [(η⁵-C₅H₅)(L)Pd] (**2**): $Tl(C_5H_5)$ (0.03 g, 0.12 mmol) was added to a solution of $[Pd(\mu\text{-}Cl)(L)]_2$ (0.1 g, 0.06 mmol) in benzene (10 ml) and the mixture was stirred under nitrogen. After 4 h, the mixture was filtered and the dark filtrate was concentrated in a rotary evaporator. Recrystallization of the solid residue from chloroform/ethanol afforded the product as a dark blue microcrystalline solid. Yield 0.083 g (80%). − ^1H NMR (300 MHz, $CDCl_3$): δ = 8.28 (d, J = 8.6 Hz, 1 H, H^6), 8.17 (d, J = 8.8 Hz, 2 H, $H^{a,d}$), 8.16 (d, J = 8.8 Hz, 2 H, $H^{a',d'}$), 7.93 (d, J = 8.8 Hz, 2 H, $H^{2',6'}$), 7.72 (d, J = 2.3 Hz, 1 H, H^3), 7.27 (d, J = 9.0 Hz, 2 H, $H^{3',5'}$), 7.08 (dd, J = 8.6, 2.3 Hz, 1 H, H^5), 6.99 (d, J = 8.8 Hz, 4 H, $H^{b,c}$ + $H^{b',c'}$), 5.88 (s, 5 H, Cp), 4.06 [t, J = 6.6 Hz, 4 H, $OCH_2(CH_2)_6CH_3$], 1.84 [m, 4 H, $OCH_2CH_2(CH_2)_5CH_3$], 1.51−1.30 [m, 20 H, $OCH_2CH_2(CH_2)_5CH_3$], 0.90 (t, J = 6.6 Hz, 6 H, CH_3). − IR (nujol): $\tilde{\nu}$ = 1724 cm^{-1} (COO). − UV/Vis (3 × 10^{-5} M $CHCl_3$ solution): λ_{max} (ε) = 264 (56300), 331 (18100), 418 (11850), 574 nm (5780). − $C_{47}H_{54}N_2O_6Pd$ (849.3): calcd. C 66.46, H 6.41, N 3.30; found C 67.02, H 6.41, N 3.05.

Preparation of [(μ-Cl)(L)Pt]₂ (**3**): A solution of $[(\mu\text{-}Cl)(\eta^3\text{-}C_4H_7)Pt]_2$ (0.08 g, 0.15 mmol) and HL ligand (0.2 g, 0.30 mmol) in 15 ml of toluene was refluxed for 12 h and then cooled. The precipitate was collected by filtration and purified by recrystallization from chloroform/diethyl ether to give a dark-red solid. Yield 0.174 g (65%). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10 (d, J = 9.1 Hz, 2 H, $H^{a,d}$), 8.07 (d, J = 9.1 Hz, 2 H, $H^{a',d'}$), 7.96 (d, J = 8.4 Hz, 1 H, H^6), 7.86 (d, J = 8.8 Hz, 2 H, $H^{2',6'}$), 7.39 (d, J = 8.8 Hz, 2 H, $H^{3',5'}$), 7.13 (d, J = 2.0 Hz, 1 H, H^3), 7.09 (dd, J = 8.4, 2.0 Hz, 1 H, H^5), 6.94 (d, J = 9.1 Hz, 2 H, $H^{b,c}$), 6.89 (d, J = 9.1 Hz, 2 H, $H^{b',c'}$), 4.04 [t, J = 6.6 Hz, 4 H, $OCH_2(CH_2)_6CH_3$], 4.00 [t, J = 6.6 Hz, 4 H, $OCH_2(CH_2)_6CH_3$]. − $C_{84}H_{98}Cl_2N_4O_{12}Pt_2$ (1816.8): calcd. C 55.53, H 5.46, N 3.08; found C 56.23, H 5.64, N 3.31.

Preparation of [(η^5-C_5H_5)(L)Pt] (**4**): A brown suspension of [(μ-Cl)(L)Pt]$_2$ (0.14 g, 0.08 mmol) in benzene/diethyl ether (50 ml, 3:2, v/v) turned dark-orange after bubbling CO through the mixture and stirring was continued for 3 h. $Tl(C_5H_5)$ (0.21 g, 0.78 mmol) was added to the mixture which turned dark-red, then dark-violet within 1 h. After filtration of the greyish solid, the solution was concentrated in a rotary evaporator to give a sticky, dark solid. The crude product was chromatographed by using silica gel with *n*-hexane/diethyl ether (1:1) as eluent. The product was eluted first as a dark-red fraction. Removal of the solvent afforded **4** as a dark-red powder. Yield 0.083 g (55%). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.33 (d, J = 8.7 Hz, 1 H, H^6), 8.18 (d, J = 8.9 Hz, 2 H, $H^{a,d}$), 8.17 (d, J = 8.9 Hz, 2 H, $H^{a',d'}$), 7.84 (d, J = 8.9 Hz, 2 H, $H^{2',6'}$), 7.82 (d, J = 2.4 Hz, 1 H, H^3), 7.27 (d, J = 8.9 Hz, 2 H, $H^{3',5'}$), 7.01 (dd, J = 8.7, 2.4 Hz, 1 H, H^5), 6.98 (d, J = 8.8 Hz, 4 H, $H^{b,c}$ + $H^{b',c'}$), 5.87 [s, ^3J(PtH) = 13 Hz, 5 H, Cp], 4.06 [t, J = 6.6 Hz, 4 H, $OCH_2(CH_2)_6CH_3$], 1.84 [m, 4 H, $OCH_2CH_2(CH_2)_5CH_3$], 1.49−1.30 [m, 20 H, $OCH_2CH_2(CH_2)_5CH_3$], 0.90 (t, J = 6.6 Hz, 6 H, CH_3). − IR (nujol): $\tilde{\nu}$ = 1722 cm^{-1} (COO). − UV/Vis (3 × 10^{-5} M $CHCl_3$ solution): λ_{max} (ε) = 263 (30270), 342 (8400), 366 (8200), 520 nm (6450). − $C_{47}H_{54}N_2O_6Pt$ (938.0): calcd. C 60.18, H 5.80, N 2.99; found C 60.40, H 5.81, N 2.91.

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