C,N,N-Cyclometallated palladium(II) complexes: a step forward to luminescent metallomesogens

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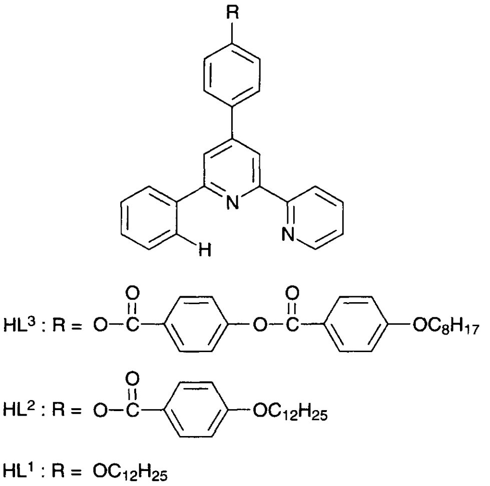
Cyclopalladation of 4′-functionalized 6′-phenyl-2,2′-bipyridine ligands (HL^n, *n* = 1–3) leads to [PdL^{n}Cl] species as demonstrated by the crystal structure of [PdL^{1}Cl]; thermotropic nematic mesomorphism is observed for HL^3 and [PdL^{3}Cl]; the latter is also photoluminescent at 77 K.

Transition-metal-based mesomorphic materials attract an ever increasing amount of attention.[1] Materials (either molecular, ionic or polymeric) span a wide range of organic ligands, metals and coordination geometries. Among them, thermotropic organometallics are the least widespread species mainly due to their intrinsic thermal instability. Cyclometallation currently represents one of the most effective synthetic strategies to generate mesomorphic materials with improved stability.[2] An alternative approach relies on versatile ferrocene[3] and ferrocenium[4] pivotal core units.

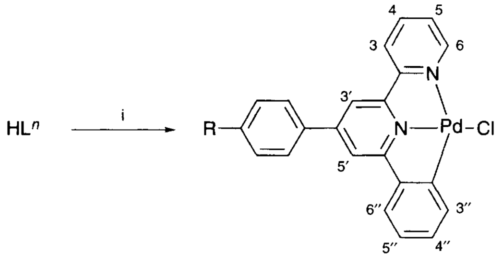
Cyclometallating ligands such as 6′-phenyl-2,2′-bipyridine,[5] 6′-(2-thienyl)-2,2′-bipyridine,[6] 2,2′ : 6′,4″-terpyridine,[7] triazine-based derivatives,[8] and related systems have good ligating properties and have been used to achieve C,N,N-cyclometallated arrangements with planar geometries. Preferred metals have a d^6 or d^8 configuration, and characteristic photophysical and/or structural properties are the subject of extensive investigation.[9,10] Trying to combine the advantages of highly stable metal chelates with the topological needs for the design of mesogenic thermotropic materials, we chose to synthesize 4′-(*R*)-6′-phenyl-2,2′-bipyridine ligands (HL^n) (Scheme 1). We report here the synthesis and thermal properties of ligands HL^n (*n* = 1–3) and their cyclopalladated counterparts [PdL^{n}Cl]. Although monotropic, [PdL^{3}Cl] represents the first example of a thermotropic organometallic mesogen with a terdentate *o*-C deprotonated ligand.

The potentially terdentate ligand 4′-(4-dodecyloxyphenyl)-6′-phenyl-2,2′-bipyridine (HL^1) was obtained as a pale brown solid by a Kröhnke-type synthesis[11] (yield 43%) starting from 1-(2-pyridyl)-3-(4-dodecyloxyphenyl)propen-1-one and *N*-phenacylpyridinium bromide. As expected, molecule HL^1 has no mesogenic behaviour (mp 86.5 °C), and metallation was exploited to achieve in the following order: (*i*) rigidification of the aromatic moiety; (*ii*) optimization of π–π interactions; (*iii*) increased polarizability of the molecule by the effect of the presence of the metal. The reaction of HL^1 with [Pd(PhCN)$_2$Cl$_2$] in MeOH–benzene (1 : 1, *v*/*v*) (Scheme 2) resulted in the formation of the cyclometallated complex [PdL^{1}Cl] as a microcrystalline green solid (yield 84%). The good solubility of the complex in chlorinated solvents allowed its characterization by ^{1}H NMR which suggested that the ligand underwent orthopalladation at the C-2″ position.

The presence of a C,N,N-type denticity of the coordinated ligand L^1 was confirmed by a single-crystal X-ray study of [PdL^{1}Cl].[‡] The crystal structure is shown in Fig. 1. The coordination geometry at the Pd atom is roughly square-planar with bite angles of the chelate rings deviating from 90°. The coordinated portion of the ligand is very nearly flat, with a dihedral angle of 1.2° between the two five-membered chelate rings. The rotationally free phenyl ring is not coplanar with the rest of the aromatic system leading to a tilt angle of 21.5(1)°. On the periphery, the dodecyloxy chain deviates strongly from an all-*anti* conformation, with torsion angles about C(27)–C(28), C(28)–C(29) and C(30)–C(31) of 85(2), 82(4) and 58(4)°, respectively. In the unit cell the centrosymmetrically related molecules tend to pair, showing the shortest Pd···Pd non-bonded intermolecular interaction (Fig. 2). These molecules are approximately superimposed along the *c* axis. The π-stacking



Scheme 1 4′-Functionalised 6′-phenyl-2,2′-bipyridine HL^n ligands



Scheme 2 Preparation of organopalladium complexes [PdL^{n}Cl] (with proton numbering scheme of the coordinated moiety of L^n). *Reagents and conditions*: i, [PdCl$_2$(PhCN)$_2$], benzene–methanol, room temp., 2–5 h.

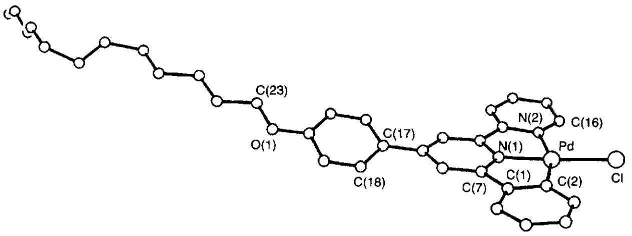


Fig. 1 Molecular structure of [PdL^{1}Cl] showing the numbering scheme adopted. Relevant parameters: Pd–Cl 2.306(3), Pd–N(1) 1.951(8), Pd–N(2) 2.105(9), Pd–C(1) 2.008(11) Å; Cl–Pd–N(1) 177.4(2), N(1)–Pd–N(2) 79.8(3), N(1)–Pd–C(2) 81.1(4)°.

interaction within the dimeric units is evident from the separation between atoms in one ligand L^1 from the mean plane of the next, ranging from 3.40 [N(1)] to 3.51 Å [C(15)].

Since complex [PdL^{1}Cl] proved to be non-mesomorphic [mp 188 °C, ΔH = 41.5 kJ mol^{-1}; data from differential scanning calorimetry (DSC), rate 10 °C min^{-1}], we thought that the rod-like molecule would benefit from both an increase in anisometry and the addition of local dipoles along the long molecular axis. The approach followed was then based on functionalization with benzoate ester groups. Esterification of the precursor 4′-(4-hydroxyphenyl)-6′-phenyl-2,2′-bipyridine[12] **1** was achieved by reaction with 4-substituted benzoic acids in the presence of DCC (DCC = 1,3-dicyclohexylcarbodiimide) and catalytic amounts of 4-pyrrolidinopyridine.[13] Use of 4-(dodecyloxy)benzoic acid afforded ligand HL^2 (37% yield after workup) as a yellowish white solid. Palladation of HL^2 led to [PdL^{2}Cl] (75% yield), recovered as a yellow solid only slightly soluble in chlorinated solvents. Again, while a stabilization of the crystal phase was achieved, both the free ligand (mp 96 °C) and its palladated derivative were not mesomorphic. [PdL^{2}Cl] melted into an isotropic liquid at 265 °C (ΔH = 40.7 kJ mol^{-1}).

Esterification of the precursor **1** with 4-(4-octyloxybenzoyloxyphenyl)benzoic acid[12] was then attempted to increase both the size and polarizability of the rigid core of the ligand. The diester HL^3 was successfully obtained as a white solid in 39% yield.[13] HL^3 showed nematic mesomorphism. The molecule entered the namatic phase at 143 °C (broad DSC peak centred at 140 °C; ΔH = 44.2 kJ mol^{-1}) and typical marbled and *schlieren* textures were consecutively observed by polarized optical microscopy. Clearing occurred at 162 °C (ΔH = 0.6 kJ mol^{-1}).

Reaction of HL^3 with [Pd(PhCN)$_2$Cl$_2$] produced the cyclometallated [PdL^{3}Cl] in high yield (90%). The yellow solid, poorly soluble in common organic solvents, was investigated for mesomorphic behaviour. During the first heating the sample darkened slightly before melting to an isotropic liquid at 306 °C (ΔH = 45.0 kJ mol^{-1}). Rapid cooling (to avoid further decomposition) led to the appearance of nematic mesomorphism below 271 °C in the form of nematic droplets followed by a *schlieren* texture. Crystallization began around 213 °C. Owing to partial crystallization (which cannot be avoided even by freezing the sample), subsequent heating cycles showed the coexistence of crystalline and frozen nematic domains up to *ca.* 226 °C, whereupon the nematic *schlieren* texture re-established itself followed by a homeotropic texture above 270 °C.

The mesogenic complex [PdL^{3}Cl] also exhibited interesting photophysical properties, in that it is photoluminescent in a rigid butyronitrile matrix at 77 K. The luminescence spectrum is structured, with maxima at 476 and 508 nm, and the luminescence lifetime is 0.11 ms. Emission is assigned to a formally triplet, ligand-centred (LC) excited state. Such an assignment is based on the structured shape of the spectrum and on the luminescence lifetime. Both the luminescence spectrum and the lifetime are typical of LC emission from polypyridine metal complexes,[14] including Pd^{II}–terpyridine species,[15] and Pd^{II} cyclometallated compounds.[16] The luminescence is quenched in dichloromethane solution at room temperature, most likely because of non-radiative deactivation by thermal population of a upper-lying metal-centred excited state.[14,16] Efforts to improve the liquid-crystalline behaviour and to better characterize the photophysical properties of this novel class of complexes are in progress.

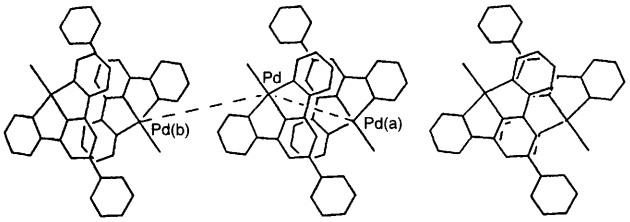


Fig. 2 Crystal packing for [PdL^{1}Cl] with alkoxy chains omitted for clarity. Projection down the *a* axis showing the alternating short [Pd···Pd(a) 5.667(2) Å] and long [Pd···Pd(b) 8.290(3) Å] Pd···Pd intermolecular contacts.

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Footnotes

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‡ Crystal data for [PdL^{1}Cl]. $C_{34}H_{39}ClN_2OPd$, M_r = 633.5, yellow–green (0.32 × 0.24 × 0.12 mm), monoclinic, space group $P2_1/c$ (no. 14), a = 12.690(3), b = 18.896(4), c = 13.258(4) Å, β = 110.20(2)°, U = 2983.6(13) Å^3, Z = 4, D_c = 1.410 g cm^{-3}, $F(000)$ = 1312, μ(Mo-Kα) = 7.41 cm^{-1}, 6132 reflections measured, 4626 independent, R_{int} = 0.015, ($1.5 < \theta < 24°$, ω scan, T = 298 K, Mo-Kα radiation, graphite monochromator, λ = 0.71073 Å) on a Siemens R3m/V diffractometer. The structure was solved by Patterson methods. Refinement of F was carried out by full-matrix least-squares techniques (SHELXTL PLUS). The hydrogen atoms were set in calculated positions and refined as riding atoms. Refinement converged at R = 0.062 [for 2653 reflections with $I > 3\sigma(I)$] [R_w = 0.060, S = 1.98; $w^{-1} = \sigma^2(F) + 0.0003\,F^2$, 292 parameters]. A final difference map showed no features outside the range $-0.57 < \Delta\rho < 0.63$ e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/246.

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