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Synthesis, characterization and thermal behaviour of *ortho*-metallated Pd(II) complexes containing *N*-benzoylthiourea derivatives

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ABSTRACT

The synthesis and characterization (elemental analysis, ^{1}H and ^{13}C NMR spectroscopy and single crystal X-ray diffraction) of the first *ortho*-metallated Pd(II) complexes containing *N*-benzoyl thiourea ligands are described. Four of these compounds showed liquid crystal properties which were investigated by mean of DSC and polarised light microscopy and their mesogenic properties are compared to those of *ortho*-metallated imine Pd(II) complexes with other types of co-ligands.

1. Introduction

Liquid crystals containing metal ions (metallomesogens) are intensively studied due to their interesting properties conferred by the presence of the metal ion, such as colour, polarizability, electrical and magnetic properties [1]. *ortho*-Metallated palladium(II) complexes with nitrogen-containing heteroaromatic ligands represent one of the most interesting and broadly studied families of metallomesogens, which form thermally stable complexes that consist of both dinuclear and mononuclear organometallic systems. Imine ligands have been extensively used in the preparation of such *ortho*-metallated species with liquid crystal properties, in particular due to the different possibilities for tuning the mesogenic properties of these compounds, as well as other physico-chemical properties [2]. A good strategy for reducing the transition temperatures and keeping a broad mesomorphic range in such systems containing the *ortho*-metallated imine fragment is to introduce various co-ligands, which lead, in most cases but not always, to mononuclear compounds with more accessible and stable mesophases compared with the dinuclear parent complexes. Amongst the various co-ligands used to prepare mononuclear species with improved mesogenic properties are β-diketones, [3] β-aminoenonates [3a,4], α-aminoacids [5], cyclopentadienyl [6] or dialkyldithiocarbamate ligands [7]. In this paper we present the synthesis and characterization of a series of *ortho*-metallated palladium complexes with different *N*-benzoyl thiourea derivatives as co-ligands in order to investigate their influence on the mesogenic behaviour of the *ortho*-metallated imine fragment. We were interested in using *N*-benzoyl thiourea derivatives as co-ligands since they possess very strong donor groups (carbonyl and thioamide) which make them very attractive for use as ligands in coordination chemistry and they are readily available by a two-step synthesis starting from benzoyl chloride and the corresponding amine, providing access to a whole range of these derivatives [8]. These ligands react with transition metals, mostly in the monoanionic and bidentate forms by deprotonation, forming neutral complexes with *S,O*-coordination [9]. These derivatives have been used previously in the design of liquid crystalline materials [10–12], but none of the examples reported so far showed their use in the preparation of metal complexes with liquid crystal properties.

2. Results and discussion

2.1. Synthesis

The synthesis of the new compounds described here is summarised in Scheme 1.

The preparation of mononuclear *ortho*-palladated complexes was carried out by a ligand exchange reaction of the acetato-bridged dinuclear Pd(II) complexes using the sodium salts of the *N*-benzoyl thiourea derivatives. The cleavage reaction of acetato-bridged Pd(II) complexes could also be carried out in the presence of simple *N*-benzoyl thiourea derivatives, but with lower yields when compared to the use of their sodium salts.

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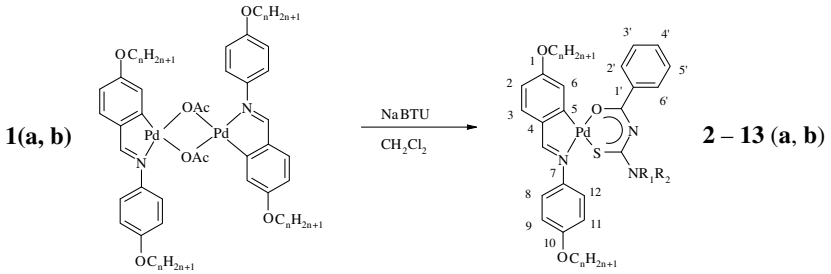

$R_1 = R_2 =$	*n*-Et	**2**	$R_1 = H, R_2 =$	Ph	**7**
	n-Pr	**3**		*p*-Me-Ph	**8**
	n-Bu	**4**		*m*-Me-Ph	**9**
	n-Hex	**5**		*p*-F-Ph	**10**
	n-Oct	**6**		*p*-Cl-Ph	**11**
				p-Br-Ph	**12**
				p-MeO-Ph	**13**

Scheme 1. Synthesis of the new complexes and the *N*-benzoyl thiourea derivatives used in this study.

The new mononuclear complexes were obtained in moderate to good yields as yellow microcrystalline solid products, which are stable under atmospheric conditions. Their structures were confirmed by elemental analysis, IR spectroscopy as well as ^{1}H and ^{13}C NMR spectroscopy and X-ray diffraction.

The coordination of the *N*-benzoyl thiourea derivatives in the deprotonated form was confirmed by the disappearance of the ν_{NH} frequency in the IR spectra of the Pd(II) complexes, which suggests the absence of the NH hydrogen located between the carbonyl and the thiocarbonyl groups of the benzoyl thioureic moiety, information that is further supported by ^{1}H NMR spectroscopy. The formation of the *ortho*-metallated mononuclear complexes can be confirmed readily by ^{1}H NMR spectroscopy where a pattern specific to 1,3,4-substitution of an aromatic ring can be seen as two doublets (H-2, H-3, $^3J_{H2,H3} = 8.4$ Hz) and a doublet of doublets (H-6, $^4J_{H2,H6} = 2.4$ Hz).

Also, the ^{1}H NMR spectra indicate the presence of only one isomer in solution (one set of signals) for all the prepared complexes, though it is possible for the complexes to exist as a mixture of two isomers with the sulfur atom of the *N*-benzoyl thiourea ligand in a *trans* or *cis* position to the nitrogen atom of the imine group of the Schiff base ligand. This information is supported by X-ray diffraction studies that showed only one isomer in the solid state for the complexes isolated as single crystals.

The ^{13}C NMR spectra show all the expected signals. The shift of the signals ($\Delta\delta \sim 13$ ppm) due to the imine and C-5 carbon atoms are consistent with the existence of a Pd–N and a Pd–C-5 bond. This deshielding effect caused by Pd bonding ($\Delta\delta = 4$–9 ppm) is also visible for the *ortho* positions with respect with the metallated position (C-4, C-6). In the case of the benzoyl moiety of the *N*-benzoyl thiourea derivative, coordination to the metal center leads to a deshielding of C-1′ ($\Delta\delta = 5$ ppm) and *para* C-4′ ($\Delta\delta = 2$ ppm), as compared with the free ligand. The signals corresponding to C=O and C=S undergo relatively large downfield and upfield chemical shifts of $\Delta\delta = 7$ and 6 ppm, respectively. This behaviour is similar to that observed for simple Pd(II) complexes with other *N*,*N*-dialkyl-*N*′-aroyl or acyl thiourea derivatives [13].

It is interesting to note that for the complexes **2–6a** the signals corresponding to the alkyl groups from the N(Alk)$_2$ moiety are not magnetically equivalent, both in the ^{1}H and ^{13}C NMR spectra. This is due to a hindered rotation about the C–N(Alk)$_2$ bond, which in turn can be explained through the conjugation between the amine and the Pd containing ring.

2.2. Structures

Single crystals of **2a**, **10a** and **13a** suitable for analysis by X-ray diffraction were obtained from a mixture of dichloromethane and ethanol (ca. 1/1 v/v) at −25 °C. Complex **13a** crystallised with two independent molecules in the structural unit. The crystallographic data are collected in Table 1, while selected bond lengths and angles for all three complexes are presented in Table 2.

The molecular structure of **2a** is shown in Fig. 1. The palladium atom is surrounded by one sulfur atom and one oxygen atom of the *N*-benzoyl thiourea ligand, one aromatic carbon atom (metallated phenyl ring) and one nitrogen atom (imine group) in an approximatively square-planar arrangement, with the sulfur atom located *cis* to the nitrogen atom of the imine group. The corresponding chelate ring around the Pd centre is essentially planar with a maximum deviation from the mean plane of 0.040 Å. However, while the metallated phenyl ring is almost coplanar with respect to the mean plane, the unmetallated ring of the imine ligand is twisted by 37.7° with respect to the core plane. The phenyl ring of the benzoyl group from the *N*,*N*-diethyl-*N*′-benzoyl thiourea ligand is also twisted by 32.9° with respect to the mean plane.

The Pd–Pd distance between two neighbouring molecules is 8.2 Å, precluding any Pd–Pd interactions. The Pd–C and Pd–N bond lengths are comparable with the values reported for similar *ortho*-palladated complexes with Schiff bases, while the Pd–O and Pd–S bond lengths are very well situated between the two values found for the simple *cis* complex of Pd(II) with *N*,*N*-diethyl-*N*′-benzoyl thiourea, which are 2.10 and 1.99 Å for the Pd–O bonds and 2.215 and 2.31 Å for the Pd–S bonds [14].

Complex **10a** (Fig. 2) crystallised with the same square-planar arrangement around the palladium atom; indeed the bond lengths and angles for the central core are all very similar to those found in

Table 1
Crystallographic data for **2a**, **10a** and **13a**

Compound	**2a**	**10a**	**13a**
Empirical formula	$C_{27}H_{29}N_3O_3PdS$	$C_{29}H_{24}FN_3O_3PdS$	$C_{30}H_{27}N_3O_4PdS$
Formula weight ($g\,mol^{-1}$)	581.99	619.97	632.01
Temperature (K)	110(2)	110(2)	110(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2(1)/n$	$P2(1)/c$
Unit cell dimensions			
a (Å)	7.6707(8)	19.813(17)	17.8784(13)
b (Å)	11.6553(12)	6.436(6)	9.3708(7)
c (Å)	15.4545(16)	20.501(17)	32.105(2)
α (°)	111.219(2)	90	90
β (°)	97.100(2)	90.18(2)	99.993(2)
γ (°)	97.386(2)	90	90
Volume (Å^3)	1255.5(2)	2614(4)	5297.1(6)
Z	2	4	8
D_{calc} ($Mg\,m^{-3}$)	1.539	1.575	1.585
Absorption coefficient (mm^{-1})	0.857	0.834	0.822
$F(000)$	596	1256	2576
Crystal	yellow	yellow	yellow
Crystal size (mm)	0.22 × 0.14 × 0.13	0.28 × 0.09 × 0.04	0.30 × 0.24 × 0.16
θ Range for data collection (°)	1.44–28.30	1.43–28.34	1.16–30.02
Index ranges	$-10 \leqslant h \leqslant 10$, $-15 \leqslant k \leqslant 15$, $-20 \leqslant l \leqslant 20$	$-26 \leqslant h \leqslant 15$, $-8 \leqslant k \leqslant 8$, $-27 \leqslant l \leqslant 26$	$-24 \leqslant h \leqslant 24$, $-13 \leqslant k \leqslant 13$, $-44 \leqslant l \leqslant 45$
Reflections collected	12837	16695	58726
Independent reflections (R_{int})	6170 (0.0204)	6420 (0.0599)	15249 (0.0429)
Completeness to $\theta = 27.48°$ (%)	99.8	98.3	98.5
Absorption correction	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents
Maximum and minimum transmission	0.890 and 0.814	0.970 and 0.724	0.877 and 0.762
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	6170/0/320	6420/0/386	15249/0/717
Goodness-of-fit on F^2	1.045	0.930	1.111
Final R indices [$F^2 > 2\sigma(F^2)$]	$R_1 = 0.0253$, $wR_2 = 0.0619$	$R_1 = 0.0387$, $wR_2 = 0.0750$	$R_1 = 0.0374$, $wR_2 = 0.0870$
R indices (all data)	$R_1 = 0.0283$, $wR_2 = 0.0632$	$R_1 = 0.0648$, $wR_2 = 0.0828$	$R_1 = 0.0487$, $wR_2 = 0.0962$
Largest difference in peak and hole (e Å^{-3})	0.592 and −0.681	0.700 and −0.530	1.605 and −0.774

Table 2
Selected bond lengths (Å) and angles (°)

	2a	**10a**	**13a**	
			Molecule A	Molecule B
Pd–C	1.9856(17)	1.984(3)	1.988(2)	1.977(2)
Pd–N	2.1003(14)	2.055(3)	2.1113(18)	2.1015(19)
Pd–S	2.2382(5)	2.2394(16)	2.2457(6)	2.2382(6)
Pd–O	2.0847(12)	2.063(2)	2.0877(15)	2.0759(16)
N–C(Ph)	1.325(2)	1.342(4)	1.330(3)	1.335(3)
N–C(S)	1.342(2)	1.321(4)	1.342(3)	1.343(3)
N–C(O)	1.339(2)	1.344(4)	1.341(3)	1.347(3)
C–O	1.265(2)	1.260(3)	1.260(3)	1.257(3)
C–S	1.7345(18)	1.745(3)	1.723(2)	1.723(2)
C(O)–C(Ph)	1.503(2)	1.487(4)	1.504(3)	1.499(3)
C–N (imine)	1.295(2)	1.306(3)	1.300(3)	1.301(3)
C–Pd–N	81.35(7)	81.17(11)	81.17(3)	81.41(9)
N–Pd–O	95.63(1)	92.61(8)	96.74(7)	96.24(7)
O–Pd–S	92.38(4)	92.28(6)	92.78(4)	91.87(5)
S–Pd–C	90.67(5)	93.84(9)	89.58(6)	90.32(7)

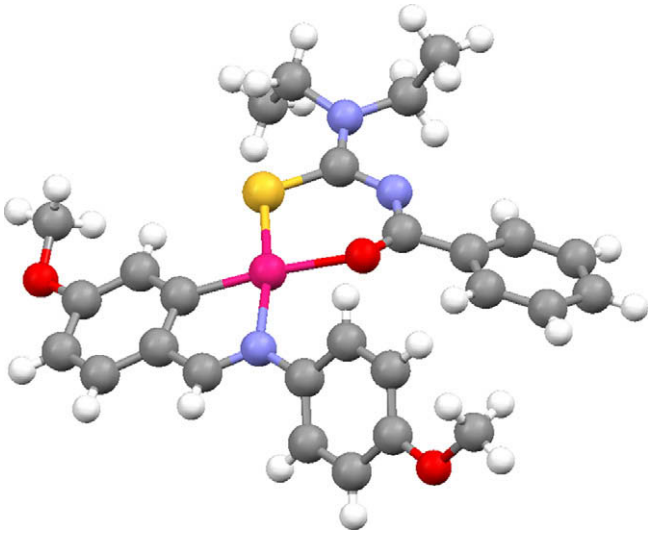

Fig. 1. The molecular structure of **2a**.

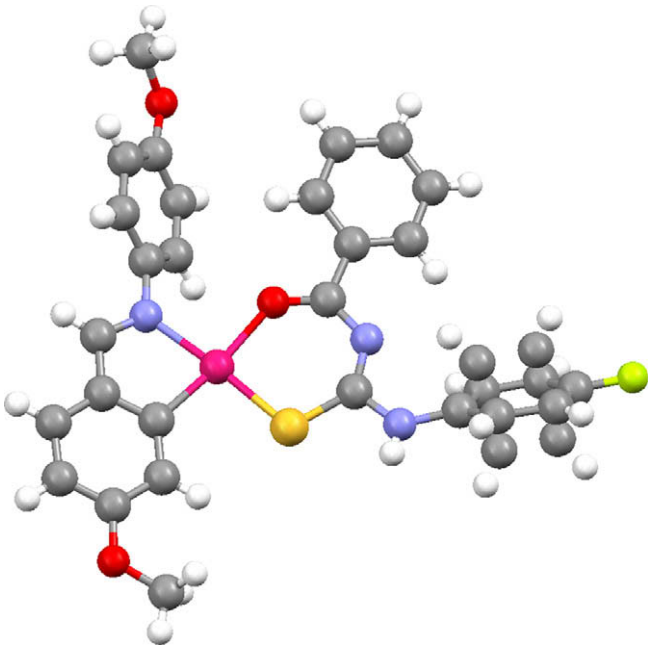

Fig. 2. The molecular structure of **10a**.

2a. The same orientation with respect to the core plane was found for the unmetallated ring of the imine ligand, which is twisted by 54.2°, a larger value when compared to **2a**. The phenyl ring of the benzoyl group from the *N*-benzoyl thiourea ligand is also twisted in respect to the core plane by 14.2°, a smaller value compare to that found for **2a**. An interesting feature of this complex is the two possible configurations adopted by the *p*-F-phenyl ring of the *N*-benzoyl thiourea ligand, with a twist of 73.6°, each with 50% probability as revealed by the site occupancy factors. In both cases there is a twist of this ring by 49.4° and 57.2° with respect to the core plane. Another factor that contributes to the crystal packing of **10a** are intermolecular –C–H···F–C– interactions, found between the fluorine atom of the *N*-benzoyl thiourea ligand and the methoxy group of the metallated ring of the imine ligand. The measured H···F distance is 2.50 Å, which is smaller than the sum of the van der Waals' radii of fluorine and hydrogen of 2.67 Å (the van der Waals' radius of fluorine is 1.47 Å)[15].

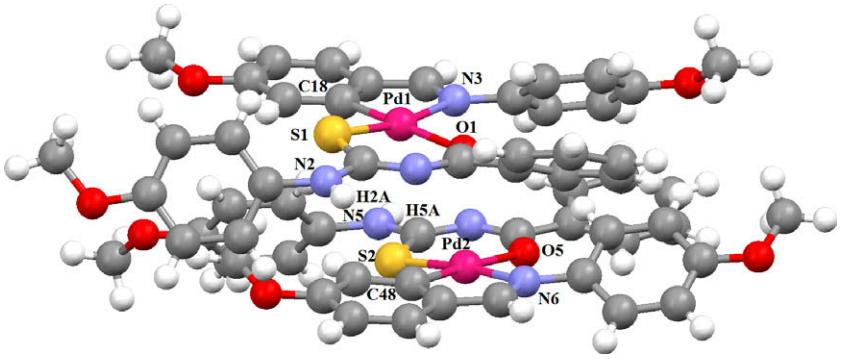

Fig. 3. The molecular structure of **13a**.

Complex **13a** crystallises in the monoclinic crystal system, group *P2*(1)/*c*, as a dimer (Fig. 3). The crystal structure of this compound shows Pd(II) in a square-planar environment bound to the imine ligand in an *ortho*-metallated fashion and chelated to the *N*-benzoyl thiourea derivative with the same coordinated atoms (one aromatic C atom (metallated ring), one N atom (imine group), one O atom (carbonyl group) and one S atom (thiocarbonyl group)) as found for **2a** and **10a**. The two five- and six-membered chelate rings are almost co-planar with the metallated ring of the imine ligand while the unmetallated ring is twisted in respect to the core plane by 34.9° for one molecule, and by 36.3° for the second.

For this compound the maximum deviation from the mean plane is 0.063 and 0.047 Å for Pd_1 and Pd_2, respectively. In this case, the complexes are arranged so that one sits over another with a short Pd–Pd distance of 3.92 Å. This distance is greater than twice the van der Waals' radius of Pd. Additionally, within the dimer the Pd···Pd vector deviates from orthogonality to the coordination plane (25° angle with the plane normal) and so the relative disposition of the complexes is not felt to be due to any intermolecular metal–metal interaction. The C–O and C–S bond lengths of the *N*-benzoyl thiourea ligand in **13a** are longer than those found in the free ligand (1.231 and 1.659 Å, respectively) while the N–C(S) and N–C(O) bond lengths are shorter in **13a** than in the free ligand (1.392 and 1.376 Å, respectively) as a consequence of the coordination of the ligand to the palladium centre in the deprotonated form which leads to the partial double-bond character of the C–N bonds [16]. An important factor that contributes to the crystal packing of **13a** is intermolecular N–H···S hydrogen bonds, found between the S atom of the thiocarbonyl group and the hydrogen atom of the amino –NHR group from the *N*-benzoyl thiourea ligand.[1] This type of interaction is usually found in the uncomplexed *N*-benzoyl thiourea ligands and is typically shorter than the interactions found for **13a** [17,18].

2.3. Thermal behaviour

The palladium complexes, bearing alkoxy groups with six carbon atoms chains (**2**–**13b**), were investigated for their potential liquid crystal properties by hot stage polarising optical microscopy and differential scanning calorimetry (DSC). DSC data were recorded only for those compounds showing mesomorphic behaviour. The thermal data are summarised in Table 3. Mesophases were assigned by their optical texture and two examples are shown in Fig. 4.

[1] Hydrogen bonds for **13a**: N(5)–H(5A)···S(2)#1, 3.772(2) Å and N(2)–H(2A)···S(1)#2, 3.6967(19) Å. Symmetry transformations used to generate equivalent atoms: (1) $-x+1, y-1/2, -z+1/2$; (2) $-x, y+1/2, -z+1/2$.

Table 3
Thermal data for the palladium(II) complexes

Compound	Transition	T (°C)	ΔH (kJ mol^{-1})
2b	Cr–I (N–I)[b]	110 (61)	23.8 (0.3[d])
3b	Cr–I (I–N) (N–Cr)	104 (64[a])	30.8 (20.4[c])
5b	Cr–Cr′ Cr′–I (I–N) (N–Cr)	102 108 (78[a])	18.2 21.5 (29.8[c])
6b	Cr–Cr′ Cr′–I (I–N) (N–Cr)	53 95 (58[a])	3.4 29.9 (22.2[c])

[a] These values represent the temperatures taken from microscopy.
[b] In this case $T_{(N-I)}$ is quoted as the sample was cooled from isotropic to nematic and then re-heated back to the isotropic phase.
[c] The two transitions could not be separated and the values represent the combined enthalpies.
[d] Compound **2b** was the only compound for which it was possible to extract the enthalpy parameter associated with the isotropic to nematic phase transition. The nematic phase of **2b** is stable up to room temperature for several hours after which a slow crystallization process occurs.

This family of complexes offers a broad and systematic picture of the possibility to use *N*-benzoyl thiourea derivatives in designing liquid crystalline materials as well as the effects of changing the substituents on this type of ligand on the mesogenic behaviour. The nature of the *N*-benzoyl thiourea derivative, more specific the R_1 and R_2 substituents, has a major influence on the mesogenic properties of these complexes (Table 3), though it is very clear that their mesogenic behaviour is driven by the *ortho*-metallated imine fragment. Thus, complexes **7**–**13b** show no mesomorphic properties and this behaviour could be assigned to the more flexible structures adopted by the *N*-benzoyl thiourea derivatives bearing aromatic fragments, in particular due to the aromatic groups linked to the nitrogen atom, which imposes a less favourable molecular shape in connection with the intermolecular hydrogen bonds N–H···S that can be formed between the S atom of the thiocarbonyl group and the hydrogen atom of the amino –NHR group. This type of intermolecular interaction (hydrogen bonding between the NH_2 and the carboxyl groups within the amino acids groups) within the crystal lattice was supposed to be responsible for increasing the melting points of the liquid crystals based on *ortho*-metallated Pd imine complexes with amino acids [5b]. On the other hand, the Pd(II) complexes with *N*,*N*-dialkyl-*N*′-benzoyl thiourea derivatives (**2**–**6b**) show a monotropic nematic phase on cooling, except for **4b** ($R_1 = R_2 =$ Bu) for which no mesophase was seen either on heating or cooling. This behaviour could be dis-

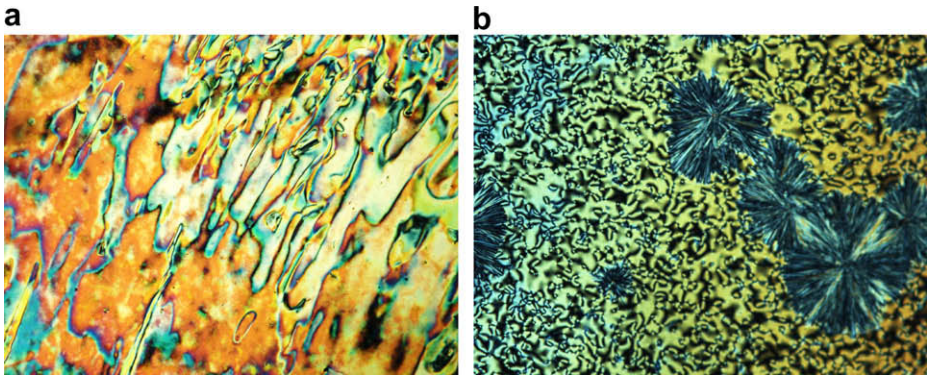

Fig. 4. Polarised optical micrograph of the nematic phase of **2b** at 60 °C (a) and of **6b** at 58 °C (b). In the later case the transition to the nematic phase occurs just before the crystallisation process.

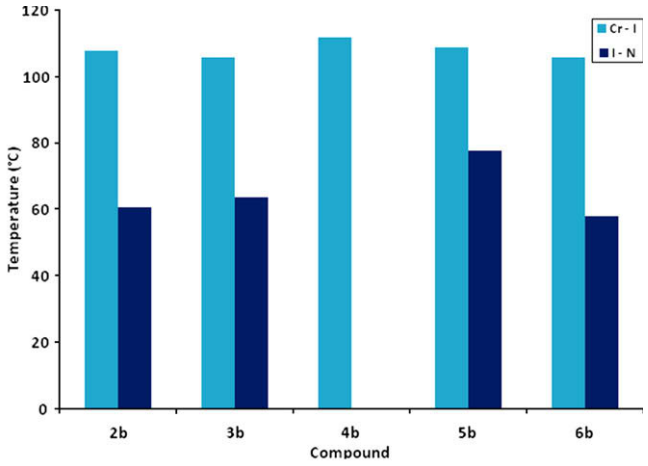

Fig. 5. Thermotropic behaviour of Pd(II) complexes **2–6b.**

cussed in terms of molecular anisotropy of these complexes, e.g. the length-to-breadth ratio [19]. As the terminal alkoxy chains of the imine are not changed, increasing the length of the alkyl chain of the *N*-benzoyl thiourea derivative leads to an increase of the breadth of the molecule with immediate consequences on the mesogenic behaviour. One can assume that the maximum breadth of the molecule is reached for $R_1 = R_2 =$ butyl, when the mesogenic behaviour is being totally suppressed.

Fig. 5 shows the influence of the chain length on the mesogenic properties of Pd(II) complexes with *N*,*N*-dialkyl-*N*′-benzoyl thiourea derivatives. Though the melting points and the temperature of the transition from isotropic to nematic phase do not follow the same trend, there is a clear tendency of increase of T_{I-N} with the increasing chain length up to hexyl groups, followed by a significant drop, 20 °C, on going from hexyl to octyl groups. The same effect of decreasing the transition temperatures with increasing the alkyl chain length from ethyl to octyl has been seen for *ortho*-metallated imine Pd(II) complexes with dialkyldithiocarbamates as chelating ligands [7].

It is very clear that compared with the other types of co-ligands, such as β-diketones or β-aminoenonates, the use of *N*-benzoyl thiourea derivatives as co-ligands destabilise the mesogenic behaviour to such an extent that only monotropic behaviour is seen, with the transitions to the nematic mesophase occurring at approximately 30–50 °C below the clearing point. While changing β-diketones to β-aminoenonate co-ligands leads to more accessible nematic phase but over slightly narrower temperature [3a], the effect of introducing the *N*-benzoyl thiourea derivatives is to further decrease the melting points and the mesophase range together with a change of transition type.

3. Conclusions

A series of organometallic palladium(II) complexes bearing imine ligands and different types of *N*-benzoyl thiourea derivatives as co-ligands were prepared and investigated for their liquid crystal properties. The structures of three of the complexes have been solved by X-ray diffraction.

The first liquid crystals based on metal complexes containing the *N*-benzoyl thiourea moiety are reported here and their mesogenic properties are compared to those of palladium complexes with other types of co-ligands. The use of *N*-benzoyl thiourea derivatives as co-ligands in company of the *ortho*-palladated imine fragment destabilise the mesogenic behaviour of these complexes. Thus, in the case of complexes bearing *N*,*N*-dialkyl-*N*′-benzoyl thiourea derivatives only monotropic behaviour is seen, with the transitions to nematic mesophase occurring approximately 30–50 °C below the clearing point, while in the case where *N*-aryl-*N*′-benzoyl thiourea derivatives were employed, the mesomorphic behaviour was totally suppressed.

These results suggest the possibility of using these simple *N*-benzoyl thiourea derivatives in designing liquid crystals together with the *ortho*-metallated imine fragment but, probably, the mesogenic behaviour of such compounds can be considerably improved by changing the type of imine ligand employed.

4. Experimental

Dichloromethane was distilled from phosphorus pentaoxide, while acetone was distilled from calcium chloride; other chemicals were used as supplied. Proton and carbon NMR spectra were recorded on a Varian Gemini 300 BB spectrometer operating at 300 MHz, using $CDCl_3$ as solvent. ^1H chemical shifts were referenced to the solvent peak position, δ 7.26 ppm. Analysis by DSC was carried out using a Perkin–Elmer DSC7 instrument using a 10 °C/min heating rate. Mesomorphism was studied by hot stage polarising microscopy using a Nikon 50i Pol microscope equipped with a Linkam THMS600 hot stage and a TMS94 temperature controller. Mesophases were assigned by their optical texture [20].

Diffraction data were collected at 110 K on a Bruker Smart Apex diffractometer with Mo Kα radiation (λ = 0.71073 Å) using a SMART CCD camera. Diffractometer control, data collection and initial unit cell determination was performed using "SMART" (v5.625 Bruker-AXS). Frame integration and unit-cell refinement was carried out with the "SAINT+" (v6.22, Bruker AXS) sofware. Absorption correc-

tions were applied by SADABS (v2.03, Sheldrick). Structures were solved by "direct methods" using SHELXS-97 [21] and refined by full-matrix least squares using SHELXL-97 [21]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms (except for NH hydrogens) were placed using a "riding model" and were included in the refinement at calculated positions. NH hydrogens were found by a difference map after all other atoms were found.

The synthesis of the μ-acetato bridged Pd(II) complexes (**1a**,**b**) was carried out as described elsewhere [22]. The *N*-benzoyl thiourea derivatives used in this work were prepared according to the methods published in literature [8].

4.1. Preparation of the sodium salts of N-benzoyl thiourea derivatives

The sodium salts of *N*-benzoyl thiourea derivatives were prepared by reacting the corresponding *N*-benzoyl thiourea with sodium ethoxide (1:1 molar ratio) in petroleum ether for 2 h under reflux. A white or off-white precipitate developed for all *N*-benzoyl thiourea derivatives, which was filtered off and washed with petroleum ether several times. The sodium salts were used in the next step without further purification. Their formation was checked by IR spectroscopy. Their IR spectra confirmed the loss of the proton by the disappearance of ν_{NH} (~3300 cm^{-1}) and $\nu_{C=O}$ (~1670 cm^{-1}) frequencies (compare to the IR spectra of the free ligands) together with a shift of ν_{C-N} frequency towards lower wavenumbers.

4.2. Synthesis of **2a**

The solid sodium salt of *N*,*N*-diethyl-*N*'-benzoyl thiourea (0.0715 g, 0.27 mmol) was added to a solution of the binuclear palladium complex (0.075 g, 0.09 mmol) in CH_2Cl_2 (15 cm^3) and the mixture was stirred at room temperature for 24 h. Evaporation of the solvent gave a yellow solid, which was purified by chromatography on silica using CH_2Cl_2 as the eluant to give a yellow solid. This was recrystallised from a mixture of CH_2Cl_2/C_2H_5OH (1/1) at −25 °C.

4.2.1. Compound **2a**

Yield: 52%, m.p. 144 °C. *Anal.* Calc. for $C_{27}H_{29}N_3O_3PdS$: C, 55.7; H, 4.6; N, 7.2. Found: C, 55.3; H, 4.1; N, 7.5%.

^{1}H NMR (300 MHz, $CDCl_3$): 8.13 (s, 1H), 7.73 (m, 2H), 7.41–7.18 (m, 6H), 7.03 (d, ^4J = 2.4 Hz, 1H), 6.97 (AA′BB′ system, ^3J = 8.8 Hz, 2H), 6.60 (dd, ^3J = 8.4 Hz, ^4J = 2.4 Hz, 1H), 3.99 (q, ^3J = 7.1 Hz, 2H), 3.88–3.82 (m, 8H), 1.40 (t, ^3J = 7.1 Hz, 3H), 1.25 (t, ^3J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 172.7 (C–S), 170.9 (CH=N), 170.2 (C-O), 160.3, 158.6, 158.2, 141.6, 140.4, 138.2 (C-1, C-4, C-5, C-7, C-10, C-1′), 130.7 (C-4′), 130.2 (C-3), 129.4 (C-3′, C-5′), 127.3 (C-2′, C-6′), 124.4 (C-8, C-12), 118.9 (C-6), 113.9 (C-9, C-11), 109.2 (C-2). IR (cm^{-1}): 1582($\nu_{C=N}$); 1496(δ_{NH}); 1418(ν_{CN+CS}).

4.3. Synthesis of **2b** and **3–13a**,*b*

Compounds **2b** and **3–13a,b** were prepared in the same manner as **2a** by using the binuclear palladium complex/sodium salt of *N*-benzoyl thiourea in a molar ratio of 1:3.

4.3.1. Compound **2b**

Yield: 50%, m.p. 108 °C. *Anal.* Calc. for $C_{37}H_{49}N_3O_3PdS$: C, 61.5; H, 6.8; N, 5.8. Found: C, 61.3; H, 6.4; N, 5.3%.

^{1}H NMR (300 MHz, $CDCl_3$): 8.04 (s, 1H), 7.66 (m, 2H), 7.32–7.11 (m, 6H), 6.93 (d, ^4J = 2.4 Hz, 1H), 6.89 (AA′BB′ system, ^3J = 8.9 Hz, 2H), 6.51 (dd, ^3J = 8.4 Hz, ^4J = 2.5 Hz, 1H), 3.94 (m, 6H), 3.78 (q, ^3J = 7.0 Hz, 2H), 1.80–1.22 (m, 19H), 1.18 (t, ^3J = 7.0 Hz, 3H), 0.84 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 172.9 (C–S), 170.9 (CH=N), 170.2 (C–O), 160.3, 158.2, 141.5, 140.2, 138.4 (C-1, C-4, C-5, C-7, C-10, C-1′), 130.7 (C-4′), 130.3 (C-3), 129.4 (C-3′, C-5′), 127.4 (C-2′, C-6′), 124.3 (C-8, C-12), 119.1 (C-6), 114.5 (C-9, C-11), 109.9 (C-2). IR (cm^{-1}): 1585($\nu_{C=N}$); 1525(δ_{NH}); 1418(ν_{CN+CS}).

4.3.2. Compound **3a**

Yield: 55%, m.p. 161 °C. *Anal.* Calc. for $C_{29}H_{33}N_3O_3PdS$: C, 57.1; H, 5.4; N, 6.9. Found: C, 56.9; H, 5.9; N, 6.5%.

^{1}H NMR (300 MHz, $CDCl_3$): 8.14 (s, 1H), 7.74–7.70 (m, 2H), 7.42–7.18 (m, 6H), 7.02 (d, ^4J = 2.3 Hz, 1H), 6.97 (AA′BB′ system, ^3J = 8.9 Hz, 2H), 6.59 (dd, ^3J = 8.3 Hz, ^4J = 2.4 Hz, 1H), 3.90–3.71 (m, 10H), 1.95–1.67 (m, 4H), 1.03 (t, ^3J = 7.3 Hz, 3H), 0.92 (t, ^3J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 173.0 (C–S), 170.9 (CH=N), 170.2 (C–O), 160.3, 158.6, 158.4, 141.1, 140.3, 138.3 (C-1, C-4, C-5, C-7, C-10, C-1′), 130.6 (C-4′), 130.1 (C-3), 129.4 (C-3′, C-5′), 127.3 (C-2′, C-6′), 124.3 (C-8, C-12), 117.8 (C-6), 113.9 (C-9, C-11), 110.0 (C-2). IR (cm^{-1}): 1582($\nu_{C=N}$); 1507(δ_{NH}); 1418 (ν_{CN+CS}).

4.3.3. Compound **3b**

Yield: 51%, m.p. 106 °C. *Anal.* Calc. for $C_{39}H_{55}N_3O_3PdS$: C, 62.3; H, 7.3; N, 5.6. Found: C, 62.0; H, 7.7; N, 5.3%.

^{1}H NMR (300 MHz, $CDCl_3$): 8.11 (s, 1H), 7.73 (m, 2H), 7.40–7.19 (m, 6H), 7.01 (d, ^4J = 2.4 Hz, 1H), 6.96 (AA′BB′ system, ^3J = 8.9 Hz, 2H), 6.59 (dd, ^3J = 8.4 Hz, ^4J = 2.5 Hz, 1H), 4.03 (m, 4H), 3.90–3.74 (m, 4H), 1.95–1.31 (m, 20H), 1.04 (t, ^3J = 7.4 Hz, 3H), 0.93 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): 172.9 (C-S), 170.9 (CH=N), 170.2 (C–O), 160.1, 158.6, 158.3, 141.7, 140.3, 138.5 (C-1, C-4, C-5, C-7, C-10, C-1′), 130.7 (C-4′), 130.2 (C-3), 129.4 (C-3′, C-5′), 127.4 (C-2′, C-6′), 124.5 (C-8, C-12), 118.6 (C-6), 114.6 (C-9, C-11), 110.7 (C-2). IR (cm^{-1}): 1582($\nu_{C=N}$); 1540(δ_{NH}); 1420(ν_{CN+CS}).

4.3.4. Compound **4a**

Yield: 60%, m.p. 140 °C. *Anal.* Calc. for $C_{31}H_{37}N_3O_3PdS$: C, 58.4; H, 5.8; N, 6.6. Found: C, 57.9; H, 5.9; N, 6.2%.

^{1}H NMR (300 MHz, $CDCl_3$): 8.13 (s, 1H), 7.72 (m, 2H), 7.41–7.17 (m, 6H), 7.02 (d, ^4J = 2.4 Hz, 1H), 6.97 (AA′BB′ system, ^3J = 8.9 Hz, 2H), 6.59 (dd, ^3J = 8.4 Hz, ^4J = 2.5 Hz, 1H), 3.99 (q, ^3J = 7.1 Hz, 2H), 3.94–3.77 (m, 10H), 1.88–1.28 (m, 8H), 1.02 (t, ^3J = 7.3 Hz, 3H), 0.91 (t, ^3J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 173.0 (C–S), 168.7 (CH=N), 171.0 (C–O), 160.4, 158.7, 158.5, 141.7, 140.3, 138.3 (C-1, C-4, C-5, C-7, C-10, C-1′), 130.7 (C-3), 130.2 (C-4′), 129.5 (C-3′, C-5′), 127.4 (C-2′, C-6′), 124.4 (C-8, C-12), 118.9 (C-6), 113.9 (C-9, C-11), 110 (C-2). IR (cm^{-1}): 1581($\nu_{C=N}$); 1511(δ_{NH}); 1418(ν_{CN+CS}).

4.3.5. Compound **4b**

Yield: 43%, m.p. 112 °C. *Anal.* Calc. for $C_{41}H_{57}N_3O_3PdS$: C, 63.3; H, 7.3; N, 5.4. Found: C, 62.9; H, 7.0; N, 5.0%.

^{1}H NMR (300 MHz, $CDCl_3$): 8.11 (s, 1H), 7.75 (m, 2H), 7.40–7.19 (m, 6H), 7.02 (d, ^4J = 2.4 Hz, 1H), 6.97 (AA′BB′ system, ^3J = 8.8 Hz, 2H), 6.59 (dd, ^3J = 8.4 Hz, ^4J = 2.4 Hz, 1H), 4.06–3.75 (m, 8H), 1.92–1.29 (m, 24H), 1.04 (t, ^3J = 7.3 Hz, 3H), 0.91 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): 173.0 (C–S), 170.9 (CH=N), 170.2 (C–O), 160.3, 158.6, 158.4, 141.1, 140.3, 138.3 (C-1, C-4, C-5, C-7, C-10, C-1′), 130.8 (C-3), 130.3 (C-4′), 129.7 (C-3′, C-5′), 127.5 (C-2′, C-6′), 124.5 (C-8, C-12), 118.3 (C-6), 114.6 (C-9, C-11), 110.9 (C-2). IR (cm^{-1}): 1582($\nu_{C=N}$); 1540, 1516(δ_{NH}); 1420(ν_{CN+CS}).

4.3.6. Compound **5a**

Yield: 69%, m.p. 138 °C. *Anal.* Calc. for $C_{35}H_{47}N_3O_3PdS$: C, 60.6; H, 6.5; N, 6.1. Found: C, 60.2; H, 6.1; N, 6.2%.

^{1}H NMR (300 MHz, $CDCl_3$): 8.13 (s, 1H), 7.73 (m, 2H), 7.42–7.18 (m, 6H), 7.03 (d, ^4J = 2.5 Hz, 1H), 6.98 (AA′BB′ system, ^3J = 8.9 Hz, 2H), 6.60 (dd, ^3J = 8.3 Hz, ^4J = 2.4 Hz, 1H), 3.92–3.75 (m, 10H),

1.87–1.23 (m, 16H), 0.94–0.82 (m, 6H). IR (cm^{-1}): 1583($\nu_{C=N}$); 1522(δ_{NH}); 1421(ν_{CN+CS}).

4.3.7. Compound ***5b***

Yield: 59%, m.p. 109 °C. *Anal.* Calc. for $C_{45}H_{65}N_3O_3PdS$: C, 64.8; H, 7.8; N, 5.0. Found: C, 64.3; H, 7.4; N, 4.8%.

^1H NMR (300 MHz, $CDCl_3$): 8.10 (s, 1H), 7.76 (m, 2H), 7.40–7.19 (m, 6H), 7.02 (d, ^4J = 2.5 Hz, 1H), 6.97 (AA′BB′ system, ^3J = 8.9 Hz, 2H), 6.58 (dd, ^3J = 8.2 Hz, ^4J = 2.3 Hz, 1H), 4.05–3.77 (m, 8H), 1.96–1.27 (m, 32H), 0.95–0.83 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): 173.3 (C–S), 171.0 (CH=N), 170.2 (C–O), 160.1, 158.5, 158.3, 141.7, 140.3, 138.5 (C-1, C-4, C-5, C-7, C-10, C-1′), 130.8 (C-3), 130.4 (C-4′), 129.6 (C-3′, C-5′), 127.5 (C-2′, C-6′), 124.5 (C-8, C-12), 118.6 (C-6), 114.6 (C-9, C-11), 110.6 (C-2). IR (cm^{-1}): 1582($\nu_{C=N}$); 1518(δ_{NH}); 1419(ν_{CN+CS}).

4.3.8. Compound ***6b***

Yield: 51%, m.p. 106 °C. *Anal.* Calc. for $C_{49}H_{73}N_3O_3PdS$: C, 66.0; H, 8.4; N, 4.7. Found: C, 65.6; H, 8.7; N, 4.4%.

^1H NMR (300 MHz, $CDCl_3$): 8.06 (s, 1H), 7.70 (m, 2H), 7.35–7.13 (m, 6H), 6.96 (d, ^4J = 2.4 Hz, 1H), 6.91 (AA′BB′ system, ^3J = 8.9 Hz, 2H), 6.54 (dd, ^3J = 8.4 Hz, ^4J = 2.3 Hz, 1H), 3.98 (q, ^3J = 6.6 Hz, 4H), 3.87–3.71 (m, 4H), 1.84–1.16 (m, 38H), 0.91–0.78 (m, 12H).

4.3.9. Compound ***7a***

Yield: 60%, m.p. 145 °C. *Anal.* Calc. for $C_{29}H_{25}N_3O_3PdS$: C, 57.9; H, 4.2; N, 7.0. Found: C, 57.3; H, 4.6; N, 6.6%.

^1H NMR (300 MHz, $CDCl_3$): 8.13 (s, 1H), 7.72 (m, 2H), 7.58 (m, 2H), 7.42–7.20 (m, 9H), 6.99 (AA′BB′ system, ^3J = 8.9 Hz, 2H), 6.90 (d, ^3J = 2.3 Hz, 1H), 6.61 (dd, ^3J = 8.4 Hz, ^4J = 2.5 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H). IR (cm^{-1}): 3295(ν_{NH}); 1585($\nu_{C=N}$); 1526, 1501(δ_{NH}); 1428(ν_{CN+CS}).

4.3.10. Compound ***7b***

Yield: 47%, m.p. 115 °C. *Anal.* Calc. for $C_{39}H_{45}N_3O_3PdS$: C, 63.1; H, 6.0; N, 5.7. Found: C, 63.0; H, 6.5; N, 5.3%.

^1H NMR (300 MHz, $CDCl_3$): 8.10 (s, 1H), 7.75 (broad d, 2H), 7.58 (m, 2H), 7.43–7.18 (m, 9H), 6.97 (AA′BB′ system, ^3J = 8.8 Hz, 2H), 6.89 (broad s, 1H), 6.60 (m, 1H), 4.02 (t, ^3J = 6.6 Hz, 4H), 1.94–1.25 (m, 16H), 0.94 (m, 6H). IR (cm^{-1}): 3128(ν_{NH}); 1585($\nu_{C=N}$); 1540, 1502(δ_{NH}); 1422(ν_{CN+CS}).

4.3.11. Compound ***8a***

Yield: 47%, m.p. 218 °C. *Anal.* Calc. for $C_{30}H_{27}N_3O_3PdS$: C, 58.5; H, 4.4; N, 6.8. Found: C, 58.1; H, 4.8; N, 6.4%.

^1H NMR (300 MHz, $CDCl_3$): 8.13 (s, 1H), 7.72 (d broad, 2H), 7.47–7.16 (m, 10H), 6.98 (AA′BB′ system, ^3J = 8.9 Hz, 2H), 6.90 (s broad, 1H), 6.60 (dd, ^3J = 8.2 Hz, ^4J = 2.4 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 2.35 (s, 3H). IR (cm^{-1}): 3363(ν_{NH}); 1583($\nu_{C=N}$); 1520(δ_{NH}); 1419(ν_{CN+CS}).

4.3.12. Compound ***8b***

Yield: 45%, m.p. 156 °C. *Anal.* Calc. for $C_{40}H_{47}N_3O_3PdS$: C, 63.5; H, 6.2; N, 5.6. Found: C, 63.8; H, 6.0; N, 5.2%.

^1H NMR (300 MHz, $CDCl_3$): 8.11 (s, 1H), 7.75 (broad d, 2H), 7.48–7.17 (m, 10H), 6.98 (AA′BB′ system, ^3J = 8.9 Hz, 2H), 6.90 (d broad, 1H), 6.60 (dd, ^3J = 8.3 Hz, ^4J = 2.4 Hz, 1H), 4.03 (t, ^3J = 6.6 Hz, 4H), 2.36 (s, 3H), 1.90–1.34 (m, 16H), 0.93 (m, 6H). IR (cm^{-1}): 3321(ν_{NH}); 1584($\nu_{C=N}$); 1510(δ_{NH}); 1425(ν_{CN+CS}).

4.3.13. Compound ***9a***

Yield: 81%, m.p. 153 °C. *Anal.* Calc. for $C_{30}H_{27}N_3O_3PdS$: C, 58.5; H, 4.4; N, 6.8. Found: C, 58.2; H, 4.8; N, 6.7%.

^1H NMR (300 MHz, $CDCl_3$): 8.12 (s, 1H), 7.74 (m, 2H), 7.41–7.20 (m, 10H), 6.99 (AA′BB′ system, ^3J = 8.9 Hz, 2H), 6.90 (d, ^4J = 2.4 Hz, 1H), 6.61 (dd, ^3J = 8.4 Hz, ^4J = 2.4 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 2.36 (s, 3H). IR (cm^{-1}): 3298(ν_{NH}); 1584($\nu_{C=N}$); 1501(δ_{NH}); 1399(ν_{CN+CS}).

4.3.14. Compound ***9b***

Yield: 45%, m.p. 179 °C. *Anal.* Calc. for $C_{40}H_{47}N_3O_3PdS$: C, 63.5; H, 6.2; N, 5.6. Found: C, 63.9; H, 6.0; N, 5.3%.

^1H NMR (300 MHz, $CDCl_3$): 8.14 (s, 1H), 7.85 (broad d, 2H), 7.53–7.02 (m, 12H), 6.98 (d broad, 1H), 6.65 (dd, ^3J = 8.4 Hz, ^4J = 2.3 Hz, 1H), 4.08 (t, ^3J = 6.5 Hz, 4H), 2.43 (s, 3H), 1.95–1.40 (m, 16H), 1.01 (m, 6H). IR (cm^{-1}): 3126(ν_{NH}); 1584($\nu_{C=N}$); 1508(δ_{NH}); 1451(ν_{CN+CS}).

4.3.15. Compound ***10a***

Yield: 52%, m.p. 171 °C. *Anal.* Calc. for $C_{29}H_{24}FN_3O_3PdS$: C, 56.2; H, 3.9; N, 6.8. Found: C, 55.9; H, 3.5; N, 6.4%.

^1H NMR (300 MHz, $CDCl_3$): 8.12 (s, 1H), 7.79 (broad d, 2H), 7.53–7.19 (m, 8H), 7.06 (AA′MXX system, ^3J = 8.3 Hz, 2H), 6.98 (AA′BB′ system, ^3J = 8.9 Hz, 2H), 6.87 (broad s, 1H), 6.61 (dd, ^3J = 8.3 Hz, ^4J = 2.4 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 2.36 (s, 3H). IR (cm^{-1}): 3267(ν_{NH}); 1583($\nu_{C=N}$); 1536, 1503(δ_{NH}); 1405(ν_{CN+CS}).

4.3.16. Compound ***10b***

Yield: 41%, m.p. 171 °C. *Anal.* Calc. for $C_{39}H_{44}FN_3O_3PdS$: C, 60.3; H, 5.7; N, 5.4. Found: C, 59.8; H, 5.4; N, 5.0%.

^1H NMR (300 MHz, $CDCl_3$): 8.03 (s, 1H), 7.62 (broad d, 2H), 7.43 (AA′MXX system, ^3J = 8.3 Hz, $^4J_{HF}$ = 4.9 Hz, 2H), 7.35–7.12 (m, 6H), 6.99 (AA′MXX system, ^3J = 8.4 Hz, 2H), 6.89 (AA′BB′ system, ^3J = 9.0 Hz, 2H), 6.78 (broad s, 1H), 6.52 (dd, ^3J = 8.3 Hz, ^4J = 2.4 Hz, 1H), 3.94 (t, ^3J = 6.6 Hz, 4H), 1.91–1.24 (m, 16H), 0.84 (m, 6H). IR (cm^{-1}): 3111(ν_{NH}); 1583($\nu_{C=N}$); 1544, 1507(δ_{NH}); 1400(ν_{CN+CS}).

4.3.17. Compound ***11a***

Yield: 61%, m.p. 199 °C. *Anal.* Calc. for $C_{29}H_{24}ClN_3O_3PdS$: C, 54.7; H, 3.8; N, 6.6. Found: C, 54.3; H, 3.9; N, 6.2%.

^1H NMR (300 MHz, $CDCl_3$): 8.13 (s, 1H), 7.69 (d broad, 2H), 7.52 (AA′BB′ system, ^3J = 8.8 Hz, 2H), 7.45–7.21 (m, 8H), 6.98 (AA′BB′ system, ^3J = 8.9 Hz, 2H), 6.87 (d, ^4J = 2.3 Hz, 1H), 6.61 (dd, ^3J = 8.3 Hz, ^4J = 2.4 Hz, 1H), 3.88 (s, 3H), 3.85 (s, 3H). IR (cm^{-1}): 3209(ν_{NH}); 1582($\nu_{C=N}$); 1527(δ_{NH}); 1415(ν_{CN+CS}).

4.3.18. Compound ***11b***

Yield: 43%, m.p. 199 °C. *Anal.* Calc. for $C_{39}H_{44}ClN_3O_3PdS$: C, 60.3; H, 5.7; N, 5.4. Found: C, 60.0; H, 5.8; N, 5.0%.

^1H NMR (300 MHz, $CDCl_3$): 8.10 (s, 1H), 7.71 (broad d, 2H), 7.52 (AA′BB′ system, ^3J = 8.9 Hz, 2H), 7.44–7.21 (m, 8H), 6.97 (AA′BB′ system, ^3J = 8.9 Hz, 2H), 6.87 (d, ^4J = 2.4 Hz, 1H), 6.60 (dd, ^3J = 8.3 Hz, ^4J = 2.4 Hz, 1H), 4.02 (t, ^3J = 6.6 Hz, 4H), 1.89–1.32 (m, 16H), 0.93 (m, 6H). IR (cm^{-1}): 3209(ν_{NH}); 1584($\nu_{C=N}$); 1525(δ_{NH}); 1424(ν_{CN+CS}).

4.3.19. Compound ***12a***

Yield: 66%, m.p. 201 °C. *Anal.* Calc. for $C_{29}H_{24}BrN_3O_3PdS$: C, 51.1; H, 3.5; N, 6.2. Found: C, 50.9; H, 3.9; N, 6.9%.

^1H NMR (300 MHz, $CDCl_3$): 8.13 (s, 1H), 7.69 (m, 2H), 7.47–7.21 (m, 10H), 6.99 (AA′BB′ system, ^3J = 8.7 Hz, 2H), 6.87 (d, ^4J = 2.4 Hz, 1H), 6.61 (dd, ^3J = 8.2 Hz, ^4J = 2.4 Hz, 1H), 3.88 (s, 3H), 3.85 (s, 3H). IR (cm^{-1}): 3298(ν_{NH}); 1584($\nu_{C=N}$); 1501(δ_{NH}); 1399(ν_{CN+CS}).

4.3.20. Compound ***12b***

Yield: 33%, m.p. 191 °C. *Anal.* Calc. for $C_{39}H_{44}BrN_3O_3PdS$: C, 57.0; H, 5.4; N, 5.1. Found: C, 56.8; H, 5.0; N, 4.9%.

^1H NMR (300 MHz, $CDCl_3$): 8.02 (s, 1H), 7.64 (m, 2H), 7.36–7.14 (m, 10H), 6.90 (AA′BB′ system, ^3J = 8.8 Hz, 2H), 6.79 (d, ^4J = 2.4 Hz,

1H), 6.52 (dd, ^3J = 8.4 Hz, ^4J = 2.4 Hz, 1H), 3.94 (t, ^3J = 6.6 Hz, 4H), 1.80–1.24 (m, 16H), 0.86 (m, 6H). IR (cm^{-1}): 3210(ν_{NH}); 1584($\nu_{C=N}$); 1510(δ_{NH}); 1423(ν_{CN+CS}).

*4.3.21. Compound **13a***

Yield: 56%, m.p. 162 °C. *Anal.* Calc. for $C_{30}H_{27}N_3O_4PdS$: C, 57.0; H, 4.3; N, 6.7. Found: C, 56.9; H, 4.6; N, 6.3%.

^1H NMR (300 MHz, $CDCl_3$): 8.11 (s, 1H), 7.67 (m, 2H), 7.57–7.19 (m, 10H), 6.99–6.87 (m, 3H), 6.59 (dd, ^3J = 8.2 Hz, ^4J = 2.4 Hz, 1H), 3.86 (s, 3H), 3.81 (s, 3H). IR (cm^{-1}): 3298(ν_{NH}); 1584($\nu_{C=N}$); 1501(δ_{NH}); 1399(ν_{CN+CS}).

*4.3.22. Compound **13b***

Yield: 51%, m.p. 165 °C. *Anal.* Calc. for $C_{40}H_{47}N_3O_4PdS$: C, 62.4; H, 6.2; N, 5.5. Found: C, 61.9; H, 6.0; N, 5.2%.

^1H NMR (300 MHz, $CDCl_3$): 8.10 (s, 1H), 7.72 (br, 2H), 7.49–7.20 (m, 10H), 6.97 (AA′BB′ system, ^3J = 8.8 Hz, 2H), 6.92 (d, ^4J = 2.4 Hz, 1H), 6.52 (dd, ^3J = 8.4 Hz, ^4J = 2.4 Hz, 1H), 4.01 (t, ^3J = 6.6 Hz, 2H), 3.82 (t, ^3J = 6.6 Hz, 2H), 1.90–1.32 (m, 16H), 0.91 (m, 6H). IR (cm^{-1}): 3220(ν_{NH}); 1585($\nu_{C=N}$); 1509(δ_{NH}); 1420(ν_{CN+CS}).

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Appendix A. Supplementary data

CCDC 684867, 684868 and 684869 contain the supplementary crystallographic data for **2a**, **10a** and **13a**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.08.023.

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