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Synthesis and liquid crystal properties of dinuclear cyclopalladated 5-alkyl-2-(4′-alkoxyphenyl)pyrimidine and 3-(4′-alkoxyphenyl)-6-alkoxypyridazine complexes

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The dinuclear cyclopalladated complexes $[Pd(L_1 \text{ or } L_2)(\mu\text{-}X)]_2$ (HL_1 = 5-alkyl-2-(4′-alkoxyphenyl)pyrimidine, HL_2 = 3-(4′-alkoxyphenyl)-6-alkoxypyridazine, $X = Cl^-$, CH_2ClCOO^-, CH_2BrCOO^-, $CH_3CHBrCOO^-$, $CH_2BrCH_2COO^-$, CH_3COO^-) have been synthesized and characterized; their mesogenic properities were determined by DSC and polarizing microscopy. The effect of the bulk and the polarity of the bridging ligands on their mesogenic properties is discussed. The effect of the length of the alkyl chains on the mesogenic properties of these organometallic complexes has also been investigated.

1. Introduction

In recent years, a number of palladium(II)-containing liquid crystals have been reported and attracted much attention owing to their great potential application as highly functional optio-electronic materials [1–4]. Ghedini *et al*. have recently synthesized dimeric cyclopalladated complexes based on the 5-alkyl-2-(4-alkoxyphenyl)pyrimidine ligand and reported that all μ-halo complexes possess mesogenic properties, while all μ-acetate complexes are non-mesogenic [5]. The effect of the molecular structures of dinulear organometallic liquid crystals on their mesomorphism has not yet been studied in detail. In a continuation of our previous studies of the mesomorphism of cyclopalladated dinuclear complexes of azine, imine and azo derivatives [6–8], we have synthesized 5-hexyl-2-(4′-alkoxyphenyl)pyrimidines (HL_1) and their dinuclear cyclopalladated complexes I–VI. In order to investigate the effect of the position of the nitrogen atoms in the heterocyclic ring on mesophase type and stability, 3-(4′-alkoxyphenyl)-6-alkoxypyridazines (HL_2) and their dinuclear cyclopalladated complexes VII–X have also been synthesized. The effects of the bridging group, the length of the alkyl chains and the central ligands on the type and stability of mesophases of the complexes is discussed in detail.

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2. Results and discussion

2.1. *Synthesis of the ligands and complexes*

The synthesis of the ligands HL_1, HL_2 and the corresponding organometallic complexes of series I–X is outlined in schemes 1 and 2, respectively. The ligands HL_1, HL_2 were prepared according to similar methods previously described [9, 10]. The organometallic complexes of series I and VII were synthesized by the reaction of $[Pd(PhCN)_2Cl_2]$ with HL_1 and HL_2, respectively, in good yields. The complexes of series II–VI and VIII–X were obtained through exchange reaction of the compounds I, and VII with the appropriate sodium acetate, respectively. The structure and purity of all compounds were confirmed by IR, ^{1}H NMR and elemental analysis.

2.2. *Mesomorphism*

The phase behaviour determined by DSC and polarizing microscopy of the organic ligand and organometallic complexes I–VI ($m = 6$) and VII–X (n, $m = 10$) are shown in table 1.

2.2.1. *Effect of the central metal on mesomorphic properties*

From table 1 we find that the mesogenic temperature ranges of the organometallic complexes (except for the acetate-bridging complexes) are not only wider, but the mesogenic performances are better, than those of ligands. The organic ligands may display nematic

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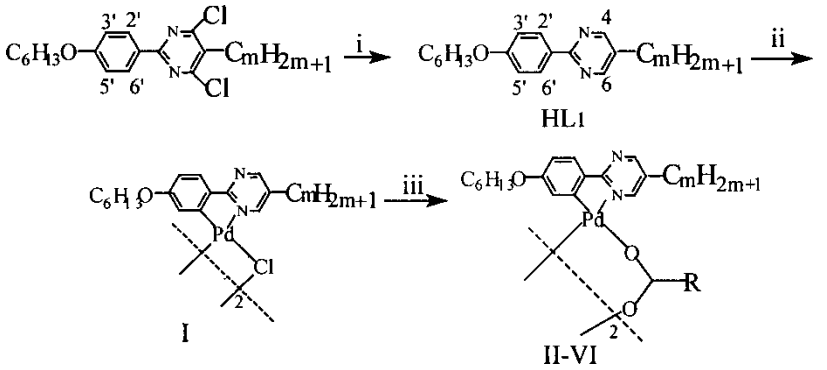
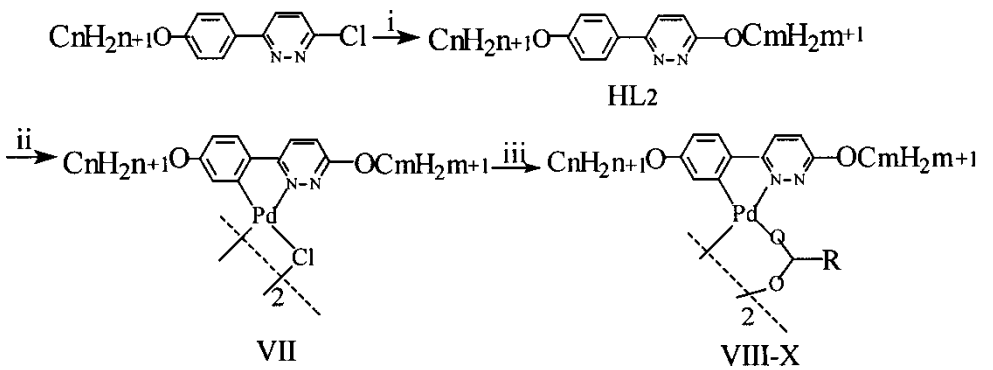


Scheme 1. (i) Pd/C, H_2; (ii) Pd $(PhCN)_2Cl_2$, EtOH; (iii) RCO_2Na, acetone. II: $R=-CH_3$; III: $R=-CH_2Cl$; IV: $R=-CH_2Br$; V: $R=-CHBrCH_3$; V: $R=-CH_2CH_2Br$.



Scheme 2. (i) Na, $C_mH_{2m+1}OH$; (ii) Pd $(PhCN)_2Cl_2$, EtOH; (iii) RCO_2Na, acetone. VIII: $R=-CH_3$; IX: $R=-CH_2Cl$; X: $R=-CH_2Br$.

Table 1. Phase transition of organic ligand and organometallic complexes.

Compound	Transition	T °C	ΔH kJ mol^{-1}
$HL_1(m=6)$	Cr–N	39	53.6
	N–I	62	3.8
I($m=6$)	Cr–SmA	125	42.7
	SmA–I	209	17.5
II($m=6$)	Cr–I	158	
III($m=6$)	Cr–SmC	130	36.6
	SmC–SmA	213	14.5
	SmA–I	218	5.6
IV($m=6$)	Cr–SmC	102	26.6
	SmC–I	113	4.3
V($m=6$)	Cr–SmC	104	8.6
	SmC–I	114	6.2
VI($m=6$)	Cr–SmC	148	38.5
	SmC–I	192	14.1
$HL_2(n,\ m=10)$	Cr–SmA	79	24.1
	SmA–I	102	17.1
VII($n,\ m=10$)	Cr–SmA	163	38.3
	SmA–I	212	10.3
VIII($n,\ m=10$)	Cr–I	185	
IX($n,\ m=10$)	Cr–SmA	160	42.1
	SmA–I	185	9.7
X($n,\ m=10$)	Cr–SmA	160	33.0
	SmA–I	174	12.6

or smectic phases, while the organometallic mesogens exhibit only smectic phases. This improvement of the mesomorphic behaviour may be attributed to two factors: (i) larger and polarizable electronic density of the Pd^{2+} metal further increases the molecular anisotropy; (ii) planar five-membered metallocycles enhance the rigidity of the organometallic mesogenic molecules, promoting ordered intermolecular arrangement [4]. Both of these aspects lead to organized arrangements between the molecules and facilitate the formation of smectic phases.

2.2.2. *Effect of the bridging group on the mesogenic properties*

From table 1 the influence of the central bridge X ($X=Cl^-, CH_2ClCOO^-, CH_2BrCOO^-, CH_3CHBrCOO^-, CH_2BrCH_2COO^-, CH_3COO^-$) on the mesogenic properties of the complexes can be seen. When the bridge is the Cl^- ion, the central bimetallic core of the complexes may be a planar structure [5, 8], which is advantageous for promoting an intermolecular ordered arrangement and facilitating mesomorphism. When X is an acetate bridge ($RCOO^-$), the two coordination

planes may be a 'half-open book', with the *R* group of the acetates in the spine of the book and the main axis of the pyrimidine or pyridazine ligand arranged parallel to this spine [11–13]. When *R* is the CH_3 group, the two coordination planes form a dihedral angle of about 25°, which is expected to disfavour the molecular arrangement and decrease the rigidity of the complexes [5]. Therefore, none of compounds of series II, VII display mesomorphism. In contrast, all the halo-substituted acetate-bridged complexes of the III–VI and IX, X series exhibit an enantiotropic phase. Two factors may contribute to this improvement of mesogenic behaviour: (i) the more bulky halo-substituted acetates depress the two coordination planes of the complexes and reduce the dihedral angel below that of the acetate bridged complexes, thus promoting ordered molecular arrangement; (ii) the polarity of the halogen atoms increases the polarizability anisopy of the complexes and the intermolecular interactions. Both of these factors are advantageous for the formation of mesomorphism, so all the halo-substituted acetate-bridged complexes display mesogenic phases.

2.2.3. *Effect of the central ligand on the mesogenic properties of the organometallic complexes*

To describe the effect of the ligand on mesoganic properties, we take the ligands HL_1 ($n=6$, $m=10$), HL_2 ($n=6$, $m=10$) and their corresponding complexes as examples. The experimental results of the phase transition temperature and the enthalpy measurements are shown in table 2.

The data in table 2 show that the mesogenic temperature ranges of the ligand HL_1 ($n=6$, $m=10$) and the complexes I, III, IV are wider than the ligand HL_2 ($n=6$, $m=10$) and its corresponding complexes; the mesomorphisms of the former are also better than those of the latter. The main difference between the ligand HL_1 ($n=6$, $m=10$) and HL_2 ($n=6$, $m=10$) is the arrangement of the two N atoms in the heterocyclic ring. The two N atoms in the pyrimidine ring in HL_1 ($m=10$) give rise to a strong dipole moment parallel to the molecular axis, while the two N atoms in the pyridazine ring HL_2 ($n=6$, $m=10$) give rise to a strong dipole moment perpendicular to the molecular axis [10]. The perpendicular dipole moments may counteract in the organometallic molecules and decrease the rigidity of the complex compounds, factors which do not facilitate the formation of liquid crystal phases.

Table 2. Phase transition and enthalpy of ligands and complexes.

	Transition	T °C	ΔH kJ mol^{-1}
HL_1($m=10$)	Cr–SmC	41	16.4
	SmC–SmA	63	7.6
	SmA–I	78	5.8
I($m=10$)	Cr–SmA	141	45.2
	SmA–I	212	9.7
III($m=10$)	Cr–C′	118	2.5
	C′–SmA	180	19.8
	SmA–I	237	6.9
IV($m=10$)	Cr–SmC	118	42.7
	SmC–SmA	132	13.9
	SmA–I	178	5.1
HL_2($n=6$, $m=10$)	Cr–SmA	79	24.1
	SmA–I	102	17.1
VII($n=6$, $m=10$)	Cr–SmA	148	33.8
	SmA–I	204	12.7
IX($n=6$, $m=10$)	Cr–SmA	128	32.1
	SmA–I	149	12.5
X($n=6$, $m=10$)	Cr–I	160	15.8

2.2.4. *Effect of the length of the alkyl chains on mesogenic properties*

The experimental results are shown in table 3 and figures 1, 2, 3. The influence of the terminal chain length of the ligands on the mesogenic properties of the complexes III can be seen in figure 1. There is a decrease in transition temperature as the length of the terminal chain increases, and a slight anti-odd-even effect is observed in the mesogenic phase to isotropic liquid transitions. It is also found that the complexes display more mesogenic phases and wider mesogenic temperature ranges with the long terminal chains.

Figure 2 shows that the clearing point temperatures of complexes IV follow an odd-even dependence on the length of alkyl chain. When the terminal carbon number is 12, the melting point decreases greatly and the mesogenic temperature range becomes wider than for other analogous complexes. We also find when the terminal carbon number is 8, 10, 12, the complexes exhibit two types of mesogenic phase, SmA and SmC; when the terminal carbon number is odd, all the complexes display only the SmA phase.

Figure 3 shows that all the complexes, except for IX ($n=6$, $m=10$), display the SmA phase, and that clearing points of the mesogens follow an odd-even dependence on the terminal carbon number. The mesomorphism temperature range does not change greatly, except for complex IX ($n=9$, $m=10$), which has a much wider range.

Generally, the effect of alkyl chain length on mesogenic properties is variable, being related to nature of the central ligand, the acetate-bridge group, the rigidity of the organometallic molecule, and the planarity of the structure of the molecule.

Table 3. Phase transition and enthalpy of organometallic mesogens.

Compound	Transition	T °C	ΔH kJ mol^{-1}
III($m=6$)	Cr–SmC	130	39.5
	SmC–SmA	213	15.6
	SmA–I	218	6.0
III($m=7$)	Cr–C′	77	20.6
	C′–SmA	106	23.8
	SmA–I	135	5.5
III($m=8$)	Cr–SmA	137	42.9
	SmA–I	232	7.7
III($m=9$)	Cr–SmA	156	34.7
	SmA–I	230	15.2
III($m=10$)	Cr–C′	118	2.5
	C′–SmA	180	19.8
	SmA–I	237	6.9
III($m=11$)	Cr–SmC	64	30.8
	SmC–SmA	147	14.1
	SmA–I	182	10.7
III($m=12$)	Cr–SmC	58	32.2
	SmC–SmA	142	17.7
	SA–I	219	11.0
IV($m=6$)	Cr–SmC	102	31.0
	SmC–I	113	5.0
IV($m=7$)	Cr–SmA	105	56.7
	SmA–I	211	10.8
IV($m=8$)	Cr–SmC	118	48.1
	SmC–SmA	147	15.3
	SmA–I	192	10.1
IV($m=9$)	Cr–SmA	146	51.4
	SmA–I	210	10.9
IV($m=10$)	Cr–SmC	118	42.7
	SmC–SmA	132	13.9
	SmA–I	178	5.1
IV($m=11$)	Cr–SmA	130	41.7
	SmA–I	194	9.5
IV($m=12$)	Cr–SmC	58	44.8
	SmC–SmA	114	14.0
	SmA–I	210	6.4
IX($n=10$, $m=6$)	Cr–I	172	17.9
IX($n=10$, $m=7$)	Cr–SmA	152	16.7
	SmA–I	185	17.8
IX($n=10$, $m=8$)	Cr–SmA	148	21.6
	SmA–I	177	12.3
IX($n=10$, $m=9$)	Cr–SA	128	32.9
	SmA–I	196	14.9
IX($n=10$, $m=10$)	Cr–SmA	160	42.1
	SmA–I	185	9.7
IX($n=10$, $m=11$)	Cr–SmA	154	28.5
	SmA–I	182	15.8
IX($n=10$, $m=12$)	Cr–SmA	161	34.6
	SmA–I	177	13.9

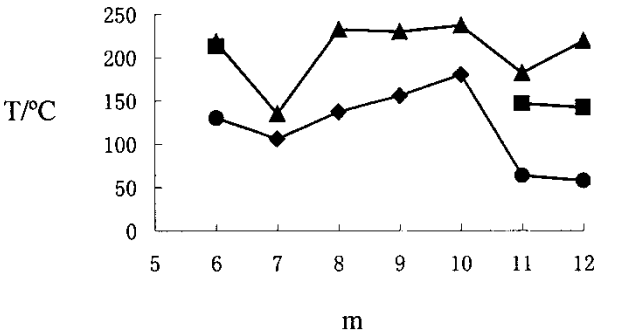


Figure 1. Effect of the length of the alkyl chain on the mesomorphism of III. ◆ Cr–SmA ●Cr–SmC ■SmC–SmA ▲SmA–I.

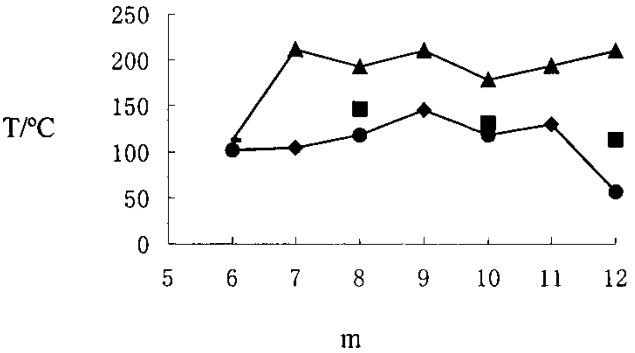


Figure 2. Effect of the length of the alkyl chain on the mesomorphism of IV. ◆Cr–SmA ●Cr–SmC ■SmC–SmA ▲SmA–I –SmC–I.

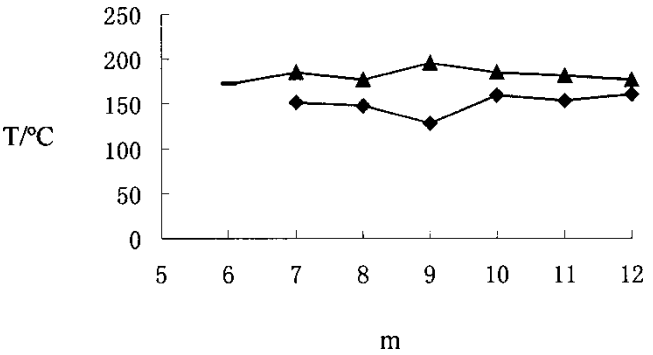


Figure 3. Effect of the length of the alkyl chain on the mesomorphism of IX. –Cr–I ◆Cr–SmA ▲SmA–I.

3. Experimental

3.1. *Characterization*

^{1}H NMR spectra were recorded on a 300 MHz Bruker AC-P300 spectrometer, using $CDCl_3$ as solvent and TMS as internal standard. The IR spectra (nujol) were performed on a Nicolet FT-MX-IE spectrometer. Elemental analyses were obtained with a Carlo Erba-1106 microanalyser. The transition temperatures and thermal behaviour were determined by DSC (Perkin-Elmer 7 series analysis system) operated at a scanning rate of 10°C min^{-1}. The mesophases were identified according to the textures observed under an Orthlux-II POLBK polarizing microscope [14]. The mesogenic textures of the representative title complexes are shown in figures 4 and 5.

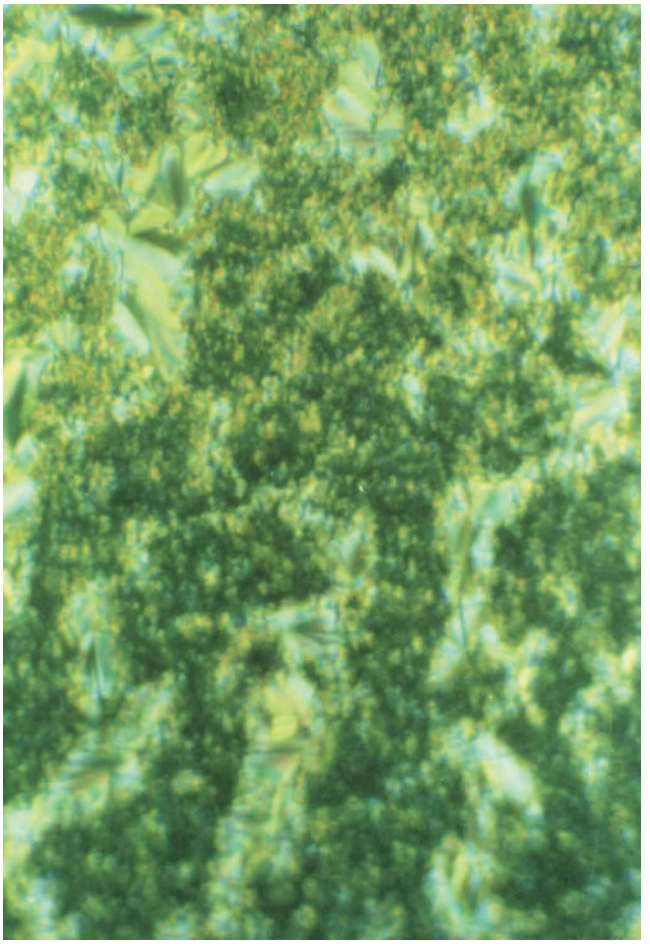


Figure 4. Texture of the complex III ($m=11$) under crossed polarizers, 110°C, heating, SmC, ×250.

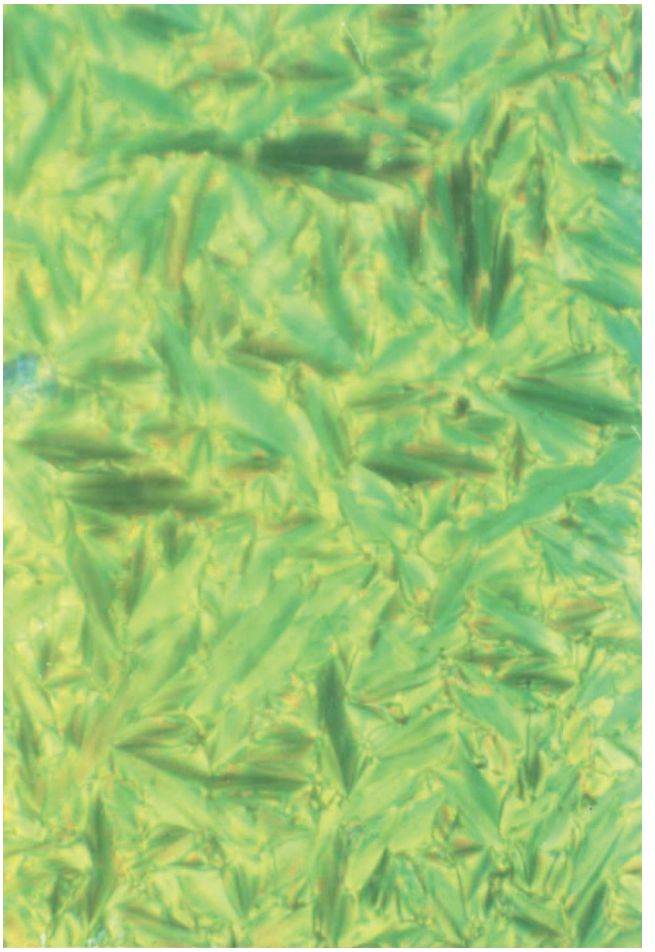


Figure 5. Texture of the complex IX ($n=10$, $m=11$) under crossed polarizers, 170°C, heating, SmA, ×250.

3.2. *Synthesis*

3.2.1. *5-(1-Hexyl)-2-[4′-(1-hexyloxy)phenyl]-pyrimidine HL_1 ($m=6$)*

A 100 ml round-bottom flask containing absolute ethanol (50 ml) and Pd/C (0.2 g, 5%Pd) was evacuated and filled with argon, then evacuated again and filled with hydrogen; finally a balloon filled with hydrogen was connected. 4,6-Dichloro-5-(1-hexyl)-2-[4′-(1-hexyloxy) phenyl]pyrimidine (4.09 g, 0.01 mol) was added and the mixture was stirred vigorously for 6 h at 50°C. The Pd/C was filtered off and the solvent evaporated. The product was rescrystallized from ethanol to give 3.04 g HL_1 ($m=6$) as a white solid; yield 90%. IR (KBr, cm^{-1}): 1610 (s, Ar), 858 (s, Ar), 1429 (m, O–O). ^1H NMR ($CDCl_3$, ppm): δ 8.40 (s, 2H, H^4 and H^6), 8.23 (2H, d, $J=8.9$ Hz, $H^{3'}$ and $H^{5'}$), 6.60 (2H, d, $J=8.8$ Hz, $H^{2'}$ and $H^{6'}$), 3.90 (2H, t, $J=6.0$ Hz), 2.70 (2H, t, $J=5.6$ Hz), 1.80–0.77 (m, 22H). Anal: calcd for $C_{22}H_{32}N_2O$ C 77.64, H 9.41, N 8.23; found C 77.80, H 9.31, N 8.27%.

3.2.2. *3-[4′-(1-Hexyloxy)phenyl]-6-(1-hexyloxy)-pyridazine HL_2 ($n=6$, $m=10$)*

Sodium (460 mg, 20 mmol) was added to a solution of *n*-decyl alcohol (320 mg, 2 mmol) in 20 ml of dried toluene, and the mixture stirred for 2 h until no additional hydrogen gas was released. A solution of chloropyridazine (300 mg, 1 mmol) in 30 ml of toluene was added and the mixture heated at reflux for 2 h. This solution was filtered and the filtrate was concentrated *in vacuo*. The residue was rescrystallized from hexane to give 220 mg HL_2 ($n=6$, $m=10$); yield 53%. IR (KBr, cm^{-1}): 1610 (m, Ar), 825 (s). ^1H NMR ($CDCl_3$, ppm): δ 7.99 (1H, d, $J=9.2$ Hz, H^5), 7.88 (1H, d, $J=9.2$ Hz, H^3), 7.66 (2H, d, $J=7.6$ Hz, $H^{3'}$ and $H^{5'}$), 7.00 (2H, d, $H^{2'}$, $H^{6'}$, $J=7.6$ Hz), 4.05 (4H, m), 1.76–0.84 (m, 30H).

Anal: calcd for $C_{26}H_{40}N_2O_2$ C 75.73, H 9.71, N 6.80; found C 75.75, H 9.71, N 6.80%.

3.2.3. *Complexes [Pd(L1)(μ-Cl)]2 (I) and [Pd(L2)(μ-Cl)]2 (VII)*

These were prepared according to a typical method reported in the literature as follows: $[Pd(PhCN)_2Cl_2]$ (383.5 mg, 1 mmol) and a stoichiometric amount of the appropriate HL_1 or HL_2 ligand were suspended in acetone (20 ml) with stirring at room temperature for 3 h. The mixture was filtered, and the yellow solid product was obtained after washing with petroleum ether and drying under vacuum.

$Pd(L_1)(\mu\text{-}Cl)]_2$ ($m=6$): yield 93%. IR (KBr, cm^{-1}): 1586 (s, Ar), 883 (m), 788 (s). ^1H NMR ($CDCl_3$, ppm): δ 8.45 (2H, br, s, H^6), 8.43 (2H, br, s, H^4), 7.56 (2H, d, $J=8.0$ Hz, $H^{5'}$), 6.62 (1H, d, $J=8.0$ Hz, $H^{6'}$), 7.00 (2H, br, s, $H^{3'}$), 4.00 (m, 4H), 2.75 (m, 4H), 1.80–0.90 (m, 44H). Anal: calcd for $C_{44}H_{62}Cl_2N_4O_2Pd_2$ C 54.84, H 6.44, N 5.82; found C 54.52, H 6.34, N 5.76%.

$[Pd(L_2)(\mu\text{-}Cl)]_2$ ($n=6$, $m=10$): yield 95%. IR (KBr, cm^{-1}): 1590 (s, Ar), 810, 835. ^1H NMR ($CDCl_3$, ppm): δ 8.20 (2H, d, $J=9.4$ Hz, H^4), 8.05 (2H, d, $J=9.4$ Hz, H^5), 7.30 (2H, d, $J=8.2$ Hz, $H^{5'}$), 7.02 (2H, s, $H^{3'}$), 6.82 (2H, d, $J=8.2$ Hz, $H^{6'}$), 4.00 (8H, m), 1.80–0.78 (m, 60H). Anal: calcd for $C_{52}H_{78}Cl_2N_4O_4Pd_2$ C 56.42, H 7.05, N 5.06; found C 56.55, H 7.14, N 4.91%.

3.2.4. *Complexes [Pd(L1)(μ-O2C-R)]2 (II–VI) and [Pd(L2)(μ-O2C-R)]2 (VIII–X)*

These were synthesized through the exchange reaction of the complexes I and VII with the corresponding sodium acetate. To a suspension of the appropriate complex I or VII (0.5 mmol) in acetone (25 ml) was added an equimolar amount of the appropriate sodium acetate (*R*COONa). The mixture was heated at reflux for 24 h, and the white precipitate filtered off. The solvent was removed from the filtrate to obtain the corresponding complexes II–VI and VIII–X as yellow solids.

$[Pd(L_1)(\mu\text{-}O_2CCH_3)]_2$, II ($m=6$): yield 92%. IR (KBr, cm^{-1}): 1588 (s, Ar), 881 (m), 788 (s). ^1H NMR ($CDCl_3$, ppm): δ 8.47 (2H, br, s, H^6), 8.38 (2H, br, s, H^4), 7.54 (2H, d, $J=8.0$ Hz, $H^{5'}$), 6.62 (1H, d, $J=8.0$ Hz, $H^{6'}$), 7.03 (2H, br, s, $H^{3'}$), 4.04 (m, 4H), 2.70 (m, 4H), 2.14 (s, 6H), 1.82–0.86 (m, 44H). Anal: calcd for $C_{48}H_{68}N_4O_6Pd_2$ C 57.10, H 6.74, N 5.50; found C 56.94, H 6.95, N 5.45%.

$[Pd(L_1)(\mu\text{-}O_2CCH_2Cl)]_2$, III ($m=6$): yield 86%. IR (KBr, cm^{-1}): 1586 (s, Ar), 1250 (s), 881 (m), 786 (s). ^1H NMR ($CDCl_3$, ppm): δ 8.48 (2H, br, s, H^6), 8.42 (2H, br, s, H^4), 7.54 (2H, d, $J=8.0$ Hz, $H^{5'}$), 6.61 (1H, d, $J=8.0$ Hz, $H^{6'}$), 7.06 (2H, br, s, $H^{3'}$), 4.02 (m, 4H), 4.50 (s, 4H), 2.75 (m, 4H), 1.76–0.82 (m, 44H). Anal: calcd for $C_{48}H_{66}Cl_2N_4O_6Pd_2$ C 53.44, H 6.12, N 5.19; found C 53.63, H 6.32, N 5.38%.

$[Pd(L_1)(\mu\text{-}O_2CCH_2Br)]_2$, IV ($m=6$): yield 88%. IR (KBr, cm^{-1}): 1586 (s, Ar), 1254 (s), 883 (m), 788 (s). ^1H NMR ($CDCl_3$, ppm): δ 8.47 (2H, br, s, H^6), 8.42 (2H, br, s, H^4), 7.56 (2H, d, $J=8.0$ Hz, $H^{5'}$), 6.58 (1H, d, $J=8.0$ Hz, $H^{6'}$), 6.90 (2H, br, s, $H^{3'}$), 4.20 (s, 4H), 4.02 (m, 4H), 2.76 (m, 4H), 1.88–0.82 (m, 44H). Anal: calcd for $C_{48}H_{66}Br_2N_4O_6Pd_2$ C 49.36, H 5.66, N 4.80; found C 49.45, H 5.43, N 4.62%.

$[Pd(L_1)(\mu\text{-}O_2CCHBrCH_3)]_2$, V ($m=6$): yield 78%. IR (KBr, cm^{-1}): 1586 (s, Ar), 1248 (s), 883 (m), 788 (s). ^1H NMR ($CDCl_3$, ppm): δ 8.46 (2H, br, s, H^6), 8.41 (2H, br, s, H^4), 7.54 (2H, d, $J=8.0$ Hz, $H^{5'}$), 6.66 (1H, d, $J=8.0$ Hz, $H^{6'}$), 6.96 (2H, br, s, $H^{3'}$), 4.32 (m, 2H), 4.06 (m, 4H), 2.75 (m, 4H), 1.90–0.82 (m, 50H). Anal: calcd for $C_{50}H_{70}Br_2N_4O_6Pd_2$ C 50.21, H 5.86, N 4.69; found C 50.42, H 6.04, N 4.53%.

$[Pd(L_1)(\mu\text{-}O_2CH_2CH_2Br)]_2$, VI ($m=6$): yield 82%. IR (KBr, cm^{-1}): 1586 (s, Ar), 1243 (s), 883 (m), 788 (s). ^1H NMR ($CDCl_3$, ppm): δ 8.44 (2H, br, s, H^6), 8.36 (2H, br, s, H^4), 7.58 (2H, d, $J=8.0$ Hz, $H^{5'}$), 6.60 (1H, d, $J=8.0$ Hz, $H^{6'}$), 7.04 (2H, br, s, $H^{3'}$), 3.94 (m, 4H), 2.70 (m, 4H), 2.42 (m, 4H), 2.16 (m, 4H), 1.80–0.86 (m, 44H). Anal: calcd for $C_{50}H_{70}Br_2N_4O_6Pd_2$ C 50.21, H 5.86, N 4.69; found C 50.48, H 6.10, N 4.42%.

$[Pd(L_2)(\mu\text{-}O_2CCH_3)]_2$, VIII ($n=6$, $m=10$): yield 87%. IR (KBr, cm^{-1}): 1590 (s, Ar), 1246 (s), 810, 835. ^1H NMR ($CDCl_3$, ppm): δ 8.22 (2H, d, $J=9.4$ Hz, H^4), 8.03 (2H, d, $J=9.4$ Hz, H^5), 7.30 (2H, d, $J=8.2$ Hz, $H^{5'}$), 7.04 (2H, s, $H^{3'}$), 6.82 (2H, d, $J=8.2$ Hz, $H^{6'}$) 4.05 (8H, m) 2.10 (s, 6H), 1.82–0.84 (52H). Anal: calcd for $C_{56}H_{84}N_4O_8Pd_2$ C 58.29, H 7.29, N 4.86; found C 58.40, H 7.08, N 4.62%.

$[Pd(L_2)(\mu\text{-}O_2CCH_2Cl)]_2$, IX ($n=6$, $m=10$): yield 84%. IR (KBr, cm^{-1}): 1594 (s, Ar), 1248 (s), 806, 840. ^1H NMR ($CDCl_3$, ppm): δ 8.26 (2H, d, $J=9.4$ Hz, H^4), 8.06 (2H, d, $J=9.4$ Hz, H^5), 7.32 (2H, d, $J=8.2$ Hz, $H^{5'}$), 7.04 (2H, s, $H^{3'}$), 6.80 (2H, d, $J=8.2$ Hz, $H^{6'}$), 4.46 (s, 4H), 4.06 (8 H, m), 1.86–0.80 (52H). Anal: calcd for $C_{56}H_{82}Cl_2N_4O_8Pd_2$ C 55.00, H 6.71, N 4.58; found C 55.26, H 6.97, N 4.42%.

$[Pd(L_2)(\mu\text{-}O_2CCH_2Br)]_2$, X ($n=6$, $m=10$): yield 85%. IR (KBr, cm^{-1}): 1594 (s, Ar), 1245 (s), 808, 835. ^1H NMR ($CDCl_3$, ppm): δ 8.22 (2H, d, $J=9.4$ Hz, H^4), 8.04 (2H, d, $J=9.4$ Hz, H^5), 7.26 (2H, d, $J=8.2$ Hz, $H^{5'}$), 7.00 (2H, s, $H^{3'}$), 6.82 (2H, d, $J=8.2$ Hz, $H^{6'}$), 4.16 (s, 4H), 4.00 (8 H, m), 1.82–0.84 (52H). Anal: calcd for $C_{56}H_{82}Br_2N_4O_8Pd_2$ C 51.27, H 6.26, N 4.27; found C 51.40, H 6.51, N 4.14%.

4. Conclusion

Several series of halo-substituted acetate dinuclear cyclopalladated complexes have been synthesized and their mesogenic properties studied; these are greatly affected by the bulk, polarity and polarizablity of the bridging ligands. The effect of the length of the alkyl chain on the mesogenic properties of different series of complexes varies, and is related to the bridging ligand between two metallic nuclei, the rigidity of the organometallic molecule, and the planarity of the structure of the molecule.

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