Chem. Mater. **1991**, *3*, 65-72 65

While confirming the high conductivity of the spinless state, our investigation assigns polarons a quite different role in conductivity properties, i.e., that of partners in a mixed-valence (redox) mechanism. Features of the conductivity/potential relationship similar to ours, i.e., a maximum in conductivity shifted to an oxidation potential higher than that of maximum spin concentration, have also been observed in polyaniline.[18,19] The absence of these features in the results of ref 7 may be due to the fact that small inorganic anions (such as BF_4^-) give a much less ordered material than that produced by relatively large aromatic anions such as tosylate as shown by X-ray diffraction,[20] neutron scattering,[21] and cyclic voltammetry.[22] Thus, although relative order of materials is required for mixed-valence conduction, it may be a general case for conducting polyconjugated polymers.

Last, it must be noted that mixed-valence conductivity in polypyrrole operates between polaron and bipolaron states and not between neutral and polaron states. In fact theoretical investigations on polyconjugated polymers[23] show that conformational changes from twisted to planar configurations are expected from the undoped to the doped form and, since polarons and bipolarons are topologically quite similar,[24] it is conceivable that the major conformational change takes place at the neutral-to-polar transition. Thus, electron hopping is easier between polaron and bipolaron than between neutral an polaron as the similar planarity of the former couple of states implies lower conformational activation energy.

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Registry No. TEATos, 733-44-8; polypyrrole, 30604-81-0.

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Transition Metals Complexed to Ordered Mesophases.[1] Synthesis Characterization and Mesomorphic Properties of Binuclear Cyclopalladated Phenylpyrimidine Species. Crystal Structure of Bis{(5-(1-hexyl)-2-[(4′-methoxy)phenyl-2′-ato]pyrimidine-$N',C^{2'}$)-μ-acetato}dipalladium(II)

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To prepare new mesogenic materials, the dinuclear palladium(II) complexes $[Pd(L)(\mu\text{-}Cl)]_2$ have been synthesized by cyclometalation of the HL*n* species (HL*n* = 5-R-2-(4′-R′-phenyl)pyrimidine; HL1, R = C_6H_{13}, R′ = CH_3; HL2, R = C_9H_{19}, R′ = CH_3; HL3, R = C_6H_{13}, R′ = $C_{11}H_{23}$; HL4: R = C_9H_{19}, R′ = C_9H_{19}). With these complexes as precursors, a number of $[Pd(L)(\mu\text{-}X)]_2$ compounds (X = Cl, Br, I, OAc) have been obtained by metathetical reactions. The molecular structure of $[Pd(L1)(\mu\text{-}OAc)]_2$ has been determined by a single-crystal X-ray analysis. The crystals are triclinic, space group $P1$ with $Z = 2$. Unit cell parameters are $a = 10.454$ (1) Å, $b = 13.229$ (1) Å, $c = 14.674$ (2) Å, $\alpha = 80.20$ (1)°, $\beta = 79.97$ (1)°, $\gamma = 72.87$ (1)°, $V = 1894.5$ (4) Å^3, D(calcd) = 1.36 g cm^{-3} for mol wt 869.62. Each palladium(II) ion in a square-planar geometry is bonded to a nitrogen atom and to an ortho carbon of pyridine and phenyl rings respectively (Pd(1)–N(2) = 2.013 (6) Å, Pd(2)–N(4) = 2.011 (5) Å; Pd(1)–C(1) = 1.947 (7) Å, Pd(2)–C(18) = 1.950 (7) Å) and to oxygen atoms of two different acetato groups (Pd(1)–O(1) = 2.142 (5) Å, Pd(1)–O(2) = 2.045 (5) Å; Pd(2)–O(3) = 2.159 (5) Å, Pd(2)–O(4) = 2.044 (5) Å). The two palladium coordination planes are folded at 25.66 (2)° with a Pd–Pd separation of 2.871 (1) Å. The HL2–HL4 ligands are nematic liquid crystals, while their mesogenic cyclopalladated derivatives display smectic mesophases only.

Introduction

A new class of materials with liquid-crystalline properties has recently been obtained by incorporation of transition metals into an organic structure. These metallomesogens, organometallic or coordination compounds, when derived by complexation of metal atoms to appropriate thermotropic ligands usually display the mesomorphism at temperatures higher than those exhibited by their mesogenic parents.[2-11] On the other hand, to be of

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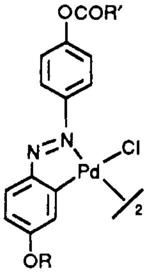
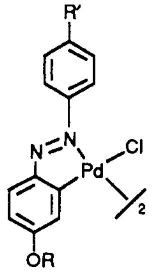
use in technological applications, these new materials must have both good thermal stability and low mesophase temperature range. Bearing this in mind, extensive investigations should be devoted to the study of the relationships between molecular structure, nature of the metal center, and mesomorphic behavior.

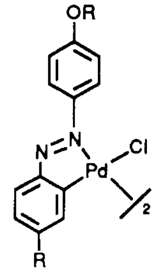
In light of this, a number of cyclopalladated species obtained from organic liquid crystals containing the diphenylazo fragment were previously described.[2a-c] The mesogenic ligands were *p*-alkoxy-*p*′-alkanoate azobenzenes[2a,b] as well as *p*-alkoxy-*p*′-alkylazobenzenes,[2c] the former affording complexes I, the latter giving rise to mixtures containg both compounds II and III (1:1 molar ratio).



I



II

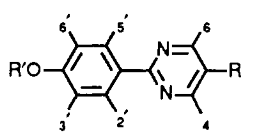


III

With reference to the para,para′ substituents, the thermotropic properties, i.e., thermal stability and mesomorphic range, were found better for the compounds containing alkyl and alkoxy groups than for the alkoxy and alkanoate homologous. However the latter species were tested as (II + III) mixtures; thus we were not able to say whether such results can actually be attributed to the different nature of the para′ substituents.

The *p*-alkyl-*p*′-alkoxyazobenzene rings are not selectively cyclometalated; therefore, to evaluate the role played by the para substituents, we need different liquid-crystalline ligands in which the metalation can occur only on one phenyl ring. For this purpose we have selected a species containing the 2-phenylpyrimidine group,[12] which in principle can react with palladium(II) affording the organometallic core IV.[13]

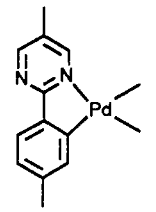
Chart I. 2-Phenylpyrimidine Ligands and Aromatic Proton Numbering



	R	R′
HL 1	C_6H_{13}	CH_3
HL 2	C_9H_{19}	CH_3
HL 3	C_6H_{13}	$C_{11}H_{23}$
HL 4	C_9H_{19}	C_9H_{19}

Table I. Crystallographic Data for Complex 1d

formula	$C_{38}H_{48}N_4O_6Pd_2$	α, deg	80.20 (1)
mol wt	869.62	β, deg	79.97 (1)
color	yellow	γ, deg	72.87 (1)
space group	$P1$	V, Å^3	1894.5 (4)
temp, K	298	Z	2
a, Å	10.454 (1)	μ (Mo Kα), cm^{-1}	9.65
b, Å	13.229 (1)	R	0.039
c, Å	14.674 (2)	wR	0.043
		S	0.794



IV

In this paper we report on the synthesis, characterization, and mesomorphic properties of a series of palladated complexes obtained from the ligands of general formula shown in Chart I.

Experimental Section

General Procedures. IR spectra in the 4000–400-cm^{-1} region were recorded on a Perkin-Elmer 1330 spectrometer as KBr pellets. ^{1}H NMR spectra were taken on a Bruker WM-300 spectrometer in $CDCl_3$ solutions with Me_4Si as internal standard.

Elemental analyses were obtained from the Microanalysis Laboratory of the Dipartimento di Chimica, Universitá della Calabria, Italy.

The textures of the mesophases were observed with a Zeiss Axioskop polarizing microscope equipped for photography and with a Linkam CO 600 heating stage. The transition temperatures and the enthalpies were measured by differential scanning calorimetry (DSC) with a Mettler FP 80 thermosystem, equipped with an FP 85 microscopy cell, operating at a scanning rate of 5 °C min^{-1}.

X-ray Structural Analysis. Yellow crystals of $[(C_6H_{13}C_4N_2H_2C_6H_3OMePd]_2(\mu\text{-}O_2CMe)_2$, **1d**, suitable for single-crystal X-ray analysis were obtained from ethanol. The diffraction data were collected on a Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation. The structure was solved by Patterson methods and completed by Fourier recycling. Full-matrix least-squares refinement was carried out minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and the calculated structure amplitudes. The employed weighting scheme was

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$$w = 1/\sigma^2|F_o| + q|F_o|^2$$

where $\sigma^2|F_o|$ is the variance of each observation obtained from counting statistics and q is an adjustable parameter (formal value $q = 0.003\,307$). All calculations were performed with the SHELX 76[14] and PARST[15] programs on the VAX/VMS computer of the Universitâ della Calabria.

Crystal data and summary of intensity data collection and structure refinement are reported in Table S1 (supplementary material), of which Table I is a reduced form.

Synthesis of the Complexes. All manipulations were carried out in air. The standard chemicals (Aldrich Chemical Co.) and $Pd(OAc)_2$ (Fluka A.G.) and the ligands HL1–4 (Merk E.) were used as supplied. $[Pd(PhCN)_2Cl_2]$ was prepared as reported in the literature.[16] Typical preparations were as follows (all analogous complexes were prepared in the same way):

$[Pd(L)(\mu\text{-}Cl)]_2$, 1a–4a. $[Pd(PhCN)_2Cl_2]$ (283.5 mg, 0.74 mmol) and a stoichiometric amount of the appropriate HL ligand were suspended in ethanol (30 mL) and stirred at room temperature (3 h). The mixture was then filtered off, and the pale-yellow solid product was obtained after washing with petroleum ether and drying under vacuum. $[Pd(L1)(\mu\text{-}Cl)]_2$, **1a**. Anal. Calcd for $C_{34}H_{42}Cl_2N_4O_2Pd_2$: C, 49.65; H, 5.15; N, 6.81. Found: C, 49.62; H, 5.03; N, 6.38. Yield, 75%. $[Pd(L2)(\mu\text{-}Cl)]_2$, **2a**. Anal. Calcd for $C_{40}H_{54}Cl_2N_4O_2Pd_2$: C, 52.89; H, 6.00; N, 6.18. Found: C, 54.37; H, 6.22; N, 6.18. Yield, 68%. $[Pd(L3)(\mu\text{-}Cl)]_2$, **3a**. Anal. Calcd for $C_{54}H_{82}Cl_2N_4O_2Pd_2$: C, 58.80; H, 7.49; N 5.08. Found: C, 58.65; H, 7.57; N, 5.15. Yield, 92%. ^{1}H NMR δ 8.59 (1 H, br s, H^6), 8.53 (1 H, br s, H^4), 7.60 (1 H, d, $J^{6',5'} = 8.3$ Hz, $H^{6'}$), 6.98 (1 H, br s, $H^{3'}$), 6.68 (1 H, m, H^5). $[Pd(L4)(\mu\text{-}Cl)]_2$,. **4a**. Anal. Calcd. for $C_{56}H_{86}Cl_2N_4O_2Pd_2$: C, 59.47; H, 7.66; N, 4.95. Found; C, 59.04; H, 7.00; N, 4.98. Yield, 86%. ^{1}H NMR δ 8.63 (1 H, br s, H^6), 8.55 (1 H, br s, H^4), 7.63 (1 H, d, $J^{6',5'} = 8.5$, $H^{6'}$), 7.00 (1 H, br s, $H^{3'}$), 6.70 (1 H, m, $H^{5'}$).

$[Pd(L)(\mu\text{-}Br)]_2$, 1b–4b. To a suspension of 0.15 mmol of $[PdCl(L)]_2$ in acetone (8 mL) was added an excess (2.9 mmol) of NaBr. The mixture was stirred at room temperature (4 days), after which the pale-yellow product was filtered off and washed several times with water, ethanol, and diethyl ether (**3b** was washed with water and acetone) and dried under vacuum. $[Pd(L1)(\mu\text{-}Br)]_2$, **1b**. Anal. Calcd for $C_{34}H_{42}Br_2N_4O_2Pd_2$: C, 44.81; H, 4.65; N, 6.15. Found: C, 44.67; H, 4.67; N, 5.99. Yield, 59%. $[Pd(L2)(\mu\text{-}Br)]_2$, **2b**. Anal. Calcd for $C_{40}H_{54}Br_2N_4O_2Pd_2$: C, 48.26, H, 5.47; N, 5.63. Found: C, 48.34; H, 5.66; N, 5.35. Yield, 53%. ^{1}H NMR δ 8.72 (1 H, br s, H^6), 8.51 (1 H, br s, H^4), 7.62 (1 H, d, $J^{6',5'} = 8.4$ Hz, $H^{6'}$), 7.14 (1 H, br s, $H^{3'}$), 6.67 (1 H, dd, $J^{5',6'} = 8.5$ Hz, $J^{5',3'} = 2.0$ Hz, $H^{5'}$). $[Pd(L3)(\mu\text{-}Br)]_2$, **3b**. Anal. Calcd for $C_{54}H_{82}Br_2N_4O_2Pd_2$: C, 54.42; H, 6.93; N, 4.70. Found: C, 54.32; H, 6.99; N, 4.59. Yield, 89%. ^{1}H NMR δ 8.73 (1 H, br s, H^6), 8.50 (1 H, br s, H^4), 7.61 (1 H, d, $J = 8.4$ Hz, $H^{6'}$), 7.13 (1 H, br s, $H^{3'}$), 6.66 (1 H, dd, $J^{5',6'} = 8.5$ Hz, $J^{5',3'} = 2.0$ Hz, $H^{5'}$). $[Pd(L4)(\mu\text{-}Br)]_2$, **4b**. Anal. Calcd for $C_{56}H_{86}Br_2N_4O_2Pd_2$: C, 55.13; H, 7.11; N, 4.59. Found: C, 55.44; H, 7.39; N, 4.59. Yield 76%. ^{1}H NMR δ 8.74 (1 H, br s, H^6), 8.53 (1 H, br s, H^4), 7.63 (1 H, d, $J = 8.4$ Hz, $H^{6'}$), 7.15 (1 H, br s, $H^{3'}$), 6.67 (1 H, dd, $J^{5',6'} = 8.4$ Hz, $J^{5',3'} = 2.0$ Hz, $H^{5'}$].

$[Pd(L)(\mu\text{-}I)]_2$, **1c–4c.** To the $[Pd(L)(\mu\text{-}Cl)]_2$ dimer (0.14 mmol), suspended in 8 mL of acetone, was added KI in a 1:20 dimer to iodine molar ratio, and the flask was covered to avoid exposure to light. After this stirred at room temperature (3 h) a white precipitate (KCl) was filtered off, and to the filtrate was added diethyl ether. The precipitated orange product was filtered, washed with water, ethanol, and diethyl ether, and dried in vacuo. $[Pd(L1)(\mu\text{-}I)]_2$, **1c**. Anal. Calcd for $C_{34}H_{42}I_2N_4O_2Pd_2$: C, 40.62; H, 4.14; N, 5.57. Found: C, 40.69; H, 4.05; N, 5.39. Yield, 90%. $[Pd(L2)(\mu\text{-}I)_2$, **2c**. Anal. Calcd for $C_{40}H_{54}I_2N_4O_2Pd_2$: C, 44.09; H, 4.99; N, 5.14. Found: C, 43.57; H, 4.95; N, 4.95. Yield, 72%. ^{1}H NMR δ 8.92 (1 H, br s, H^6), 8.52 (1 H, d, $J = 1.9$ Hz, H^4), 7.71 (1 H, d, $J = 8.5$ Hz, $H^{6'}$), 7.42 (1 H, br s, $H^{3'}$), 6.67 (1 H, dd, $J^{5',6'} = 8.5$ Hz, $J^{5',3'} = 2.2$ Hz, $H^{5'}$). $[Pd(L3)(\mu\text{-}I)]_2$, **3c**. Anal. Calcd for $C_{54}H_{82}I_2N_4O_2Pd_2$: C, 50.44; H, 6.43; N, 4.36. Found: C, 50.29; H, 6.39; N, 4.13. Yield, 90%. ^{1}H NMR δ 8.93 (1 H, br s, H^6), 8.49 (1 H, d, $J = 8.5$ Hz, $H^{6'}$), 7.4 (1 H, br s, $H^{3'}$), 6.66 (1 H, dd, $J^{5',6'} = 8.5$ Hz, $J^{5',3'} = 2.1$ Hz, $H^{5'}$). $[Pd(L4)(\mu\text{-}I)]_2$, **4c**. Anal. Calcd for $C_{56}H_{86}I_2N_4O_2Pd_2$: C, 51.19; H, 6.59; N, 4.26. Found: C, 50.81; H, 6.52; N, 4.20. Yield, 81%. ^{1}H NMR δ 8.94 (1 H, br s, H^6), 8.52 (1 H, br s, H^4), 7.72 (1 H, d, $J = 8.5$ Hz, $H^{6'}$), 7.41 (1 H, br s, $H^{3'}$), 6.68 (1 H, dd, $J^{5',6'} = 8.5$ Hz, $J^{5',3'} = 2.0$ Hz, $H^{5'}$).

$[Pd(L)(\mu\text{-}OAc)]_2$, 1d–4d. To a suspension of the appropriate HL (0.74 mmol) in ethanol (30 mL) was added an equimolar amount of $Pd(OAc)_2$. After this stirred (12 h) at room temperature, the yellow precipitate was filtered and extracted with diethyl ether (40 mL), and the solution cooled at −10 °C. The $[Pd(OAc)(L)]_2$ complex was obtained as yellow (**1d** and **3d**), brown (**4d**), or green (**2d**) crystals. $[Pd(L1)(\mu\text{-}OAc)]_2$, **1d**. Anal. Calcd for $C_{38}H_{48}N_4O_6Pd_2$: C, 52.48; H, 5.56; N, 6.44. Found: C, 52.11; H, 5.56; N, 6.50. Yield, 22%. ^{1}H NMR δ 8.17 (1 H, d, $J = 2.5$ Hz, H^6), 7.73 (1 H, d, $J = 8.7$ Hz, $H^{6'}$), 7.23 (1 H, d, $J = 8.7$ Hz, $H^{6'}$), 6.44 (2 H, m, $H^{5'}$ and $H^{3'}$). $[Pd(L2)(\mu\text{-}OAc)]_2$, **2d**. Anal. Calcd for $C_{44}H_{60}N_4O_6Pd_2$: C, 52.41; H, 6.34; N, 5.87. Found: C, 52.11; H, 5.53; N, 6.16. Yield, 64%. ^{1}H NMR δ 8.17 (1 H, d, $J = 2.6$ Hz, H^6), 7.73 (1 H, d, $J = 2.7$ Hz, H^4), 7.22 (1 H, d, $J = 8.5$ Hz, $H^{6'}$), 6.44 (2 H, m, $H^{5'}$ and $H^{3'}$). $[Pd(L3)(\mu\text{-}OAc)]_2$, **3d**. Anal. Calcd for $C_{58}H_{88}N_4O_6Pd_2$: C, 60.57; H, 7.71; N, 4.87. Found: C, 59.36; H, 7.76; N, 4.85. Yield, 18%. ^{1}H NMR δ 8.16 (1 H, d, $J = 2.5$ Hz, H^6), 7.72 (1 H, d, $J = 2.5$ Hz, H^4), 7.20 (1 H, d, $J = 8.9$ Hz, $H^{6'}$), 6.42 (2 H, m, $H^{5'}$ and $H^{3'}$). $[Pd(L4)(\mu\text{-}OAc)]_2$, **4d**. Anal. Calcd for $C_{60}H_{90}N_4O_6Pd_2$: C, 61.27; H, 7.71; N, 4.76. Found: C, 59.49; H, 7.83; N, 4.65. Yield, 69%. ^{1}H NMR δ 8.16 (1 H, d, $J = 2.4$ Hz, H^6), 7.72 (1 H, d, $J = 2.3$ Hz, H^4), 7.19 (1 H, d, $J = 9.0$ Hz, $H^{6'}$), 6.42 (2 H, m, $H^{5'}$ and $H^{3'}$). Alternatively, the complex $[Pd(L3)(\mu\text{-}OAc)]_2$, **3d**, was synthesized through metathetical reactions from $[Pd(L3)(\mu\text{-}Cl)]_2$, **3a**, and AcONa or AcOAg.

Reaction with AcONa. To the **3a** dimer (0.18 mmol) in acetone (15 mL) was added 5 equiv of AcONa (0.90 mmol) to give a yellow solution with a white precipitate (NaCl). After this stirred (24 h) at room temperature, the solid was filtered, and the solvent removed from the filtrate to obtain **3d** as a yellow solid, in 61% yield.

Reaction with AcOAg. To the **3a** dimer (0.09 mmol) in 15 mL of diethyl ether, AcOAg was added in a 1:2 dimer to acetato molar ratio. The mixture was stirred at room temperature (12 h) and then filtered from the AgCl so formed. After removal of the solvent from the filtrate, **3d**, as a yellow solid, washed with petroleum ether was obtained in 89% yield.

^{1}H NMR data for the uncomplexed HL1–HL4 ligands: For sake of comparison, the ^{1}H NMR data concerning the HL1–HL4 protons are reported. HL1: δ 8.56 (2 H, s, H^4 and H^6), 8.37 (2 H, d, $J^{3',2';6',5'} = 8.9$ Hz, $H^{3'}$ and $H^{6'}$), 6.98 (2 H, d, $J^{2',3';5',6'} = 9.0$ Hz, $H^{2'}$ and $H^{6'}$). HL2: δ 8.57 (2 H, s, H^4 and H^6), 8.35 (2 H, d, $J = 8.8$ Hz, $H^{3'}$ and $H^{6'}$), 6.99 (2 H, d, $J = 8.8$ Hz, $H^{2'}$, and $H^{5'}$). HL3: δ 8.56 (2 H, s, H^4 and H^6), 8.35 (2 H, d, $J^{3',2';6',5'} = 8.9$ Hz, $H^{3'}$ and $H^{6'}$), 6.98 (2 H, d, $J^{2',3';5',6'} = 8.8$ Hz, $H^{2'}$ and $H^{5'}$). HL4: δ 8.56 (2 H, s, H^4 and H^6), 8.35 (2 H, d, $J = 8.9$ Hz, $H^{3'}$ and $H^{6'}$), 6.97 (2 H, d, $J = 8.9$ Hz, $H^{2'}$ and $H^{5'}$).

Results and Discussion

Synthesis and Characterization of the Complexes. Heteroaromatic compounds such as 2-phenylpyridine[17] or 2-*p*-tolylbenzthiazole[18] react with palladium(II) salts giving rise to the respective cyclopalladated derivates; similar products obtained from the 5,4′-disubstituted-2-phenylpyrimidines reported in Chart I are now described.

The ligands HL1–HL4 reacting with $[Pd(PhCN)_2Cl_2]$ (1:1 molar ratio) afford in good yields the yellow products **1a–4a**, respectively, whose elemental analyses are in agreement with the expected $[Pd(L)_2(\mu\text{-}Cl)]_2$ stoichiometry. Moreover, these compounds have been characterized by IR (KBr pellets) and, when allowed by the solubility (**2a**

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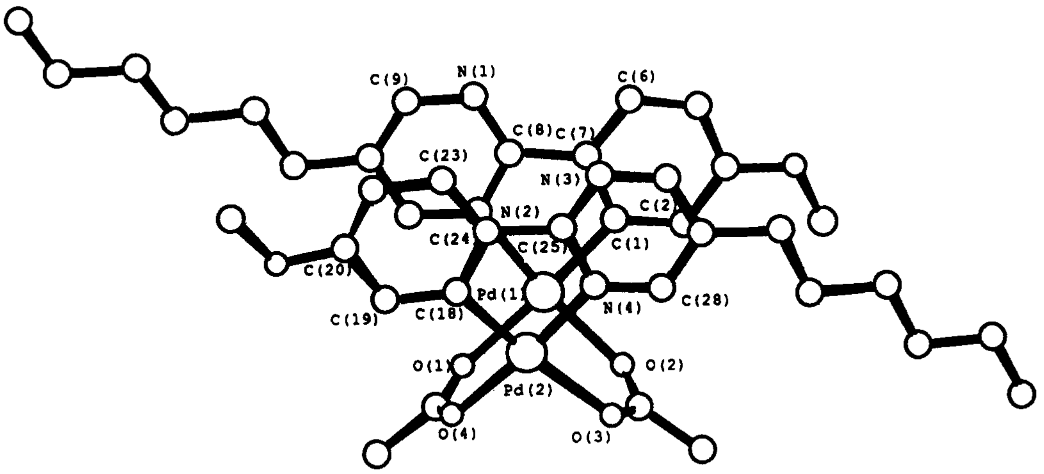
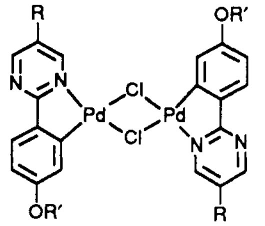


Figure 1. Molecular structure of complex **1d** with the scheme used for atom labeling.

Chart II. Sketch of the Molecular Structure Proposed for Complexes 1a–4a



	R	R′
1a	C_6H_{13}	CH_3
2a	C_9H_{19}	CH_3
3a	C_6H_{13}	$C_{11}H_{23}$
4a	C_9H_{19}	C_9H_{19}

and **3a**), by ^{1}H NMR spectroscopy. As far as the ^{1}H NMR data are concerned (Experimental Section), all the investigated complexes show a single broad resonance attributable to the H$^{3'}$ proton (in the spectra of the free ligands H$^{3'}$ appears as a doublet with $J^{3',2'}$ = 8.9 Hz); therefore, the metalation occurring on the phenyl ring is apparent. Accordingly, for the homologous **1a**–**4a** complexes the usual binuclear chloro-bridged molecular structure depicted in Chart II is suggested.

Complexes **1a**–**4a** are very useful starting materials for the preparation of their isostructural derivates of general formula $[Pd(L)(\mu\text{-}X)]_2$. Thus, by methatetical reactions with NaBr or KI (Experimental Section) the homologous bromide-containing (**1b**-**4b**) or iodide-containing (**1c**–**4c**) compounds have been obtained.

A further series of similar compounds, the acetato-bridged $[Pd(L)(\mu\text{-}OAc)]_2$, **1d**–**4d**, has been synthesized by treatment of the appropriate HL ligand with palladium(II) acetate. Alternatively, as found for $[Pd(L3)(\mu\text{-}OAc)]_2$, **3d** (Experimental Section), the whole series of **1d**–**4d** compounds could be prepared also by reacting the proper $[Pd(L)(\mu\text{-}Cl)]_2$ dimer with sodium or silver acetate. All the new complexes have been characterized by elemental analysis and spectroscopic methods. In particular, in the ^{1}H NMR spectra the position of the H$^{3'}$ resonance is noteworthy. In fact, it is found nearly superimposed with the H$^{5'}$ resonance and high-field shifted by about 0.5 ppm with respect to the values obtained for the halo-bridged complexes. In the acetato-bridged orthopalladated imine complex $[Pd(C_{10}H_{21}OC_6H_4CH{=}NC_6H_4OC_{10}H_{21})(\mu\text{-}OAc)]_2$, a similar upfield shift, observed for the methinic proton, was attributed to the magnetic anisotropic field originated by the ortho-palladated ring of the other ligand.[10b] In the present case such a result likely can be attributed to the shielding effect exerted by a neighboring aromatic ring; consequently, on the basis of this evidence, we suggest that for the acetato-bridged compounds the two 2-phenylpyrimidine moieties in solution preserve the same arrangement exhibited as solids (vide infra).

Table II. Selected Interatomic Distances (angstroms) and Angles (degrees) for Complex 1d

Pd(1)-Pd(2)	2.871 (1)		
Pd(1)-O(1)	2.142 (5)	Pd(2)-O(3)	2.159 (5)
Pd(1)-O(2)	2.045 (5)	Pd(2)-O(4)	2.044 (5)
Pd(1)-N(2)	2.013 (6)	Pd(2)-N(4)	2.011 (5)
Pd(1)-C(1)	1.947 (7)	Pd(2)-C(18)	1.950 (7)
C(1)-C(7)	1.407 (11)	C(18)-C(24)	1.422 (11)
C(7)-C(8)	1.443 (9)	C(24)-C(25)	1.446 (9)
C(8)-N(2)	1.358 (10)	C(25)-N(4)	1.353 (10)
O(1)-Pd(1)-O(2)	92.6 (2)	O(3)-Pd(2)-O(4)	92.0 (2)
O(1)-Pd(1)-N(2)	94.6 (2)	O(3)-Pd(2)-N(4)	92.8 (2)
O(2)-Pd(1)-C(1)	91.3 (2)	O(4)-Pd(2)-C(18)	93.3 (2)
N(2)-Pd(1)-C(1)	81.6 (3)	N(4)-Pd(2)-C(18)	81.8 (2)
Pd(1)-C(1)-C(2)	127.2 (5)	Pd(2)-C(18)-C(19)	127.3 (5)
Pd(1)-C(1)-C(7)	113.8 (5)	Pd(2)-C(18)-C(24)	113.6 (5)
C(2)-C(1)-C(7)	119.1 (6)	C(19)-C(18)-C(24)	119.0 (6)
C(1)-C(7)-C(6)	120.2 (7)	C(18)-C(19)-C(20)	120.3 (6)
C(1)-C(7)-C(8)	115.5 (6)	C(18)-C(24)-C(25)	115.2 (6)
C(6)-C(7)-C(8)	124.2 (7)	C(23)-C(24)-C(25)	125.4 (6)
Pd(1)-N(2)-C(8)	114.6 (4)	Pd(2)-N(4)-C(25)	115.1 (4)
Pd(1)-N(2)-C(11)	126.0 (4)	Pd(2)-N(4)-C(28)	125.3 (4)
C(8)-N(2)-C(11)	119.2 (6)	C(25)-N(4)-C(28)	118.8 (5)

The molecular structure of **1d** has been determined by single-crystal X-ray analysis.

Crystal Structure of $[(C_6H_{13}C_4N_2H_2C_6H_3OMe)Pd]_2(\mu\text{-}O_2CMe)_2$, 1d. Selected interatomic distances and angles and their estimated standard deviations are listed in Table II (atomic coordinates and other data presented in Table IIIand in the supplementary material); a view of the **1d** complex, with the atomic labeling scheme is shown in Figure 1.

The crystal structure consists of discrete dinuclear molecules with each palladium(II) atom surrounded in a square-planar arrangement by a nitrogen atom of the pyrimidine ring, an ortho carbon atom of the phenyl ring, and two oxygen atoms (one from each of the μ-acetate ligands).

This molecular structure is closely similar to those previously reported for the acetate-bridged dimers obtained by cyclometalation of 2-*p*-tolylbenzthiazole and 2-*p*-tolylbenzoxazole with palladium(II) acetate.[18] The 2-phenylpyrimidine systems form five-membered chelate rings with "bite" angles, [C(1)–Pd(1)–N(2) and C(18)–Pd(2)–N(4)], of 81.6 (3)° and 81.8(2)°. The Pd(1)–Pd(2)

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[18] Churchill, M. R.; Wasserman, H. J.; Young, G. J. *Inorg. Chem.* 1980, *19*, 762.

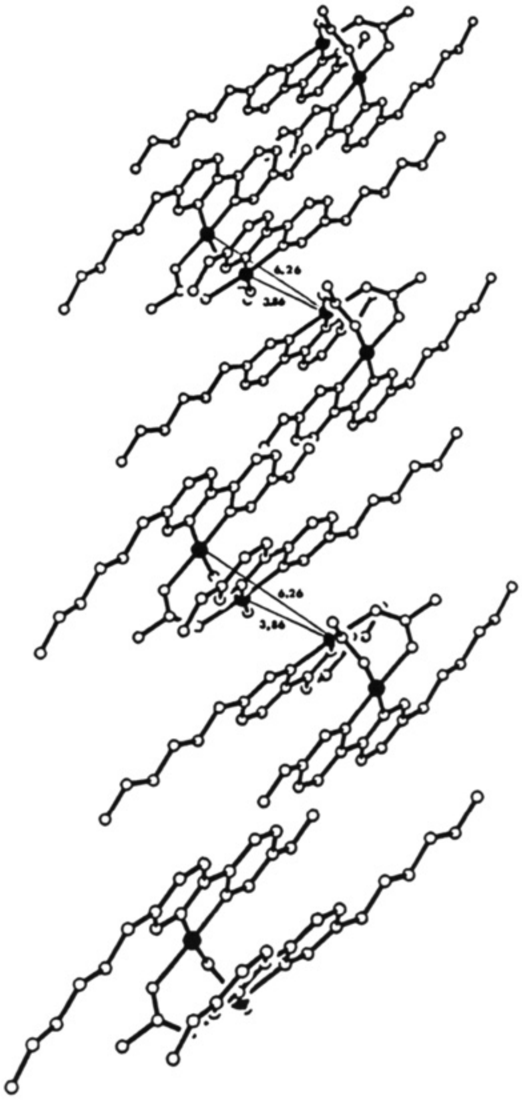

Figure 2. Molecular packing in **1d**, viewed along the [0,−1,1] direction.

separation is 2.871 (1) Å, and the angle between their coordination planes is 25.66 (2)°. As a result, the two phenylpyrimidine moieties, in a mutually transoid geometry, are forced to lie above one another and with phenyl and pyrimidine rings in a face-to-face arrangement. The four aromatic rings, although separately planar, are not coplanar in the L1 ligands. The tilt angles they form are 8.00 (2)° in L1 binding Pd(1) and 2.91 (2)° in L1 bonded to Pd(2).

In the unit cell, the two molecules are parallel to the z axis with the shortest intermetallic separation of 14.357 (2) Å, while the molecular packing (Figure 2) shows a stacked structure, along the [0,−1,1] direction, with alternate metal–metal distances of 3.860 (1) and 6.264 (1) Å.

Mesomorphic Properties. The thermal behavior of both the free ligands and their palladium(II) complexes are reported in Table IV. These data show that the HL2–HL4 species are nematic liquid crystals while the **2d**–**4d**, **2c**, and **4a** compounds, together with HL1 and its derivatives, do not display mesomorphism. By contrast, all the remaining HL2–HL4 halo-bridged cyclopalladated complexes exhibit a smectic A mesophase.[19]

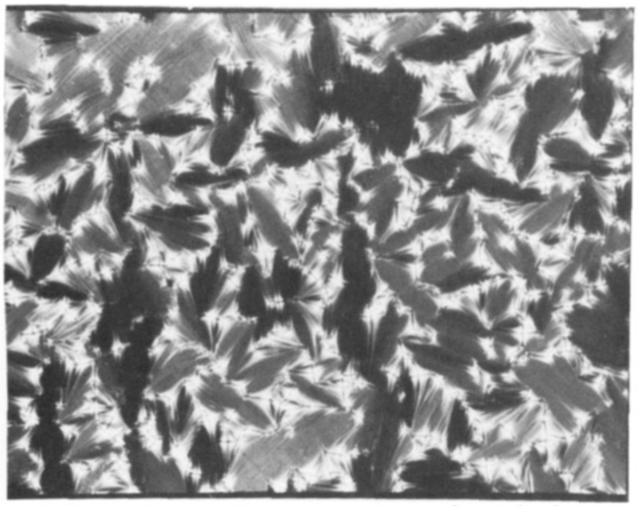

Figure 3. Complex **4c**, S_A polygonal texture. Crossed polarizers, 110 °C, ×150.

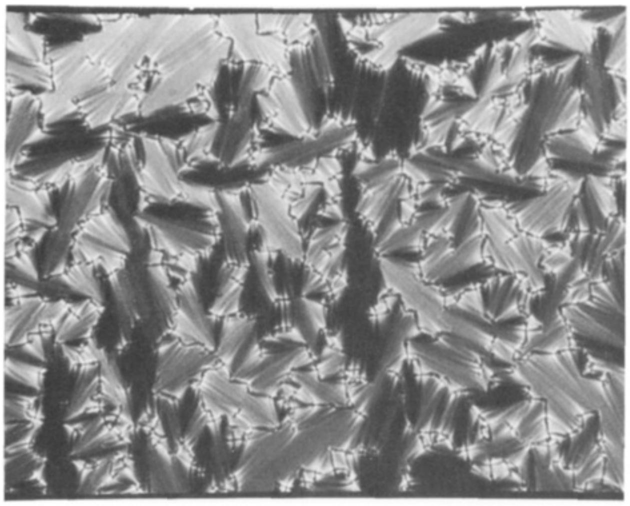

Figure 4. Complex **4c**, S_X polygonal texture. Crossed polarizers, 130 °C, ×150. Same section as Figure 3.

Regarding the metallomesogens, general trends are observed: the range of stability is wider and the temperatures at which the mesophases appear are higher (Table IV). Futhemore, **2a**, **2b**, and **3a**–**3c** give solid-to-solid transitions (K → K′) while for both **2a** and **4c**, the smectic A phase exhibits a thermal rearrangement. Thus, as an example, compound **4c**, upon heating or cooling, reveals a S_A polygonal texture at 105.1 °C (Figure 3), which at 128.1 °C rearranges to a different smectic phase with similar texture (S_X, Figure 4).

Remarkably, for all the HL3 derivatives, the smectic phases appear at increasing temperatures, in the order I < Br < Cl. In similar halo-bridged orthopalladated imine complexes (halide = Cl, Br), the S_A phases appear at higher temperatures for the chlorinated compounds.[10a] Therefore, on the bases of such an analogy, the behavior shown by the **3a**–**c** series seems to indicate an usual sequence. On the contrary, with reference to the clearing temperatures, the **3a**–**c** compounds (for which Cl > Br > I, Table IV) and the above-mentioned imine complexes show a reverse order (Br > Cl).[10a]

Finally, the good thermal stability generally displayed by such complexes should be noted.

Conclusion

The 5,4′-disubstituted-2-phenylpyrimidine ligands HL1–HL4 react in mild conditions with $[Pd(PhCN)_2Cl_2]$

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[19] Demus, D.; Richter, L. *Texture of Liquid Crystals*; Verlag Chemie: Weinheim, West Germany, 1978.

Table III. Fractional Atomic Coordinates (×10^4) with Esd's in Parentheses for the Non-Hydrogen Atoms of Complex 1d

atom	x/a	y/b	z/c
Pd(1)	3248 (1)	1001 (1)	10222 (1)
Pd(2)	1553 (1)	2742 (1)	9152 (1)
O(1)	3428 (5)	463 (4)	8897 (3)
O(2)	1520 (5)	545 (4)	10706 (3)
O(3)	157 (4)	1874 (4)	9904 (3)
O(4)	2075 (5)	1805 (4)	8101 (3)
O(5)	1808 (7)	1494 (6)	13891 (4)
O(6)	5096 (6)	4087 (5)	6530 (4)
N(1)	6019 (6)	2625 (5)	10388 (4)
N(2)	4877 (5)	1572 (4)	9882 (4)
N(3)	2084 (7)	4897 (5)	10684 (5)
N(4)	1213 (5)	3691 (4)	10154 (3)
C(1)	3249 (6)	1450 (5)	11418 (4)
C(2)	2439 (7)	1252 (6)	12260 (5)
C(3)	2540 (9)	1648 (6)	13038 (5)
C(4)	1122 (11)	712 (10)	14026 (6)
C(5)	3422 (10)	2280 (7)	13000 (6)
C(6)	4243 (8)	2460 (6)	12185 (6)
C(7)	4175 (6)	2043 (5)	11395 (5)
C(8)	5069 (6)	2112 (5)	10533 (5)
C(9)	6790 (7)	2587 (6)	9567 (6)
C(10)	6706 (7)	2027 (5)	8883 (5)
C(11)	5680 (6)	1540 (5)	9066 (5)
C(12)	7623 (8)	1909 (7)	7959 (6)
C(13)	8452 (8)	2678 (7)	7715 (6)
C(14)	9347 (9)	2524 (8)	6770 (6)
C(15)	10146 (8)	3319 (7)	6477 (6)
C(16)	11094 (10)	3134 (8)	5580 (6)
C(17)	11898 (11)	3935 (9)	5284 (7)
C(18)	2775 (6)	3604 (5)	8573 (5)
C(19)	3554 (7)	3544 (5)	7708 (5)
C(20)	4434 (7)	4187 (6)	7410 (5)
C(21)	5924 (9)	4771 (8)	6153 (7)
C(22)	4579 (7)	4854 (6)	7985 (6)
C(23)	3828 (8)	4916 (6)	8853 (6)
C(24)	2915 (7)	4304 (5)	9162 (5)
C(25)	2045 (7)	4328 (5)	10044 (5)
C(26)	1256 (9)	4800 (6)	11475 (6)
C(27)	408 (7)	4168 (5)	11670 (5)
C(28)	392 (7)	3622 (5)	10960 (5)
C(29)	-455 (8)	4073 (5)	12617 (5)
C(30)	-1238 (7)	3244 (6)	12737 (5)
C(31)	-2013 (8)	3159 (7)	13715 (5)
C(32)	-2792 (8)	2316 (7)	13869 (6)
C(33)	-3481 (11)	2147 (9)	14845 (7)
C(34)	-4197 (12)	1273 (12)	15015 (9)
C(35)	2907 (6)	896 (5)	8189 (5)
C(36)	3274 (9)	308 (6)	7342 (5)
C(37)	387 (7)	1076 (6)	10499 (5)
C(38)	-819 (8)	735 (7)	11018 (6)

Chart III. Representation of the Molecular Structure of Complexes 1-4

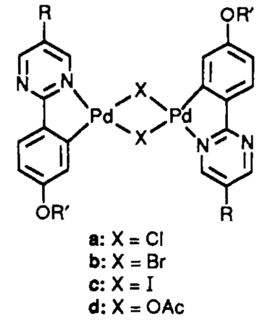
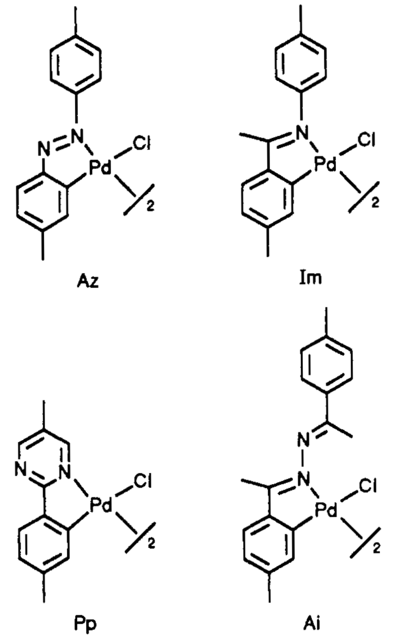


Chart IV. Sketch of the Molecular Structure of the Mesogenic Cyclopalladated Dimers Reported in Table V



or Pd(OAc)$_2$ to give the complexes **1a**–**4a** and **1d**–**4d**, respectively. Moreover, **1a**–**4a** by further treatment with NaBr or KI form compounds **1b**–**4b** and **1c**–**4c**.

The four **a**–**d** homologous series contain a dimetallic core (Chart III) in which each palladium(II) atom is in a square-planar geometry.

Table IV. Thermal and Thermodynamic Data for the Ligands HL1-HL4 and Complexes 1-4

compd	phases^a and transition temp, °C	ΔH, J g^{-1}
HL1	K → 53.5 (I)	
[PdCl(L1)]$_2$, **1a**	K → 215.0 (I)	
[PdBr(L1)]$_2$, **1b**	K → 202.0 (I)	
[PdI(L1)]$_2$, **1c**	K → 205.0 (I)	
[Pd(OAc)(L1)]$_2$, **1d**	K → 183.0 (I)	
HL2	K $\xrightarrow{1}$ 32.5 (N) $\xrightarrow{2}$ 37.5 (I)	1 = 114.64; 2 = 8.33
[PdCl(L2)]$_2$, **2a**	K $\xrightarrow{1}$ 100.0 (K′) $\xrightarrow{2}$ 128.9 (S_A) $\xrightarrow{3}$ 137.2 (S_X) $\xrightarrow{4}$ 168.3 (I)	1 = 1.01; 2 = 11.69; 3 = 25.10; 4 = 8.18
[PdBr(L2)]$_2$, **2b**	K $\xrightarrow{1}$ 115.8 (K′) $\xrightarrow{2}$ 129.8 (S_A) $\xrightarrow{3}$ 174.5 (I)	1 = 12.5; 2 = 14.8; 3 = 53.0
[PdI(L2)]$_2$, **2c**	K → 195.0 (I)	
[Pd(OAc)(L2)]$_2$, **2d**	K → 128.0 (I)	
HL3	K $\xrightarrow{1}$ 47.7 (N) $\xrightarrow{2}$ 59.0 (I)	1 = 112.33; 2 = 2.53
[PdCl(L3)]$_2$, **3a**	K $\xrightarrow{1}$ 100.0 (K′) $\xrightarrow{2}$ 177.2 (S_A) $\xrightarrow{3}$ 218.8 (I)	1 = 38.27; 2 = 9.73; 3 = 2.36
[PdBr(L3)]$_2$, **3b**	K $\xrightarrow{1}$ 112.0 (K′) $\xrightarrow{2}$ 171.3 (S_A) $\xrightarrow{3}$ 202.1 (I)	1 = 61.8; 2 = 10.8; 3 = 7.37
[PdI(L3)]$_2$, **3c**	K $\xrightarrow{1}$ 109.7 (K′) $\xrightarrow{2}$ 148.6 (S_A) $\xrightarrow{3}$ 192.9 (I)	1 = 30.8; 2 = 6.9; 3 = 5.77
[Pd(OAc)(L3)]$_2$, **3d**	K → 139.6 (I)	
HL4	K $\xrightarrow{1}$ 33.5 (N) $\xrightarrow{2}$ 72.0 (I)	1 = 100.41; 2 = 17.9
[PdCl(L4)]$_2$, **4a**	K → 207.0 (I)	
[PdBr(L4)]$_2$, **4b**	K $\xrightarrow{1}$ 105.9 (S_A) $\xrightarrow{2}$ 196.6 (I)	1 = 13.75; 2 = 0.27
[PdI(L4)]$_2$, **4c**	K $\xrightarrow{1}$ 105.1 (S_A) $\xrightarrow{2}$ 128.1 (S_X) $\xrightarrow{3}$ 202.5 (I)	1 = 30.11; 2 = 5.95; 3 = 6.85
[Pd(OAc)(L4)]$_2$, **4d**	K → 135.0 (I)	

^{a} K = crystal; N = nematic; S = smectic.

Table V. Summary of the Mesomorphic Behavior Displayed by Selected Cyclopalladated Dimers Containing the Pd(μ-Cl)$_2$Pd Core

	uncomplexed ligands				palladium complexes					
ligand[a]	phases[b]	T_M[c]	T_I[d]	$T_I - T_M$	phases[b]	T_M[c]	T_I[d]	$T_I - T_M$	R[e]	ref
Az(C_2H_5O, $C_4H_9CO_2$)	N	78.0	126.0	48.0	N	212.0	215.0	3.0	0.06	2a
Az(C_2H_5, $C_5H_{11}CO_2$)	N	73.0	127.0	54.0	N, S_A, S_B	210.0	225.0	15.0	0.27	2a
Az(C_2H_5O, $C_6H_{13}CO_2$)	N	59.0	112.0	53.0	N	190.0	205.0	15.0	0.28	2a
Az(C_2H_5O, $CH_2CH(CH_2)_8CO_2$)	N	64.0	107.0	43.0	N	165.0	185.0	20.0	0.46	2a
Az(CH_3O, CH_3)			108.0		N	229.0	254.0	25.0		2c
Az(C_2H_5O, CH_3)	N[f]	97.0	117.0	20.0	N	214.0	235.0	21.0	1.05	2c
Az($C_7H_{15}O$, CH_3)	N[f]	68.0	77.0	9.0	N	175.0	194.0	19.0	2.11	2c
Az($C_{12}H_{25}O$, CH_3)	N[f]	75.5	76.1	0.6	N	150.0	174.0	24.0		2c
Az($C_{12}H_{25}O$, C_2H_5)	N[f]	70.0	71.0	1.0	N	163.0	170.0	7.0	7.00	2c
Im($C_{10}H_{21}O$, $C_{10}H_{21}$)	S_F, S_A	53.3	89.1	35.8	S_C, S_A	112.4	237.6	125.2	3.49	10a
Im($C_{10}H_{21}O$, $C_{10}H_{21}O$)	S_C	102.3	110.9	8.6	S_C, S_A	132.7	242.8	110.1	13.76	10a
Im(CH_3O, C_4H_9)	N	20.0	47.0	27.0	S_A, N	218.0	251.0	33.0	1.22	1
Ai($C_{10}H_{21}O$, $C_{10}H_{21}O$)	S_C, N	123.2	135.5	12.3	S_C	102.0	226.0	124.0	10.08	24, 10d
Pp($C_9H_{19}O$, CH_3)	N	32.5	37.5	5.0	S_A	128.9	168.3	39.4	7.88	[g]
Pp($C_6H_{13}O$, $C_{11}H_{23}$)	N	47.7	59.0	11.3	S_A	177.2	218.8	41.6	3.68	[g]
Pp($C_9H_{19}O$, C_9H_{19})	N	35.5	72.0	36.5	S_A		207.0			[g]

[a] Az = azobenzene; Im = imine; Ai = azine; Pp = 2-phenylpyrimidine; para, para′ substituents in parentheses. [b] Texture of the mesophases. [c] T_M = lowest temperature (°C) at which the mesophases appear. [d] T_I = clearing point (°C). [e] R is (T_I = T_M) complex/(T_I − T_M)ligand. [f] Monotropic. [g] This paper.

In the solid state, when X = OAc, the two coordination planes form a dihedral angle of about 25° and a similar geometry, as confirmed by ^{1}H NMR evidences, is preserved in solution. Otherwise, for X = halide, the Pd_2X_2 core may be either planar[20] or bent. In the latter case the extimated value of the X⋯X hinged dihedral angle ranges approximately from 120 to 140°.[21] However, it should be pointed out that the Pd(μ-X)$_2$Pd bridge imposes to the phenylpyrimidine ligands a transoid geometry and, consequently, forces the R and R′ aliphatic chains to lie on opposite sides with respect to the Pd⋯Pd axis.

The thermal behavior can be summarized as follows:

1. The above-described palladation reaction, leading to bimetallic complexes, promotes the existence of mesophases (smectic or solid) more ordered than the nematic one.
2. The temperatures at which the mesophases appear are of some 70–115 °C higher than those displayed by the HL mesogens.
3. The palladium complexation broadens by a factor ranging between 2.5 and 8.0 (**2a**, **2b**) the temperature range in which the mesophases are stable.
4. The complexes clearing points are increased by about 135 °C.
5. None of the complexes **1**, i.e., those formed by the nonmesogenic ligand HL1, display mesomorphism. Therefore in the HL1 case, the palladium complexation, in spite of the more elongated resulting molecules,[2c,10,22] does not induce mesomorphism.
6. Although rigid roof-shaped palladium mesogens containing the acetate bridge have been recently synthesized,[10d] none of the **1d**–**4d** derivatives described in the present work exhibits mesomorphism.

The peculiar properties induced by the organic ligand could be discussed on the bases of the findings above reported in points 1–6. Liquid-crystalline cyclopalladated dimers have so far been obtained from mesogenic ligands that can be gathered in three different classes, namely, azobenzene (Az),[2a–c] imine (Im),[10a,b] and azine (Ai)[10c,d] compounds. However, for sake of comparison, only Pd(μ-Cl)$_2$Pd complexes will be considered, selecting among them those with similar para and para′ substituents (i.e., alkyl, alkoxy, or alkanoate chains).

The available data, within the limit imposed by either the different chain lengths or the clearing point temperatures, which in some cases actually are the decomposition temperatures, are collected in Table V. This evidence allow the ensuing considerations.

First, higher transition temperatures and the presence of additional mesophases are observed in both the Az (alkoxy, alkyl) and 2-phenylpyrimidine, Pp (alkoxy, alkyl), complexes. In a previous paper, dealing with a comparative study on uncomplexed Az (alkoxy, alkyl) and their palladium derivatives, we discussed such features, taking into account either the different molecular structures or the possible different molecular interactions due to the Pd(μ-Cl)$_2$Pd core.[23] Therefore, considering the close similarity of the Pp (alkoxy, alkyl) and Az (alkoxy, alkyl) molecular shapes, we suppose that the behavior shown by the 2-phenylpyrimidine compounds could be likely explained.

Moreover, the previously investigated azobenzene compounds were either *p*-alkoxy-*p*′-alkanoate[2a] or *p*-alkyl-*p*′-alkoxy[2c] substituted, and since the latter were tested as (II + III) mixtures (see Introduction), we were not able to recognize the actual task of the para,para′ groups. The Pp (alkoxy, alkyl), being selectively metalated on the phenyl ring (Chart III), give pure compounds so that they are helpful in solving the problem. In fact, for both the Az (alkoxy, alkyl) and the Pp (alkoxy, alkyl) complexes, the range of temperatures for which the mesophases are stable widens, while for the Az (alkoxy, alkanoate) it was

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found to be reduced (Table V). Hence, the mesomorphic behavior displayed by the Az (alkoxy, alkyl) series may be mainly attributed to the nature of the para,para′ groups.

Concluding, a further point concerning the role played by the ligand's aromatic molecular core can be elucidated by comparing the nature of the mesophases exhibited by the different palladium complexes with reference to the uncomplexed ligands. In particular, it may be pointed out that the nematic (enantiotropic or monotropic) azobenzene species, and the smectic imine give nematic or smectic complexes, respectively. The nematic imine Im (CH_3O, C_4H_9) gives a smectic and nematic complex while the nematic 2-phenylpyrimidine species gives smectic complexes only (Table V). With respect to the previously discussed trend, which accounts for the presence of more ordered mesophases in the palladium derivatives rather than in the ligands, we can then conclude that such an effect is enhanced for the 2-phenylpyrimidine complexes. Nevertheless, this behavior can be explained by looking at the structural features of the Az, Im, and Pp cyclopalladated dimers (Chart IV).

Thus, evident is the similarity between the Az and Im structures, wherein the nonmetalated ring is free to rotate, and their difference with the comparatively more rigid Pp geometry imposed by the heteroaromatic nitrogen atom involved in the cyclopalladated ring. Recently, Espinet and Serrano, reporting on palladated azine dimers,[10d] observed that a greater mobility to the non-ortho-palladated moiety may cause either the lowering of the transition temperatures (Table V) or the occurrence of the mesophases. Hence, in the present case, the mesomorphic behavior displayed by the 2-phenylpyrimidine complexes might be ascribed to their extremely rigid molecular structure.

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Registry No. **1a**, 130903-21-8; **1b**, 130903-25-2; **1c**, 130903-29-6; **1d**, 130903-33-2; **2a**, 130903-22-9; **2b**, 130903-26-3; **2c**, 130903-30-9; **2d**, 130903-34-3; **3a**, 130903-23-0; **3b**, 130903-27-4; **3c**, 130903-31-0; **3d**, 130903-35-4; **4a**, 130903-24-1; **4b**, 130903-28-5; **4c**, 130903-32-1; **4d**, 130903-36-5; HL1, 99895-83-7; HL2, 99895-84-8; HL3, 57202-31-0; HL4, 99895-85-9.

Supplementary Material Available: Table SI listing crystallographic data and Tables SII–SIV listing complete bond distances, bond angles, positional parameters of H atoms, and thermal parameters (14 pages). Table SV of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

Growth and Characterization of Thin Films of Thallium(III) Oxide by Organometallic Chemical Vapor Deposition

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Films containing thallium(III) oxide were grown by organometallic chemical vapor deposition in an oxygen-rich atmosphere on MgO, Al_2O_3, and Si substrates. Three organothallium precursors were used: thallium acetylacetonate, dimethylthallium acetylacetonate, and cyclopentadienylthallium. Films were characterized by using X-ray diffraction techniques and X-ray photoelectron, Auger electron, and infrared spectroscopies. The results indicate the presence of Tl_2O_3 as the major component with possible smaller amounts of Tl_2CO_3. Deposition on Si resulted in the formation of a silicate from interaction between the film and the substrate.

Introduction

Thallium(III) oxide has electrical and optical properties that make it potentially useful in solar cells and transparent electrical contacts.[1] Interest in this material has grown further with the discovery of the high-temperature superconducting material Tl–Ba–Ca–Cu oxide.[2] Although thin films of metal oxides have been deposited by a variety of techniques including evaporation, sputtering, hydrolysis, and organometallic chemical vapor deposition (OMCVD),[3] studies of Tl_2O_3 have been limited by the unique set of problems involving the toxicity, volatility, and stability of thallium compounds. To our knowledge, films of Tl_2O_3 have not been grown by OMCVD, although Tl–Ba–Ca–Cu oxide has been deposited by this technique.[4,5] In this study, we report the growth and characterization of Tl_2O_3 films from thallium acetylacetonate, dimethylthallium acetylacetonate, and cyclopentadienylthallium on MgO, Al_2O_3, and Si substrates.

Experimental Section

Organometallic Precursors. Thallium acetylacetonate (Tl(acac)) was purchased from Strem Chemicals, Inc., and sublimed at 90–120 °C and 10^{-5} Torr before use. Dimethylthallium acetylacetonate ($Me_2Tl(acac)$) was synthesized according to published procedures from the reaction of trimethylthallium and acetylacetone[6] and characterized by IR, ^1H NMR, and elemental

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