Transition Metals Complexed to Ordered Mesophases.[1] Synthesis, Characterization, and Mesomorphic Properties of New Potentially Ferroelectric Liquid Crystals: Chiral *p,p'*-Dialkoxyazobenzenes and Their Cyclopalladated Dinuclear Complexes

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To prepare chiral metallo-mesogens with ferroelectric properties, new azobenzene compounds, $HL_N(n)$, bearing a chiral substituent have been synthesized. These ligands consist of two aliphatic chains of variable length, one of which contains a stereogenic center located in the para and para' positions of an azobenzene core. The chiral groups (R*O) are as follows: $N = 1$, (*R*)-(−)-menthol; $N = 2$, (*S*)-(−)-β-citronellol, and $N = 3$, (*R*)-(−)-2-octanol; the aliphatic chains are linear *n*-alkoxy groups $C_nH_{2n+1}O$ ($n = 7, 10, 12, 14$). Only the $HL_2(n)$ species display liquid-crystalline properties giving cholesteric or smectic A mesophases. The $HL_N(n)$ ligands react with $[Pd(PhCN)_2Cl_2]$, to give the corresponding chloro-bridged dinuclear cyclopalladated products $\{Pd[L_N(n)](\mu\text{-}Cl)\}_2$ as 1:1 mixtures of isomers arising from the nonselective attack of the palladium on the benzene ring bearing the chiral alkoxy group or on the benzene with the aliphatic alkoxy chain. The $\{Pd[L_2(n)](\mu\text{-}Cl)\}_2$ compounds and the $\{Pd[L_3(n)](\mu\text{-}Cl)\}_2$ ($n = 10, 12, 14$) exhibit smectic mesophases (Sc* in $\{Pd[L_2(7)](\mu\text{-}Cl)\}_2$, $\{Pd[L_2(10)](\mu\text{-}Cl)\}_2$, $\{Pd[L_3(10)](\mu\text{-}Cl)\}_2$, and $\{Pd[L_3(14)](\mu\text{-}Cl)\}_2$, S_A in $\{Pd[L_2(12)](\mu\text{-}Cl)\}_2$, $\{Pd[L_2(14)](\mu\text{-}Cl)\}_2$, $\{Pd[L_3(12)]\mu\text{-}Cl)\}_2$). The $Pd[L_N(n)](\mu\text{-}Cl)\}_2$ compounds have been converted into the corresponding iodo analogues $\{Pd[L_N(n)](\mu\text{-}I)\}_2$. The chloro complexes display a richer mesomorphism than the respective iodo compounds.

Introduction

The metallo-mesogens are new materials designed to improve the physical properties which feature the conventional organic liquid crystals.[2] The expectations settled on these new materials have been confirmed, and recent investigations reporting on birefringence[3,4] and polarisability anisotropy[5] seem to suggest that their use for practical applications can be forecast. Presently, the chiral liquid-crystalline species, namely, those which display cholesteric or chiral smectic C phases, are widely utilized in electrooptical devices because of the optical or ferroelectric properties and of the switching time they show.[6-10] We are currently concerned with studies on metallo-mesogens,[4,11] and therefore, to investigate on possible better performances of these materials, we have extended our investigations to chiral, metal-containing mesogenic species.

Several thermotropic palladated compounds are cyclometalated complexes derived from substituted azoben-

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(2) Maitlis, P. M.; Giroud-Godquin, A. M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 375.

(3) Bruce, D. W.; Dunmur, D. A.; Maitlis, P. M.; Manterfield, M. M.; Orr, R. *J. Mater. Chem.* **1991**, *1*, 255.

(4) (a) Cipparrone, G.; Versace, C.; Duca, D.; Pucci, D.; Ghedini, M.; Umeton, C. *Mol. Cryst. Liq. Cryst.* **1992**, *212*, 217. (b) Versace, C.; Cipparrone; G.; Lucchetta, D.; Pucci, D.; Ghedini, M. *Mol. Cryst. Liq. Cryst.* **1992**, *212*, 313.

(5) Bertram, C.; Bruce, D. W.; Dunmur, D. A.; Hunt, S. E.; Maitlis, P. M.; McCann, M., *J. Chem. Soc., Chem. Commun.* **1991**, 69.

(6) Meyer, R. B.; Liebert, L.; Strzeleski, L.; Keller, P. *J. Phys. Lett.* **1975**, *36*, L69.

(7) (a) Clark, N. A.; Lagerwall, S. T. *Appl. Phys. Lett.* **1980**, *36*, 899. (b) Clark, N. A.; Handschy, M. A.; Lagerwall, S. T. *Mol. Cryst. Liq. Cryst.* **1983**, *94*, 213.

(8) (a) Yoshino, K.; Ozaki, M. *Ferroelectrics* **1984**, *59*, 145. (b) Yoshino, K.; Taniguchi, H.; Ozaki, M. *Ferroelectrics* **1989**, *91*, 267.

(9) Kelly, S. M.; Buchecker, R. *Helv. Chim. Acta* **1988**, *71*, 451 and references therein.

(10) Walba, D. M.; Slater, S. C.; Thurmes, W. N.; Clark, N. A., Handschy, M. A.; Supon, F. *J. Am. Chem. Soc.* **1986**, *108*, 5210.

(11) (a) Ghedini, M.; Pucci, D.; De Munno, G.; Viterbo, D.; Neve, F.; Armentano, S. *Chem. Mater.* **1991**, *3*, 65. (b) Ghedini, M.; Morrone, S.; Gatteschi, D.; Zanchini, C. *Chem. Mater.* **1991**, *3*, 752.

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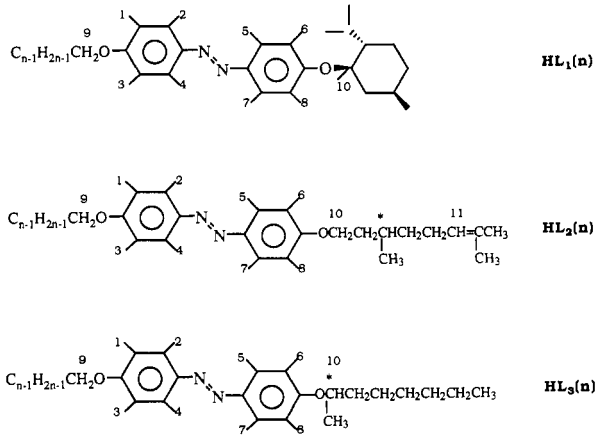
Chart I



zenes,[12,13] azoxybenzenes,[14] aromatic imines,[15] azines,[16] or phenylpyrimidines.[11,17] These ligands bear aliphatic chains in para and para' positions and most of the complexes exhibit a dinuclear halo- or carboxylate-bridged molecular structure. Our experience in metallo-mesogens have prompted us to investigate optically active palladium mesogens incorporating different chiral groups in an azobenzene structure. Worthy of note, the chiral metallo-mesogens reported up to now are chiral-at-metal iron complexes[18] and dimeric cyclopalladated imine wherein the stereogenic center is located on a carboxylate ligand bridging two palladium atoms.[19]

The azobenzene ligands considered in this investigation (Chart I) contain the chiral nonracemic group (*R*)-(−)-2-octanol (**2**) and (*S*)-(−)-β-citronellol ((*S*)-3,7-dimethyl-6-octen-1-ol) (**3**). We have focused our attention on these two chiral groups because they have proved to be efficient in giving mesogenic structures.[20,21] In addition, to test the synthetic procedures, the less expensive (*R*)-(−)-menthol ((1-*R*,2-*S*,5-*R*)-2-isopropyl-5-methylcyclohexanol) (**1**) has also been considered. The second substituent which completes the azobenzene structure consists of an *n*-alkoxy chain with 7, 10, 12, or 14 carbon atoms. Thereafter, for the sake of conciseness, these ligands will be indicated by the general formulae $HL_N(n)$, where *N* defines the chiral group and *n* the number of carbon atoms in the *n*-alkoxy chain.

Hereafter we describe the preparation and the mesomorphic behavior of a series of azobenzene ligands $HL_N(n)$ and that of the corresponding palladated complexes $\{Pd[L_N(n)](\mu\text{-}X)\}_2$ where X can be chloro or iodo bridging halogens.

Experimental Section

General Procedures. All chemicals and the commercially available (−)-menthol ((1-*R*,2-*S*,5-*R*)-2-isopropyl-5-methylcyclohexanol) (Fluka, A.G., >99% optical purity), (*S*)-(−)-β-citronellol ((*S*)-3,7-dimethyl-6-octen-1-ol) (Fluka, A.G., >99% optical purity) and (*R*)-(−)-2-octanol (Fluka, A. G., 98% optical purity) were used without further purification. $[Pd(PhCN)_2Cl_2]$,[22] *p*-nitroalkoxybenzenes (II),[23] *p*-aminoalkoxybenzenes (III),[24,25] and azo compounds (IV)[26,27] were prepared according to the literature methods.

^1H NMR spectra were recorded on a Bruker WM-300 or AW 80 spectrometers in $CDCl_3$ solutions with Me_4Si as internal standard. Infrared spectra were runned on a Perkin-Elmer 1330 spectrophotometer. Elemental analyses were performed by the Microanalysis Laboratory of the Dipartimento di Chimica, Università della Calabria, Italy.

The optical observations were made with a Zeiss Axioskop polarizing microscope equipped for photography and with a Linkam CO 600 heating stage. Transition temperatures and enthalpies were measured on a Perkin-Elmer DSC-7 differential scanning calorimeter with a heating and cooling rate of 10 °C/min. The apparatus was calibrated with indium (156.6 °C, 28.5 J/g) and tin (232.1 °C, 60.5 J/g).

The X-ray powder diffraction patterns were obtained by an INEL CPS120 powder diffractometer equipped with a position sensitive detector covering a scattering angle of 120°, with an angular resolution of 0.018°. Monochromatized Cu Kα radiation (λ = 1.54 Å) impinged on the ~1-mm-thick sample, the temperature of which was controlled to ±0.1 °C by a hot stage containing electrical resistors.

Synthesis of the Ligands. *Preparation of p-Nitroalkoxybenzenes, II.* In a typical procedure, to 64 mmol of the chiral alcohol I, dissolved in 100 mL of dimethyl sulfoxide, 64 mmol of *p*-nitrochlorobenzene was added. The resulting solution was heated to 40 °C with stirring for 10 min; 0.70 mmol of sodium hydride (55% dispersion in oil) was added and the suspension heated to 70 °C for 1.5 h. The black solution was quenched with water, acidified with 2 N hydrochloric acid, and extracted with diethyl ether (2 × 50 mL). The combined organic phases were dried over anhydrous sodium sulfate and evaporated in vacuo to give II as a black oil.

p-Nitro-2-isopropyl(5-methylcyclohexyloxy)benzene, IIa: recrystallization from methanol gave IIa as pale yellow crystals in 80% yield. Mp 66 °C; ^1H NMR (80 MHz, $CDCl_3$) δ 4.20 (m, 1H, H^{10}), 6.93 (d, 2H, $H^{6,8}$), 8.18 (d, 2H, $H^{5,7}$). Anal. Calcd for $C_{16}H_{23}NO_3$: C, 69.29; H, 8.36; N, 5.05. Found: C, 69.24; H, 8.95; N, 5.09.

p-Nitro(3,7-dimethyl-6-octen-1-oxy)benzene, IIb: the compound was purified by column chromatography (SiO_2; diethyl ether/hexane, 1/5, v/v) to give a yellow oil (88% yield). ^1H NMR (80 MHz, $CDCl_3$) δ 4.09 (t, 2H, H^{10}), 5.10 (m, 1H, H^{11}), 6.94 (d, 2H, $H^{6,8}$), 8.19 (d, 2H, $H^{5,7}$).

p-Nitro(2-octyloxy)benzene, IIc: the crude compound was purified by column chromatography (SiO_2, benzene) to give a yellow oil (90%) yield). ^1H NMR (80 MHz, $CDCl_3$) δ 4.47 (m, 1H, H^{10}), 6.91 (d, 2H, $H^{6,8}$), 8.18 (d, 2H, $H^{5,7}$).

Preparation of p-Aminoalkoxybenzenes, III. *p*-Amino(2-isopropyl-5-methylcyclohexyloxy)benzene, IIIa: A stainless steel autoclave equipped with magnetic stirring was loaded with 5.00 mmol of IIa, 0.25 g of 10% palladium-on-carbon catalyst, and 40 mL of methanol. The autoclave was pressurized to 50 atm and stirred at room temperature for 18 h: the autoclave was vented,

(12) (a) Ghedini, M.; Armentano, S.; Neve, F.; Licoccia, S. *J. Chem. Soc., Dalton Trans.* **1988**, 1565. (b) Versace, C. C.; Bartolino, R.; Ghedini, M.; Neve, F.; Armentano, S.; Petrov, M.; Kirov, N. *Liq. Cryst.* **1990**, *8*, 481. (c) Formoso, V.; Pagnotta, M. C.; Mariani, P.; Ghedini, M.; Neve, F.; Bartolino, R.; More, M.; Pépy, G. *Liq. Cryst.* **1992**, *11*, 639.

(13) Hoshino, N.; Hasegawa, H.; Matsunaga, Y. *Liq. Cryst.* **1991**, *9*, 267.

(14) Ghedini, M.; Morrone, S.; De Munno, G.; Crispini, A. *J. Organomet. Chem.* **1991**, *415*, 281.

(15) (a) Marcos, M.; Ros, M. B.; Serrano, J. L. *Liq. Cryst.* **1988**, *3*, 1129. (b) Ciriano, M. A.; Espinet, P.; Lalinde, E.; Ros, M. B.; Serrano, J. L. *J. Mol. Struct.* **1989**, *196*, 327. (c) Baena, M. J.; Espinet, P.; Ros, M. B.; Serrano, J. L. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 711. (d) Ros, M. B.; Ruiz, N.; Serrano, J. L.; Espinet, P. *Liq. Cryst.* **1991**, *9*, 77.

(16) Espinet, P.; Lalinde, E.; Marcos, M.; Perez, J.; Serrano, J. L. *Organometallics* **1990**, *9*, 555.

(17) (a) Ghedini, M.; Pucci, D. *J. Organomet. Chem.* **1990**, *395*, 105.

(18) Ziminski, L.; Malthete, J. *J. Chem. Soc., Chem. Commun.* **1990**, 1495.

(19) Espinet, P.; Extebarria, J.; Marcos, M.; Perez, J.; Remòn, A.; Serrano, J. L. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1065.

(20) (a) Gray, G. W.; Hird, M.; Toyne, K. J. *Mol. Cryst. Liq. Cryst.* **1991**, *204*, 91. (b) Anderson, G.; Flatischler, K.; Komitov, L.; Lagerwall, S. T., Skarp, K.; Stebler, B. *Ferroelectrics* **1991**, *113*, 361.

(21) (a) Sugita, S.; Takeno, H.; Teraji, T., *Mol. Cryst. Liq. Cryst.* **1991**, *206*, 139. (b) Chin, E.; Goodby, J. W.; Patel, J. S.; Geary, J. M.; Leslie, T. M. *Mol. Cryst. Liq. Cryst.* **1987**, *146*, 325.

(22) Karash, M. S.; Seyber, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 882.

(23) Sohda, T.; Mizuno, K.; Imamiya, E.; Sugiyama, Y.; Fujita, T.; Kawamatsu, Y. *Chem. Pharm. Bull.* **1982**, *30*, 3580.

(24) Secrist, A. J.; Logue, M. W. *J. Org. Chem.* **1972**, *37*, 335.

(25) Bellamy, F. D.; Ou, K. *Tetrahedron Lett.* **1984**, *25*, 839.

(26) Conant, J. B.; Lutz, R. E.; Corson, B. B. *Org. Synth.* **1941**, *Coll. Vol. I*, 49.

(27) Claisen, L.; Eisleb, O. *Justus Liebigs Ann. Chem.* **1913**, *401*, 29.

and the catalyst filtered off and washed with 10 mL of methanol; the combined filtrates were evaporated to give IIIa as a black oil. ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.83 (m, 1H, H^{10}), 6.70 (m, 4H, $H^{5,7}$ and $H^{6,8}$). Yield 89%.

p-Amino(3,7-dimethyl-6-octen-1-oxy)benzene, IIIb: IIb (5.00 g, 18.70 mmol) was dissolved in ethyl acetate (40 mL) under nitrogen, and 21.00 g (93.40 mmol) of $SnCl_2{\cdot}2H_2O$ suspended in 20 mL of ethyl acetate was added to the solution. The reaction mixture was stirred for 17 h; the mixture was neutralized with NaOH 2 N and extracted with methylene dichloride. The combined organic extracts were dried over sodium sulfate, filtered, and evaporated to dryness. The residue was purified by column chromatography (SiO_2, diethyl ether/hexane, 80/20, v/v). IIIb was isolated as a yellow oil. ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.96 (t, 2H, H^{10}), 5.13 (m, 1H, H^{11}), 6.83 (m, 4H, $H^{5,7}$ and $H^{6,8}$). Yield 50%.

p-Amino(2-octyloxy)benzene, IIIc: Compound IIIc was prepared as described for IIIa. ^{1}H NMR (80 MHz, $CDCl_3$) δ 4.20 (m, 1H, H^{10}), 6.79 (m, 4H, $H^{5,7}$ and $H^{6,8}$). Yield 91%.

Preparation of Azo Compounds IV. In a typical procedure, 7.48 mmol of IIIa were dissolved under argon in 15 mL of water and 1.93 mL of HCl (36%). The solution was cooled to 0 °C, and 8.22 mmol of $NaNO_2$, dissolved in a minimum amount of water, was added, keeping the temperature of the solution lower than 5 °C. Phenol (7.48 mmol) dissolved in 8.6 mL of 2 N NaOH was added dropwise to the solution of the diazonium salt. When the addition was complete (0.5 h), the reaction mixture was allowed to warm to room temperature and extracted with methylene dichloride; the organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product IVa was purified by column chromatography (SiO_2, hexane/diethyl ether, 60/40, v/v). Colors, melting points, ^{1}H NMR, elemental analysis, and yields for IVa–c are as follows:

p-Hydroxy-*p'*-(2-isopropyl-5-methylcyclohexyloxy)azobenzene, IVa: orange solid, mp 50 °C. ^{1}H NMR (80 MHz, $CDCl_3$) δ 4.07 (m, 1H, H^{10}), 6.90 (d, 4H, $H^{1,3}$ and $H^{6,8}$), 7.81 (d, 4H, $H^{2,4}$ and $H^{5,7}$). Anal. Calcd for $C_{22}H_{28}N_2O_2$: C, 74.97; H, 8.01; N, 7.95. Found: C, 74.62; H, 8.13; N, 7.43. Yield 40%.

p-Hydroxy-*p'*-(3,7-dimethyl-6-octen-1-oxy)azobenzene, IVb: the crude product was recrystallized from hexane. Orange solid, mp 55 °C. ^{1}H NMR (80 MHz, $CDCl_3$) δ 4.05 (t, 2H, H^{10}), 5.11 (m, 1H, H^{11}), 6.94 (d, 4H, $H^{1,3}$ and $H^{6,8}$), 7.85 (d, 4H, $H^{2,4}$ and $H^{5,7}$). Anal. Calcd for $C_{22}H_{28}N_2O_2$: C, 74.97; H, 8.01; N, 7.95. Found: C, 73.67; H, 8.17; N, 8.08. Yield 70%.

p-Hydroxy-*p'*-(2-octyloxy)azobenzene, IVc: red oil. ^{1}H NMR (80 MHz, $CDCl_3$) δ 4.45 (m, 1H, H^{10}), 6.98 (d, 4H, $H^{1,3}$ and $H^{6,8}$), 7.85 (d, 4H, $H^{2,4}$ and $H^{5,7}$). Yield 70%.

Preparation of Azo Compounds [$HL_N(n)$]. In a typical procedure, 1.00 mmol of IVa, 1.60 mmol of butyl bromide, and 4 mmol of anhydrous potassium carbonate were suspended in cyclohexanone (4 mL) and refluxed under nitrogen for 3 h. The mixture was allowed to cool and filtered to remove the solids. The filtrate was evaporated under reduced pressure, and the residue was recrystallized from ethanol. Colors, melting points, ^{1}H NMR, elemental analysis and yields for [$HL_N(n)$] compounds are as follows:

p-Butoxy-*p'*-(2-isopropyl-5-methylcyclohexyloxy)azobenzene, [$HL_1(4)$]: orange solid, mp 96 °C. ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.96 (m, 3H, $H^{9,10}$), 6.93 (d, 4H, $H^{1,3}$ and $H^{6,8}$), 7.84 (d, 4H, $H^{2,4}$ and $H^{5,7}$). Anal. Calcd for $C_{26}H_{36}N_2O_2$: C, 76.43; H, 8.88; N, 6.86. Found: C, 76.81; H, 9.21; N, 6.60. Yield 90%.

p-Heptyloxy-*p'*-(2-isopropyl-5-methylcyclohexyloxy)azobenzene, [$HL_1(7)$]: orange solid, mp 75 °C. ^{1}H NMR (80 MHz, $CDCl_3$) δ 4.00 (m, 3H, $H^{9,10}$), 6.93 (d, 4H, $H^{1,3}$ and $H^{6,8}$), 7.84 (d, 4H, $H^{2,4}$ and $H^{5,7}$). Anal. Calcd for $C_{29}H_{42}N_2O_2$: C, 77.29; H, 9.39; N, 6.21. Found: C, 77.35; H, 9.61; N, 6.00. Yield 90%.

p-Dodecyloxy-*p'*-(2-isopropyl-5-methylcyclohexyloxy)azobenzene, [$HL_1(12)$]: orange solid, mp 56 °C. ^{1}H NMR (80 MHz, $CDCl_3$) δ 4.03 (m, 3H, $H^{9,10}$), 6.98 (d, 4H, $H^{1,3}$ and $H^{6,8}$), 7.85 (d, 4H, $H^{2,4}$ and $H^{5,7}$). Anal. Calcd for $C_{34}H_{52}N_2O_2$: C, 78.41; H, 10.06; N, 5.38. Found: C, 78.12; H, 10.03; N, 4.88. Yield 80%.

p-Heptyloxy-*p'*-(3,7-dimethyl-6-octenyl-1-oxy)azobenzene, [$HL_2(7)$]: yellow solid, thermotropic behavior in Table I. ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.95 (m, 4H, $H^{9,10}$), 5.09 (m, 1H, H^{11}), 6.91 (d, 4H, $H^{1,3}$ and $H^{6,8}$), 7.85 (d, 4H, $H^{2,4}$ and $H^{5,7}$). Anal. Calcd for $C_{29}H_{42}N_2O_2$: C, 77.29; H, 9.39; N, 6.21. Found: C, 76.63; H, 9.27; N, 6.20. Yield 80%.

p-Decyloxy-*p'*-(3,7-dimethyl-6-octenyl-1-oxy)azobenzene, [$HL_2(10)$]: yellow-orange solid, thermotropic behavior in Table I. ^{1}H NMR (80 MHz, $CDCl_3$) δ 4.00 (m, 4H, $H^{9,10}$), 5.10 (m, 1H, H^{11}), 6.93 (d, 4H, $H^{1,3}$ and $H^{6,8}$), 7.84 (d, 4H, $H^{2,4}$ and $H^{5,7}$). Anal. Calcd for $C_{32}H_{48}N_2O_2$: C, 78.00; H, 9.82; N, 5.68. Found: C, 78.18; H, 9.91; N, 5.82. Yield 80%.

p-Dodecyloxy-*p'*-(3,7-dimethyl-6-octenyl-1-oxy)azobenzene, [$HL_2(12)$]: yellow solid, thermotropic behavior in Table I. ^{1}H NMR (80 MHz, $CDCl_3$) δ 4.00 (m, 4H, $H^{9,10}$), 5.10 (m, 1H, H^{11}), 6.93 (d, 4H, $H^{1,3}$ and $H^{6,8}$), 7.84 (d, 4H, $H^{2,4}$ and $H^{5,7}$). Anal. Calcd for $C_{34}H_{52}N_2O_2$: C, 78.41; H, 10.06; N, 5.38. Found: C, 78.70; H, 10.25; N, 5.25. Yield 90%.

p-Tetradecyloxy-*p'*-(3,7-dimethyl-6-octenyl-1-oxy)azobenzene, [$HL_2(14)$]: yellow solid, thermotropic behavior in Table I. ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.99 (m, 4H, $H^{9,10}$), 5.11 (m, 1H, H^{11}), 6.93 (d, 4H, $H^{1,3}$ and $H^{6,8}$), 7.82 (d, 4H, $H^{2,4}$ and $H^{5,7}$). Anal. Calcd for $C_{36}H_{56}N_2O_2$: C, 78.78; H, 10.28; N, 5.10. Found: C, 78.35; H, 10.26; N, 5.04. Yield 76%.

p-Butoxy-*p'*-(2-octyloxy)azobenzene, [$HL_3(4)$]: yellow-orange solid, mp 57 °C. ^{1}H NMR (80 MHz, $CDCl_3$) δ 4.00 (t, 2H, H^9), 4.42 (m, 1H, H^{10}), 6.95 (d, 4H, $H^{1,3}$ and $H^{6,8}$), 7.85 (d, 4H, $H^{2,4}$ and $H^{5,7}$). Anal. Calcd for $C_{24}H_{34}N_2O_2$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.51; H, 8.91; N, 7.05. Yield 80%.

p-Heptyloxy-*p'*-(2-octyloxy)azobenzene, [$HL_3(7)$]: yellow solid, mp 35 °C. ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.98 (t, 2H, H^9), 4.42 (m, 1 H, H^{10}), 6.97 (d, 4H, $H^{1,3}$ and $H^{6,8}$), 7.88 (d, 4H, $H^{2,4}$ and $H^{5,7}$). Anal. Calcd for $C_{27}H_{40}N_2O_2$: C, 76.37; H, 9.49; N, 6.60. Found: C, 76.60; H, 9.30; N, 6.00. Yield 90%.

p-Decyloxy-*p'*-2-(octyloxy)azobenzene, [$HL_3(10)$]: yellow solid, mp 59 °C. ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.98 (t, 2H, H^9), 4.40 (m, 1H, H^{10}), 6.93 (d, 4H, $H^{1,3}$ and $H^{6,8}$), 7.85 (d, 4H, $H^{2,4}$ and $H^{5,7}$). Anal. Calcd for $C_{30}H_{46}N_2O_2$: C, 77.21; H, 9.93; N, 6.00. Found: C, 76.85; H, 10.02; N, 5.83. Yield 90%.

p-Dodecyloxy-*p'*-2-(octyloxy)azobenzene, [$HL_3(12)$]: yellow solid, mp 45 °C. ^{1}H NMR (80 MHz, $CDCl_3$) δ 4.02 (t, 2H, H^9), 4.44 (m, 1H, H^{10}), 6.98 (d, 4H, $H^{1,3}$ and $H^{6,8}$), 7.86 (d, 4H, $H^{2,4}$ and $H^{5,7}$). Anal. Calcd for $C_{32}H_{50}N_2O_2$: C, 77.68; H, 10.19; N, 5.66. Found: C, 77.97; H, 10.40; N, 5.84. Yield 82%.

p-Tetradecyloxy-*p'*-(2-octyloxy)azobenzene, [$HL_3(14)$]: yellow solid, mp 47 °C. ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.99 (t, 2H, H^9), 4.42 (m, 1H, H^{10}), 6.93 (d, 4H, $H^{1,3}$ and $H^{6,8}$), 7.82 (d, 4H, $H^{2,4}$ and $H^{5,7}$). Anal. Calcd for $C_{34}H_{54}N_2O_2$: C, 78.11; H, 10.41; N, 5.36. Found: C, 78.31; H, 10.47; N, 5.41. Yield 77%.

Synthesis of the {Pd[$L_N(n)$](μ-Cl)}$_2$ Complexes. *Representative Procedure for Cyclopalladation of the [$HL_1(n)$] Ligands.* To a suspension of 0.71 mmol of [$HL_1(4)$] in methanol (30 mL), 0.71 mmol of [$Pd(PhCN)_2Cl_2$] dissolved in benzene (30 mL) was added. The mixture was stirred at room temperature (4 days); a brown insoluble byproduct was filtered off. The filtrate was evaporated under reduced pressure, leaving a brown solid which was crystallized from diethyl ether. Colors, melting points, ^{1}H NMR, analytical data, and yields for the {Pd[$L_1(N)$](μ-Cl)}$_2$ complexes are as follows:

{Pd[$L_1(4)$](μ-Cl)}$_2$: brown solid, mp 160 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.04 (m, 3H, $H^{9,10}$), 6.69 (dd, 1H, H^1 or H^6), 6.84 (br s, 1H, H^3 or H^8), 6.92 (d, 2H, $H^{6,8}$ or $H^{1,3}$), 7.72 (d, 1H, H^2 or H^5), 7.76 (d, 2H, $H^{5,7}$ or $H^{2,4}$). Anal. Calcd for $C_{52}H_{70}Cl_2N_4O_4Pd_2$: C, 58.63; H, 6.42; N, 5.09. Found: C, 55.90; H, 6.28; N, 4.83. Yield 77%.

{Pd[$L_1(7)$](μ-Cl)}$_2$: brown solid, mp 130 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.03 (m, 4H, $H^{9,10}$), 6.69 (dd, 1H, H^1 or H^6), 6.85 (br s, 1H, H^3 or H^8), 6.91 (d, 2H, $H^{6,8}$ or $H^{1,3}$), 7.71 (d, 1H, H^2 or H^5), 7.76 (d, 2H, $H^{5,7}$ or $H^{2,4}$). Anal. Calcd for $C_{58}H_{82}Cl_2N_4O_4Pd_2$: C, 58.89; H, 6.99; N, 4.73. Found: C, 58.69; H, 6.98; N, 4.38. Yield 50%.

{Pd[$L_1(12)$](μ-Cl)}$_2$: brown solid, mp 115 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.05 (t, 4H, $H^{9,10}$), 6.71 (dd, 1H, H^1 or H^6), 6.85 (br s, 1H, H^3 or H^8), 6.97 (d, 2H, $H^{6,8}$ or $H^{1,3}$), 7.69 (d, 1H, H^2 or H^5), 7.80 (d, 2H, $H^{5,7}$ or $H^{2,4}$). Anal. Calcd for $C_{68}H_{102}Cl_2N_4O_4Pd_2$: C, 61.72; H, 7.77; N, 4.23. Found: C, 59.25; H, 7.05; N, 4.34. Yield 84%.

Representative Procedure for Cyclopalladation of the $HL_2(n)$ or $HL_3(n)$ Ligands. To a suspension of 0.83 mmol of $HL_2(7)$ in ethanol (30 mL), 0.83 mmol of solid [$Pd(PhCN)_2Cl_2$] was added; the mixture was stirred at room temperature (3 days), and the brown solid formed was filtered and crystallized from chloroform/

ethanol (20/80, v/v). Colors, melting points, ^{1}H NMR, analytical data, and yields for the $\{Pd[L_N(n)](\mu\text{-}Cl)\}_2$ complexes are as follows:

$\{Pd[L_2(7)](\mu\text{-}Cl)\}_2$: yellow-orange solid, thermotropic behavior in Table II. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.02 (t, 4H, $H^{9,10}$), 5.11 (m, 1H, H^{11}), 6.68 (dd, 1H, H^1 or H^6), 6.83 (s, 1H, H^3 or H^8), 6.91 (d, 2H, $H^{6,8}$ or $H^{1,3}$), 7.70 (d, 1H, H^2 or H^5), 7.76 (d, 2H, $H^{5,7}$ or $H^{2,4}$). Anal. Calcd for $C_{58}H_{82}Cl_2N_4O_4Pd_2$: C, 58.89; H, 6.99; N, 4.73. Found: C, 58.86; H, 6.84; N, 4.94. Yield 90%.

$\{Pd[L_2(10)](\mu\text{-}Cl)\}_2$: brown-yellow solid, thermotropic behavior in Table II. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.03 (t, 4H, $H^{9,10}$), 5.12 (m, 1H, H^{11}), 6.68 (dd, 1H, H^1 or H^6), 6.84 (s, 1H, H^3 or H^8), 6.91 (d, 2H, $H^{6,8}$ or $H^{1,3}$), 7.70 (d, 1H, H^2 or H^5), 7.77 (d, 2H, $H^{5,7}$ or $H^{2,4}$). Anal. Calcd for $C_{64}H_{94}Cl_2N_4O_4Pd_2$: C, 60.66; H, 7.48; N, 4.42. Found: C, 60.75; H, 7.50; N, 4.49. Yield 92%.

$\{Pd[L_2(12)])(\mu\text{-}Cl)\}_2$: brown-yellow solid, thermotropic behavior in Table II. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.01 (t, 4H, $H^{9,10}$), 5.12 (m, 1H, H^{11}), 6.69 (dd, 1H, H^1 or H^6), 6.83 (s, 1H, H^3 or H^8), 6.92 (d, 2H, $H^{6,8}$ or $H^{1,3}$), 7.71 (d, 1H, H^2 or H^5), 7.76 (d, 2H, $H^{5,7}$ or $H^{2,4}$). Anal. Calcd for $C_{68}H_{102}Cl_2N_4O_4Pd_2$: C, 61.72; H, 7.77; N, 4.23. Found: C, 61.54; H, 7.77; N, 4.33. Yield 90%.

$\{Pd[L_2(14)](\mu\text{-}Cl)\}_2$: brown-green solid, thermotropic behavior in Table II. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.02 (t, 4H, $H^{9,10}$), 5.11 (m, 1H, H^1), 6.69 (dd, 1H, H^1 or H^6), 6.84 (s, 1H, H^3 or H^8), 6.91 (d, 2H, $H^{6,8}$ or $H^{1,3}$), 7.71 (d, 1H, H^2 or H^5), 7.77 (d, 2H, $H^{5,7}$ or $H^{2,4}$). Anal. Calcd for $C_{72}H_{110}Cl_2N_4O_4Pd_2$: C, 62.69; H, 8.04; N, 4.06. Found: C, 62.59; H, 7.96; N, 3.68. Yield 85%.

$\{Pd[L_3(4)](\mu\text{-}Cl)\}_2$: brown solid, mp 128 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.03 (t, 2H, H^9), 4.43 (m, 1H, H^{10}), 6.68 (dd, 1H, H^1 or H^6), 6.86 (s, 1H, H^3 or H^8), 6.91 (d, 2H, $H^{6,8}$ or $H^{1,3}$), 7.70 (d, 1H, H^2 or H^5), 7.76 (d, 2H, $H^{5,7}$ or $H^{2,4}$). Anal. Calcd for $C_{48}H_{66}Cl_2N_4O_4Pd_2$: C, 55.08; H, 6.35; N, 5.35. Found: C, 54.84; H, 6.28; N, 5.07. Yield 83%.

$\{Pd[L_3(7)](\mu\text{-}Cl)\}_2$: brown solid, mp 135 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.01 (t, 2H, H^9), 4.44 (m, 1H, H^{10}), 6.68 (dd, 1H, H^1 or H^6), 6.83 (s, 1H, H^3 or H^8), 6.90 (d, 2H, $H^{6,8}$ or $H^{1,3}$), 7.70 (d, 1H, H^2 or H^5), 7.76 (d, 2H, $H^{5,7}$ or $H^{2,4}$). Anal. Calcd for $C_{54}H_{78}Cl_2N_4O_4Pd_2$: C, 57.35; H, 6.95; N, 4.95. Found: C, 57.63; H, 6.95; N, 4.79. Yield 65%.

$\{Pd[L_3(10)](\mu\text{-}Cl)\}_2$: brown solid, thermotropic behavior in Table II. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.00 (t, 2H, H^9), 4.44 (m, 1H, H^{10}), 6.68 (dd, 1H, H^1 or H^6), 6.84 (s, 1H, H^3 or H^8), 6.90 (d, 2H, $H^{6,8}$ or $H^{1,3}$), 7.70 (d, 1H, H^2 or H^5), 7.77 (d, 2H, $H^{5,7}$ or $H^{2,4}$). Anal. Calcd for $C_{60}H_{90}Cl_2N_4O_4Pd_2$: C, 59.31; H, 7.46; N, 4.61. Found: C, 59.03; H, 7.50; N, 4.69. Yield 90%.

$\{Pd[L_3(12)](\mu\text{-}Cl)\}_2$: yellow solid, thermotropic behavior in Table II. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.02 (t, 2H, H^9), 4.44 (m, 1H, H^{10}), 6.69 (dd, 1H, H^1 or H^6), 6.84 (s, 1H, H^3 or H^8), 6.91 (d, 2H, $H^{6,8}$ or $H^{1,3}$), 7.71 (d, 1H, H^2 or H^5), 7.76 (d, 2H, $H^{5,7}$ or $H^{2,4}$). Anal. Calcd for $C_{64}H_{98}Cl_2N_4O_4Pd_2$: C, 60.47; H, 7.77; N, 4.41. Found: C, 60.75; H, 7.73; N, 4.64. Yield 85%.

$\{Pd[L_3(14)](\mu\text{-}Cl)\}_2$: brown solid, thermotropic behavior in Table II. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.01 (t, 2H, H^9), 4.45 (m, 1H, H^{10}), 6.67 (dd, 1H, H^1 or H^6), 6.83 (s, 1H, H^3 or H^8), 6.90 (d, 2H, $H^{6,8}$ or $H^{1,3}$), 7.70 (d, 1H, H^2 or H^5), 7.77 (d, 2H, $H^{5,7}$ or $H^{2,4}$). Anal. Calcd for $C_{68}H_{106}Cl_2N_4O_4Pd_2$: C, 61.53; H, 8.05; N, 4.22. Found: C, 61.40; H, 8.06; N, 4.18. Yield 85%.

Synthesis of the $\{Pd[L_N(n)](\mu\text{-}I)\}_2$ Complexes. In a typical procedure, 0.09 mmol of the chloro-bridged complex $\{Pd[L_1(4)](\mu\text{-}Cl)\}_2$ and 1.80 mmol of KI were dissolved in acetone (8 mL) and stirred for 3 h at room temperature. The insoluble KCl was filtered off and diethyl ether was added to the filtrate to give additional white precipitate. The solution was filtered again and was concentrated under reduced pressure. Addition of pentane gave the complex $\{Pd[L_1(4)](\mu\text{-}I)\}_2$ as an orange solid. Colors, melting points, ^{1}H NMR, analytical data, and yields of the $\{Pd[L_N(n)](\mu\text{-}I)\}_2$ complexes are as follows:

$\{Pd[L_1(4)](\mu\text{-}I)\}_2$: orange solid, mp 165 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.06 (m, 3H, $H^{9,10}$), 6.69 (dd, 1H, H^1 or H^6), 6.91 (d, 2H, $H^{6,8}$ or $H^{1,3}$), 7.34 (s, 1H, H^3 or H^6), 7.65 (d, 2H, $H^{5,7}$ or $H^{2,4}$), 7.81 (d, 1H, H^2 or H^5). Anal. Calcd for $C_{52}H_{70}I_2N_4O_4Pd_2$: C, 48.73; H, 5.50; N, 4.37. Found: C, 48.50; H, 5.47; N, 4.35. Yield 80%. $\{Pd[L_1(7)](\mu\text{-}I)\}_2$: red-orange solid, mp 65 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.07 (m, 3H, $H^{9,10}$), 6.69 (d, 1H, H^1 or H^6), 6.92 (d, 2H, $H^{6,8}$ or $H^{1,3}$), 7.37 (s, 1H, H^3 or H^8), 7.65 (d, 2H, $H^{5,7}$ or $H^{2,4}$), 7.81 (d, 1H, H^2 or H^5). Anal. Calcd for $C_{58}H_{82}I_2N_4O_4Pd_2$: C, 51.00; H, 6.05; N, 4.10. Found: C, 50.85; H, 6.07; N, 3.85. Yield 85%.

$\{Pd[L_1(12)](\mu\text{-}I)\}_2$: red-orange solid, mp 44 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.06 (m, 3H, $H^{9,10}$), 6.69 (dd, 1H, H^1 or H^6), 6.92 (d, 2H, $H^{6,8}$ or $H^{1,3}$), 7.36 (s, 1H, H^3 or H^8), 7.65 (d, 2H, $H^{5,7}$ or $H^{2,4}$), 7.81 (d, 1H, H^2 or H^5). Anal. Calcd for $C_{68}H_{102}I_2N_4O_4Pd_2$: C, 54.23; H, 6.83; N, 3.72. Found: C, 52.74; H, 6.65; N, 3.70. Yield 90%.

$\{Pd[L_2(7)](\mu\text{-}I)\}_2$: red solid, thermotropic behavior in Table III. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.03 (m, 4H, $H^{9,10}$), 5.12 (m, 1H, H^{11}), 6.69 (dd, 1H, H^1 or H^6), 6.92 (d, 2H, $H^{6,8}$ or $H^{1,3}$), 7.35 (s, 1H, H^3 or H^8), 7.66 (d, 2H, $H^{5,7}$ or $H^{2,4}$), 7.81 (d, 1H, H^2 or H^5). Anal. Calcd for $C_{58}H_{82}I_2N_4O_4Pd_2$: C, 51.00; H, 6.05; N, 4.10. Found: C, 50.10; H, 5.84; N, 4.25. Yield 80%.

$\{Pd[L_2(10)](\mu\text{-}I)\}_2$: red solid, mp 157 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.03 (m, 4H, $H^{9,10}$), 5.12 (m, 1H, H^{11}), 6.69 (dd, 1H, H^1 or H^6), 6.92 (d, 2H, $H^{6,8}$ or $H^{1,3}$), 7.35 (s, 1H, H^3 or H^8), 7.66 (d, 2H, $H^{5,7}$ or $H^{2,4}$), 7.81 (d, 1H, H^2 or H^5). Anal. Calcd for $C_{64}H_{94}I_2N_4O_4Pd_2$: C, 53.01; H, 6.53; N, 3.86. Found: C, 52.80; H, 6.45; N, 3.59. Yield 88%.

$\{Pd[L_2(12)](\mu\text{-}I)\}_2$: red solid, thermotropic behavior in Table III. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.03 (m, 4H, $H^{9,10}$), 5.12 (m, 1H, H^{11}), 6.69 (dd, 1H, H^1 or H^6), 6.92 (d, 2H, $H^{6,8}$ or $H^{1,3}$), 7.35 (s, 1H, H^3 or H^8), 7.66 (d, 2H, $H^{5,7}$ or $H^{2,4}$), 7.81 (d, 1H, H^2 or H^5). Anal. Calcd for $C_{68}H_{102}I_2N_4O_4Pd_2$: C, 54.22; H, 6.83; N, 3.72. Found: C, 56.76; H, 7.07; N, 4.10. Yield 70%.

$\{Pd[L_2(14)](\mu\text{-}I)\}_2$: red solid, thermotropic behavior in Table III. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.03 (m, 4H, $H^{9,10}$), 5.12 (m, 1H, H^{11}), 6.69 (dd, 1H, H^1 or H^6), 6.92 (d, 2H, $H^{6,8}$ or $H^{1,3}$), 7.35 (s, 1H, H^3 or H^8), 7.66 (d, 2H, $H^{5,7}$ or $H^{2,4}$), 7.81 (d, 1H, H^2 or H^5). Anal. Calcd for $C_{72}H_{110}I_2N_4O_4Pd_2$: C, 55.35; H, 7.09; N, 3.59. Found: C, 53.54; H, 6.68; N, 3.25. Yield 65%.

$\{Pd[L_3(4)](\mu\text{-}I)\}_2$: brown solid, mp 135 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.02 (t, 2H, H^9), 4.44 (m, 1H, H^{10}), 6.67 (dd, 1H, H^1 or H^6), 6.91 (d, 2H, $H^{6,8}$ or $H^{1,3}$), 7.35 (d, 1H, H^3 or H^8), 7.65 (d, 2H, $H^{5,7}$ or $H^{2,4}$), 7.80 (d, 1H, H^2 or H^5). Anal. Calcd for $C_{48}H_{66}I_2N_4O_4Pd_2$: C, 46.88; H, 5.41; N, 4.56. Found: C, 46.81; H, 5.67; N, 4.35. Yield 86%.

$\{Pd[L_3(7)](\mu\text{-}I)\}_2$: orange solid, mp 122 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.02 (t, 2H, H^9), 4.45 (m, 1H, H^{10}), 6.67 (dd, 1H, H^1 or H^6), 6.92 (d, 2H, $H^{6,8}$ or $H^{1,3}$), 7.35 (d, 1H, H^3 or H^8), 7.66 (d, 2H, $H^{5,7}$ or $H^{2,4}$), 7.81 (d, 1H, H^2 or H^5). Anal. Calcd for $C_{54}H_{78}I_2N_4O_4Pd_2$: C, 49.36; H, 5.98; N, 4.26. Found: C, 49.31; H, 6.05; N, 4.38. Yield 64%.

$\{Pd[L_3(10)](\mu\text{-}I)\}_2$: red solid, mp 100 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.01 (t, 2H, H^9), 4.43 (m, 1H, H^{10}), 6.67 (dd, 1H, H^1 or H^6), 6.91 (d, 2H, $H^{6,8}$ or $H^{1,3}$), 7.35 (d, 1H, H^3 or H^8), 7.65 (d, 2H, $H^{5,7}$ or $H^{2,4}$), 7.81 (d, 1H, H^2 or H^5). Anal. Calcd for $C_{60}H_{90}I_2N_4O_4Pd_2$: C, 51.55; H, 6.49; N, 4.01. Found: C, 49.99; H, 6.20; N, 3.67. Yield 80%.

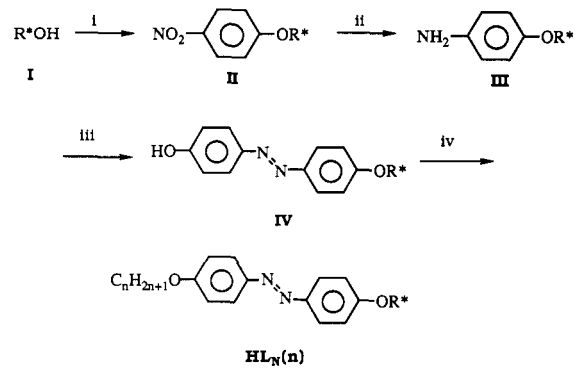
$\{Pd[L_3(12)](\mu\text{-}I)\}_2$: red-orange solid, mp 98 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.02 (t, 2H, H^9), 4.45 (m, 1H, H^{10}), 6.67 (dd, 1H, H^1 or H^6), 6.91 (d, 2H, $H^{6,8}$ or $H^{1,3}$), 7.36 (d, 1H, H^3 or H^8), 7.65 (d, 2H, $H^{5,7}$ or $H^{2,4}$), 7.80 (d, 1H, H^2 or H^5). Anal. Calcd for $C_{64}H_{98}I_2N_4O_4Pd_2$: C, 52.86; H, 6.79; N, 3.82. Found: C, 52.75; H, 6.92; N, 3.06. Yield 70%.

$\{Pd[L_3(14)](\mu\text{-}I)\}_2$: red solid, thermotropic behavior in Table III. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.02 (t, 2H, H^9), 4.45 (m, 1H, H^{10}), 6.67 (dd, 1H, H^1 or H^6), 6.91 (d, 2H, $H^{6,8}$ or $H^{1,3}$), 7.35 (d, 1H, H^3 or H^8), 7.65 (d, 2H, $H^{5,7}$ or $H^{2,4}$), 7.80 (d, 1H, H^2 or H^5). Anal. Calcd for $C_{68}H_{106}I_2N_4O_4Pd_2$: C, 54.08; H, 7.07; N, 3.71. Found: C, 53.68; H, 7.41; N, 3.51. Yield 82%.

Results and Discussion

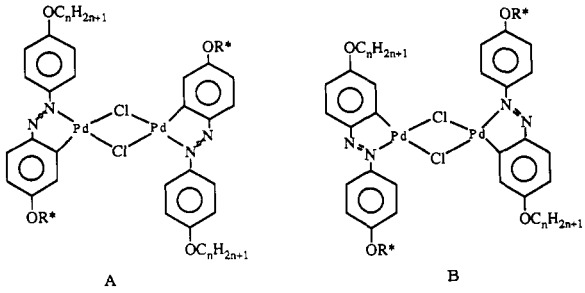
Synthesis. The synthesis of the azobenzene ligands $HL_N(n)$, summarized in Scheme I, is achieved by the following steps: the *p*-nitrochlorobenzene is reacted with the appropriate chiral alcohol I to form the optically active nitroalkoxybenzene, II, from which reduction of the nitro groups gives the corresponding substituted anilines, III. The diazotization of the aminobenzenes and the subsequent coupling with phenol afford the compounds IV; the azobenzenes $HL_N(n)$ are finally obtained in good yields

Scheme I[a]



[a] R* = (−)-menthol (HL_1), (*S*)-(−)-β-citronellol (HL_2), (*R*)-(−)-2-octanol (HL_3): (i) *p*-$NO_2C_6H_5Cl$, NaH, DMSO; (ii) H_2/Pd–C or $SnCl_2{\cdot}2H_2O$, ethyl acetate; (iii) C_6H_5OH, $NaNO_2$, HCl; (iv) $C_nH_{2n+1}Br$, K_2CO_3, cyclohexanone.

Chart II



by etherification of IV with *n*-alkyl bromides. All the compounds give satisfactory elemental analyses, and they are fully characterized (Experimental Section).

Treatment of $HL_N(n)$ with an equimolar amount of $[Pd(PhCN)_2Cl_2]$ gives the cyclopalladated dinuclear chloro-bridged complexes $\{Pd[L_N(n)](\mu\text{-}Cl)\}_2$ (Chart II); the chloro complexes are transformed into the corresponding iodo derivatives, $\{Pd[L_N(n)](\mu\text{-}I)\}_2$, by metathetical reaction with potassium iodide. The stoichiometry of all the complexes, was confirmed by elemental analysis and ^1H NMR spectroscopy (Experimental Section).

The electrophilic attack of the palladium ion on the aromatic ring leads to the cyclopalladation. Generally, in substituted azobenzenes the metalation preferably occurs at the more electron-rich phenyl ring;[28] in the $HL_N(n)$ series, either the chiral alkoxy groups (R*O) or the $C_nH_{2n+1}O$ chains are electrophilic activating groups, and therefore both the phenyl rings may undergo palladation. Actually, where the palladium carbon bond forms can be detected by NMR spectroscopy,[12a,29] but the ^1H NMR spectra of the $\{Pd[L_N(n)](\mu\text{-}Cl)\}_2$ complexes, albeit in agreement with the expected integral ratio between aromatic and aliphatic protons, show a puzzling multiplicity, and every attempt to fully assign with certainty each spectral signal failed. However, at least for the $\{Pd[L_3(n)](\mu\text{-}Cl)\}_2$ series, wherein together with a *n*-alkoxy chain the 2-octyloxy group is present, ^{13}C NMR measurements focused to the $-O-CH_2-$ and $-O-C^*H(CH_3)-$ fragments offer evidence about the nature of the palladated aromatic ring. Regarding these carbon atoms, the uncomplexed $HL_3(14)$ ligand, as an example, exhibits two resonances at 68.37 ($-O-CH_2-$) and 74.26 ppm ($-O-C^*H(CH_3)-$). Contrarily, the results arising from the investigations performed on the cyclopalladated products bearing n = 10, 12, and 14 *n*-alkoxy chain, show, for each case, two couples of signals (i.e., n = 10: 68.47 and 68.62 ppm, 74.36 and 74.61 ppm; n = 12: 68.42 and 68.60 ppm, 74.32 and 74.60 ppm; n = 14: 68.47 and 68.61 ppm, 74.35 and 74.60 ppm) concerning either the $-O-CH_2-$ or the $-O-C^*H(CH_3)-$ carbon atom and account for $-O-CH_2-$ (or $-O-C^*H(CH_3)-$) bonded to metalated and unmetalated benzene rings. The intensities of these signals, extimated by the ^{13}C NMR spectra, are as 1:1:1:1. Hence, on the basis of both the spectral multiplicity and the previous consideration about the R*O and $C_nH_{2n+1}O$ electronic effects, we suggest that all the $\{Pd[L_N(n)](\mu\text{-}Cl)\}_2$ products have to be considered 1:1 mixtures of the isomers A and B shown in Chart II.

Table I. Transition Temperatures and Enthalpy Changes of Mesogenic $HL_2(n)$ Ligands[a]

ligand	transition	T/°C	ΔH/J g^{-1}
$HL_2(7)$	K–Ch	50.7	11.12
	Ch–I	66.5	2.66
	I–Ch	65.1	2.57
	Ch–S_A	49.5	0.59
	S_A–K	47.6	8.56
$HL_2(10)$	K–I	66.4	71.41
	I–Ch	63.7	3.12
	Ch–K	53.7	59.66
$HL_2(12)$	K–S_A	63.2	53.89
	S_A–I	69.4	1.78
	I–S_A	61.9	10.69
	S_A–K	51.5	57.86
$HL_2(14)$	K–S_A	57.7	40.26
	S_A–I	64.4	5.69
	I–S_A	64.4	16.65
	S_A–K	46.2	56.62

[a] K, crystal; S, smectic; Ch, cholesteric; I, isotropic liquid.

The iodo complexes $\{Pd[L_N(n)](\mu\text{-}I)\}_2$ display an ^1H NMR spectral pattern analogous to that of the chloro-bridged precursors. The only noticeable difference is the position of the proton ortho to the carbon directly bonded to the palladium atom which resonates downfield about 0.5 ppm. A similar trend has already been observed in related complexes derived from phenylpyrimidine,[11a] imine,[15b] and azine.[16]

Mesomorphic Properties. The different mesophases are identified by optical observations carried out by a polarizing microscope; the transition temperatures are determined by the differential scanning calorimetry and, for most of the compounds, are confirmed by X-ray diffraction analysis performed on powder samples.

Mesogenic Behavior of the Ligands. The investigated azobenzenes form three different homologous series wherein the chiral group is (*R*)-(−)-menthol, (*R*)-(−)-2-octanol, and (*S*)-(−)-β-citronellol. Among them, the citronellol series only $HL_2(n)$, shows mesomorphic behavior (Table I); those containing (*R*)-(−)-menthol, $HL_1(n)$, and (*R*)-(−)-2-octanol, $HL_3(n)$ do not exhibit mesomorphism at all.

The results arising from the $HL_1(n)$ series confirms that the presence of a menthol fragment actually enlarges the rigid core so affording to molecular structures laking in mesogenic properties.[30] Contrarily, (*R*)-(−)-2-octanol in $HL_3(n)$ compounds gives mesogenic molecular structures[20] (Chart I). Nevertheless, none of the member of this series is mesogen. Therefore such behavior might be simply

(28) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403.
(29) Ghedini, M.; Armentano, S.; Neve, F. *Inorg. Chim. Acta* **1987**, *134*, 23.
(30) Bone, M. F.; Coates, D.; Gray, G. W.; Lacey, D.; Toyne, K. J.; Young, D. J. *Mol. Cryst. Liq. Cryst. Lett.* **1986**, *3*, 189.

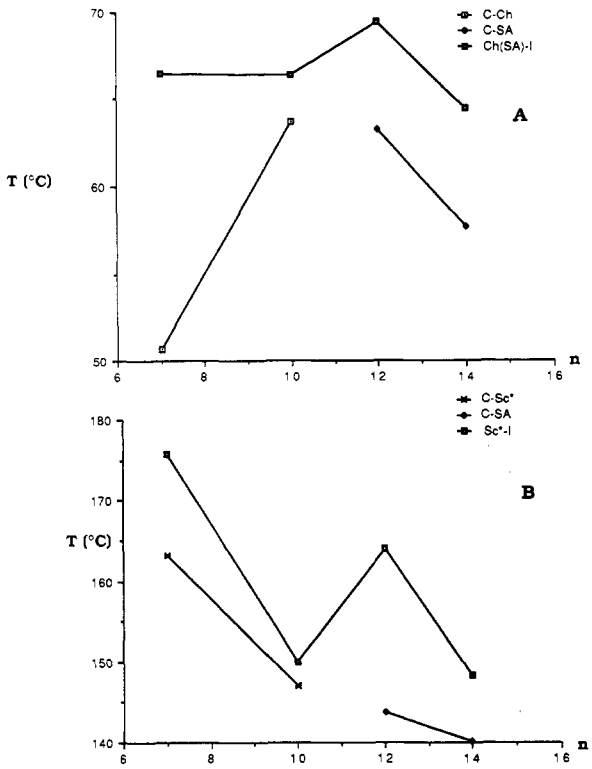


Figure 1. Plots of mesomorphic transition temperatures versus the $C_nH_{2n+1}O$ chain length (n) for $HL_2(n)$ ligands (A) and $\{Pd[L_2(n)](\mu\text{-}Cl)\}_2$ complexes (B).

ascribed to a bad choice of the tested $C_nH_{2n+1}O$ groups which are unable to provide the proper entropic contribution to the mesophases' stability.

All the $HL_2(n)$ azobenzenes are liquid crystals, enantiotropic for $HL_2(7)$, $HL_2(12)$, and $HL_2(14)$ or monotropic for $HL_2(10)$ (Table I). In particular, upon heating, $HL_2(7)$ shows, in the visible region, a cholesteric mesophase Ch, with the typical oil-streak texture, whereas $HL_2(12)$ and $HL_2(14)$ give a fan-shaped smectic A, S_A, phase. On cooling from the isotropic liquid, $HL_2(10)$ shows a Ch mesophase.

The influence exerted on the behavior of the $HL_2(n)$ by the different chain lengths of the $C_nH_{2n+1}O$ group is shown in Figure 1A, where the transition temperatures are plotted against n.

Mesogenic Behavior of the $\{Pd[L_N(n)](\mu\text{-}Cl)\}_2$ Complexes. The structures of the cyclopalladated complexes arising from $HL_N(n)$ and $[Pd(PhCN)_2Cl_2]$ are sketched in Chart II. All the $\{Pd[L_2(n)](\mu\text{-}Cl)\}_2$ complexes derived from (*S*)-(−)-β-citronellol display a mesomorphic behavior (Table II); among the (*R*)-(−)-2-octanol containing complexes, $\{Pd[L_3(n)](\mu\text{-}Cl)\}_2$, only those with n = 10, 12, and 14 are mesogenic even if the ligands do not display a mesomorphic behavior. With reference to similar organometallic species, it is not unprecedented that mesogenic materials can be obtained notwithstanding the starting materials thermotropic properties.[12a] None of the $HL_1(n)$ derivatives are mesomorphic (Table II).

The $\{Pd[L_2(n)](\mu\text{-}Cl)\}_2$ compounds, with the exception of the term n = 10, are enantiotropic liquid crystals whose mesophases on heating, chiral smectic C, S_c* (n = 7) and S_A (n = 12, 14) are stable over temperature ranges 12.5, 20.2, and 8.2 °C wide, respectively. The isotropizations occur between 148.3 (n = 14) and 175.7 °C (n = 7); S_c* (n = 7, 10) or S_A (n = 12, 14) mesophases are observed on cooling.

The mesomorphic $\{Pd[L_3(n)](\mu\text{-}Cl)\}_2$ species are monotropic with melting points quite close each other (i.e., 118.9 °C for n = 10, 115.0 °C for n = 12, and 114.2 °C for n = 14). On cooling the isotropic liquids, S_c* (n = 10, 14) and S_A (n = 12) mesophases are observed.

Table II. Transition Temperatures and Enthalpy Changes of Mesogenic $\{Pd[L_N(n)](\mu\text{-}Cl)\}_2$ Complexes[a]

complex	transition	T/°C	ΔH/J g^{-1}
$\{Pd[L_2(7)](\mu\text{-}Cl)\}_2$	K–Sc*	163.2	27.18
	Sc*–I	175.7	2.94
	I–Sc*	175.0	
	Sc*–K	154.0	
$\{Pd[L_2(10)](\mu\text{-}Cl)\}_2$	K–I	150.0	
	I–Sc*	147.0	1.07
	Sc*–K	137.9	21.73
$\{Pd[L_2(12)](\mu\text{-}Cl)\}_2$	K–S_A	143.8	20.29
	S_A–I	164.0	
	I–S_A	164.0	
	S_A–K	134.0	
$\{Pd[L_2(14)](\mu\text{-}Cl)\}_2$	K–S_A	140.1	26.48
	S_A–I	148.3	3.88
	I–S_A	137.8	2.80
	S_A–K	117.8	14.21
$\{Pd[L_3(10)](\mu\text{-}Cl)\}_2$	K–I	118.9	32.94
	I–S_C*	113.4	0.64
	S_C*–K	110.9	19.69
$\{Pd[L_3(12)](\mu\text{-}Cl)\}_2$	K–I	115.0	
	I–S_A	115.0	
	S_A–K	110.0	
$\{Pd[L_3(14)](\mu\text{-}Cl)\}_2$	K–I	114.2	39.91
	I–Sc*	109.3	4.53
	Sc*–K	91.6	15.46

[a] K, crystal; S, smectic; Ch, cholesteric; I, isotropic liquid.

The transition temperatures of all these palladium mesogens are higher than those of the uncomplexed ligands. Thus, as far as the isotropization temperature is concerned, the observed increasing of the transition temperatures is larger for the $HL_2(n)$ (about 100 °C) than for $HL_3(n)$ derivatives (about 70 °C). Comparing the mesomorphic behavior of the $HL_2(n)$ ligands and the series of palladium complexes $\{Pd[L_2(n)](\mu\text{-}Cl)\}_2$ (Figure 1), the metal complexation broadens the mesomorphic range. Regarding to the nature of the mesophases, these are preserved for n = 12 and 14 while the Ch mesophase observed in $HL_2(7)$ and $HL_2(10)$, become S_c* in the corresponding palladated complexes.

Mesogenic Behavior of the $\{Pd[L_N(n)](\mu\text{-}I)\}_2$ Complexes. In thermotropic species containing the $Pd_2(\mu\text{-}X)]_2$ core the mesomorphic behavior depends to some extent on the nature of the halogen, it has been shown that the nematic phase appears in the order Cl < Br < I[31] increasing the temperature while the smectic phases show the reverse order.[11a,32] In Table III are compiled the mesomorphic properties of the iodo complexes $\{Pd[L_N(n)](\mu\text{-}I)\}_2$ obtained by methathetical reactions from the corresponding chloro compounds.

The complexes $\{Pd[L_N(n)](\mu\text{-}I)\}_2$ with n = 7, 12, and 14 are monotropic liquid crystals which display S_A mesophases only. The data show that either the mesomorphism or the isotropic liquids appear at temperatures lower for the iodo compounds than for the parent chloro species. In the complexes $\{Pd[L_2(10)](\mu\text{-}X)\}_2$ the chloro compound is monotropic while the corresponding iodo derivatives do not show mesomorphic properties. Therefore, in this case the substitution of chloro for iodo atoms depresses the mesomorphic aptitude, transforming the liquid crystals from enantiotropic to monotropic; regarding the transition temperatures of the S_A phases, however, it should be

(31) Ghedini, M.; Licoccia, S.; Armentano, S.; Bartolino, R. *Mol. Cryst. Liq. Cryst.* 1984, *108*, 269.

Table III. Transition Temperatures and Enthalpy Changes of Mesogenic {Pd[$L_N(n)$](μ-I)}$_2$ Complexes

complex	transition	T/°C	ΔH/J g^{-1}
{Pd[$L_2(7)$](μ-I)}$_2$	K–I	159.0	
	I–S_A	158.0	
	S_A–K	140.0	
{Pd[$L_2(12)$](μ-I)}$_2$	K–I	110.0	
	I-S_A	110.0	
	S_A–K	60.0	
{Pd[$L_2(14)$](μ-I)}$_2$	K–I	144.0	
	I–S_A	140.0	
	S_A–K	139.0	
{Pd[$L_3(14)$](μ-I)}$_2$	K–S_A	56.9	18.56
	S_A–I	85.1	8.36
	I–S_A	85.1	
	S_A–K	56.9	

[a] K, crystal; S, smectic; I, isotropic liquid.

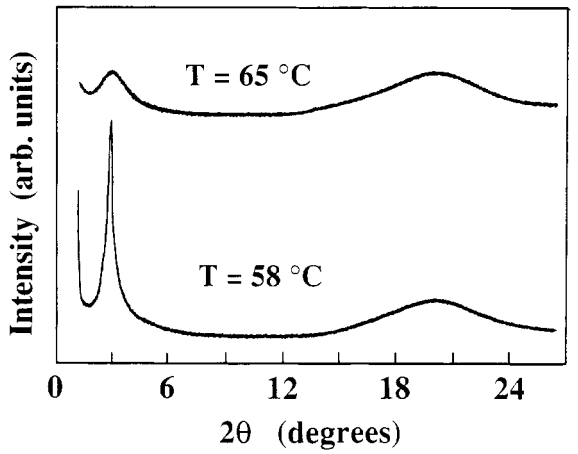


Figure 2. X-ray diffraction patterns of compound $HL_2(7)$ measured at temperatures T = 65 and 58 °C on cooling from the isotropic liquid.

pointed out that the detected trend parallels that previously observed: I < Cl.[11a,32]

In the $HL_3(n)$ series only {Pd[$L_3(14)$](μ-I)}$_2$ is a mesogen. This complex is enantiotropic with a low-temperature S_A phase (Table III) and a clearing point of 85.1 °C. The parent chloro compound shows a monotropic S_{c^*} phase on cooling. As a whole also for the $HL_3(n)$ azobenzenes, the substitution of chloro for iodo atoms reduces the mesogenic ability (with chlorine, the palladated compounds with n = 10, 12, and 14 are mesogenic). Also the mesophases, S_{c^*} in {Pd[$L_3(14)$](μ-Cl)}$_2$ and S_A in the iodo derivative, appear to follow the order I < Cl. It is remarkable, however, that in the case of the $HL_3(14)$ ligand, by changing the bridging halogen, both the mesomorphic behavior and the nature of the mesophase show different results.

X-ray Diffraction Measurements. As an example, Figures 2–4 report the measured X-ray diffraction spectra for three of the investigated compounds, namely, $HL_2(7)$, $HL_2(10)$, and {Pd[$L_2(12)$](μ-Cl)}$_2$ at temperatures where they exhibit smectic or cholestric mesophases. The patterns in Figures 1a and 2a display a sharp low-angle Bragg peak characteristic of the smectic mesophase, while the diffuse nature of the low-angle peaks in the patterns of Figures 1b and 2b clearly indicates the presence of a nematic orientational order, the local order in the cholesteric phase. Table IV reports, for all the samples investigated, the periodicity, d, characteristic of the different mesophases (as obtained by the application of the Bragg law to the low angle peaks), together with the

(32) Barberà, J.; Espinet, P.; Lalinde, E.; Marcos, M.; Serrano, J. L. *Liq. Cryst.* **1987**, *2*, 833.

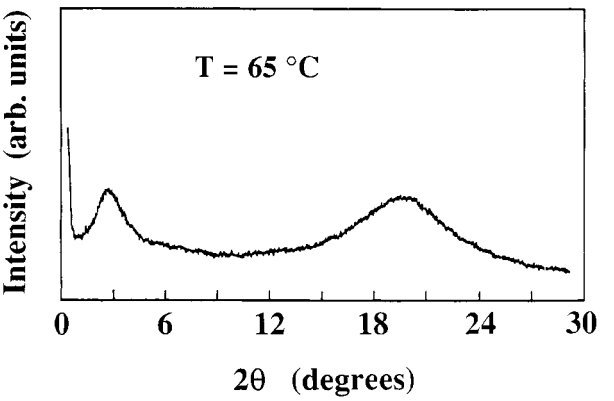


Figure 3. X-ray diffraction pattern of compound $HL_2(10)$ recorded at T = 65 °C on cooling down from the isotropic liquid.

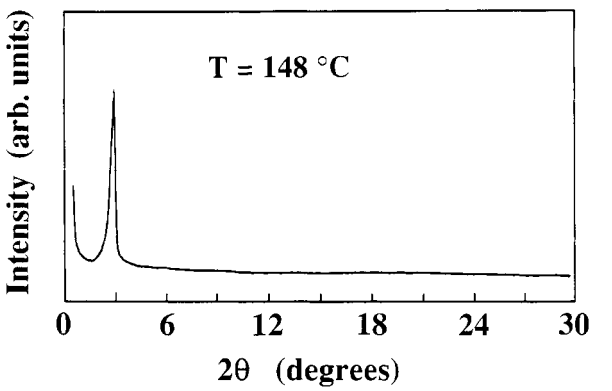


Figure 4. X-ray diffraction pattern of complex {Pd[$L_2(12)$](μ-Cl)}$_2$ measured at T = 148 °C upon heating.

Table IV. X-ray Diffraction Data

compound	phase	d,[a] Å	L,[b] Å
$HL_2(7)$	Ch	29.4	30.7
	S_A	30.1	30.7
$HL_2(10)$	Ch	34.5	34.5
$HL_2(12)$	S_A	34.3	37.0
$HL_2(14)$	S_A	35.6	39.5
{Pd[$L_2(7)$](μ-Cl)}$_2$	Sc*	27.5	32.1
{Pd[$L_2(10)$](μ-Cl)}$_2$	Sc*	29.0	36.9
{Pd[$L_2(12)$](μ-Cl)}$_2$	S_A	31.1	41.9
{Pd[$L_2(14)$](μ-Cl)}$_2$	S_A	46.0	47.0
{Pd[$L_3(10)$](μ-Cl)}$_2$	Sc*	28.0	36.9
{Pd[$L_3(12)$](μ-Cl)}$_2$	S_A	30.0	41.9
{Pd[$L_3(14)$](μ-Cl)}$_2$	Sc*	32.1	47.0
{Pd[$L_3(14)$](μ-I)}$_2$	S_A	31.3	47.0

[a] Layer spacing derived from diffraction patterns. [b] Molecular length determined by molecular modeling (alkyl chains in all trans conformation).

molecular length as estimated by molecular modeling (with the alkyl chains in the all trans conformation).

The quantity d gives the layer spacing in the smectic phase while in the nematic phase it corresponds to the average molecular length. For the cholesteric phases an excellent agreement is found between the experimentally determined average molecular length and the calculated value L. Moreover, a comparison between the values of d and L in the smectic phases shows that the layer spacing is, in any case, lower than the molecular length, which indicates a monolayer arrangement of the molecules for all compounds. Within each homologous series the ratio d/L decreases with increasing the length of the chains. In particular, for the ligands $HL_2(n)$ this ratio varies between ~1 and 0.9, which is the typical range for monolayer S_A phases. In the complexes, the ratio d/L ranges between 0.68 and 0.86 for the {Pd[$L_2(n)$](μ-Cl)}$_2$ series and takes

values between ~0.66 and 0.72 for all the other compounds. In this latter case, due to considerable lower values of the d/L ratio, liquidlike alkyl chains or random tilting of the core plus chain deformation are not sufficient to account for the shorter lamellar spacings in the S_A phases and a model where the aliphatic chains are partially melted and folded or where the chains appear strongly interdigitated must be considered for the structural conformation.

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