Rigid Chiral Building Blocks for Copper(II)- and Palladium(II)-Containing Liquid Crystals

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The possibility of metal coordination in oxazolinyl phenols has allowed the preparation of new chiral metal-containing liquid crystals in which the stereogenic center is located in the rigid mesogenic core. By using (*S*)-*β*-amino alcohols as chiral starting materials for the synthesis of the oxazoline ligands, two types of complex have been prepared: (i) mononuclear copper(II) complexes and (ii) dinuclear orthopalladated organometallic compounds with either nonplanar (acetato-bridged) or planar (chloro-bridged) geometries. The synthesis and structural characterization of all of these compounds are described. The formation of a single diastereoisomer with a trans configuration in nonplanar palladium(II) complexes has been confirmed by ^{1}H NMR spectroscopy. The complexes mainly show S_A mesomorphism, although when they are used as chiral dopants in a matrix with the phase sequence N−S_A−S_C they induce a cholesteric mesophase. The presence of stereogenic centers lying out of the coordination plane in a rigid environment must account for the formation of the helical cholesteric mesophase over broad temperature ranges.

Introduction

The design of chiral liquid crystals that show chiral mesophases deserves special attention within research on structure−activity relationships owing to the variety and importance of the properties derived from these particular organizations. These properties range from the widely investigated electrooptical effects of the S_C* phase[1] (either with ferroelectric or antiferroelectric order) to the characteristic optical behavior (such as selective reflection) of the cholesteric phase,[2] passing through the optical and electrooptical features of chiral columnar mesophases, which are yet to be fully understood.[3]

As part of our current research program on chiral liquid crystals with ferroelectric properties, we have already demonstrated the great potential of aryloxazolines derived from (*S*)-*β*-amino alcohols as chiral building blocks. Chiral liquid crystals have been prepared from these systems and have been shown either to have high spontaneous polarization values as pure compounds or to be able to behave as useful inducers of ferroelectric properties in binary mixtures.[4]

The aim of the work described here is to gain a deeper understanding of the role of the oxazoline ring derived from enantiopure *β*-amino alcohols as a promoter of chiral supramolecular organization within its mesophase. This study also encompassed an investigation into the coordination possiblities of 2-aryloxazolines with transition metals.[5] The compounds synthesized are copper(II) and palladium(II) complexes with structures such as those represented in Chart 1.

By using the appropriate design, we were able to prepare complexes with a pro-mesogenic structure similar to the well-known copper(II) salicylaldiminates and the orthopalladated imine, azo or azine complexes whose mesomorphic behavior has been extensively

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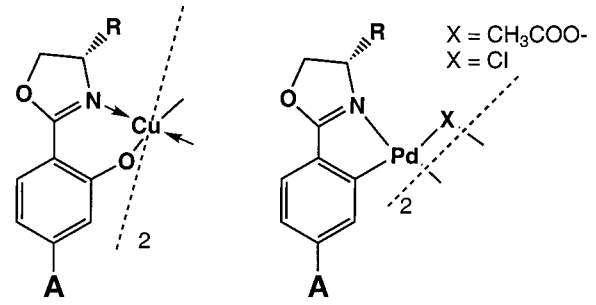
Chart 1. General structure of the Target Copper(II) and Palladium(II) Complexes



studied.[6] Undoubtedly, however, the most interesting structural aspect of these oxazoline complexes lies in the presence of stereogenic centers within a highly rigid environment in the mesogenic core. Indeed, the mesomorphic behavior of the resulting complexes, and especially their ability to induce chiral liquid crystalline organizations either in the pure state or in mixtures, must be strongly affected by the confinement of the stereogenic centers within a conformationally restricted ring in the rigid core of the molecule. This situation is in contrast to that in the chiral metallomesogens described to date that incorporate the stereogenic centers—responsible for the appearance of chiral mesophases or even ferroelectric behavior[7]—in the terminal chains of the ligands. The only two examples in which the stereogenic center is close to the mesogenic core, but is not included within it, are (i) the first ferroelectric metallomesogen described, which consists of a nonplanar (*S*)-2-chloropropionato-bridged palladium(II) complex,[8] and (ii) a cholesteric metallomesogen prepared by substitution of one of the chlorocarboxylato bridges of the former by a thiolato group.[9]

The work presented here is based on copper(II) and palladium(II) complexes of several monocatenar ligands with different mesogenic cores. The complexes belong to two classes (Chart 1): (i) planar mononuclear metallorganic copper(II) complexes obtained by complexation of (*S*)-2-(2-hydroxyaryl)oxazolines (series **I**, **II**, and **III**) and (ii) dinuclear organometallic palladium(II) complexes prepared by an orthopalladation reaction of 2-aryloxazolines to give either nonplanar acetato-bridged complexes or planar chloro-bridged complexes (series **IV** and **V**). The mesomorphic behavior of all the compounds was studied along with their ability to induce chiral mesophases in a liquid crystalline matrix typically used for experiments on ferroelectric liquid crystal (FLC) mixtures.

Synthesis and Structural Characterization. The synthesis of the chiral oxazoline ligands has been reported previously.[4] The copper(II) and acetato-bridged palladium(II) complexes were prepared by the reaction of the ligands with their corresponding metal acetates. The chloro-bridged orthopalladated complexes were obtained by exchange of the acetato bridge with chloride anions. Thus, three series of new chiral metallomesogens were synthesized; the mononuclear copper(II) complexes, the dinuclear nonplanar acetato-bridged complexes, and the planar chloro-bridged palladium(II) complexes.

Previous studies on orthopalladated mesogens have shown the possibility of cis−trans isomerism depending on the nature of the ligands. A ratio of ca. 3:1 was deduced for the trans and cis isomers in acetato-bridged palladium(II) complexes derived from benzalazine ligands.[10] In contrast, only the trans isomer is formed upon complexation of benzaldimine ligands with acetato bridges, as is the case for their chloro- and bromo-bridged derivatives.[11]

Figures 1 and 2 show the ^{1}H NMR spectra of complexes **IV-Ileu-PdOAc** (Figure 1) and **IV-Ileu-PdCl** (Figure 2). The appearance of only one set of signals for the aromatic protons (Figure 1a) reveals that a single isomer is present in the acetato-bridged complexes. Moreover, only a singlet is observed for the methyl group of the acetato bridge (Figure 1c), indicating that both methyl groups in the complex are chemically equivalent and, therefore, the only isomer formed upon complexation has the trans configuration (Figure 1d). This is in agreement with data reported for achiral oxazoline acetato-bridged palladium(II) complexes that show formation of an only stereoisomer (i.e., trans) from ^{1}H NMR studies.[12] However, the chloro-bridged complexes show additional signals for the aromatic protons (Figure 2a) as well as for the first methylene group in the alkyloxy tail (Figure 2b). These data can be accounted for by the formation of a mixture of cis and trans isomers (Figure 2d) when the acetato-bridged trans complex is converted into the chloro-bridged analogue through reaction with HCl. Steric factors related to the chiral oxazoline ring could also cause this behavior since a cis isomer in the nonplanar complex would give rise to strong steric hindrance between an H_c hydrogen and the bulky alkyl group in the stereogenic center of the second oxazoline ligand (Figure 3). The proportions of both isomers could be accurately determined for the complex **IV-Ileu-PdCl** by means of ^{13}C NMR spectroscopy. The ratio has been found to be ca. 2:1, presumably corresponding the highest proportion to the trans isomer.

Nonplanar acetato-bridged complexes lack symmetry elements other than a C_2 axis, and hence they exist as a pair of enantiomers. Benzaldimine acetato-bridged

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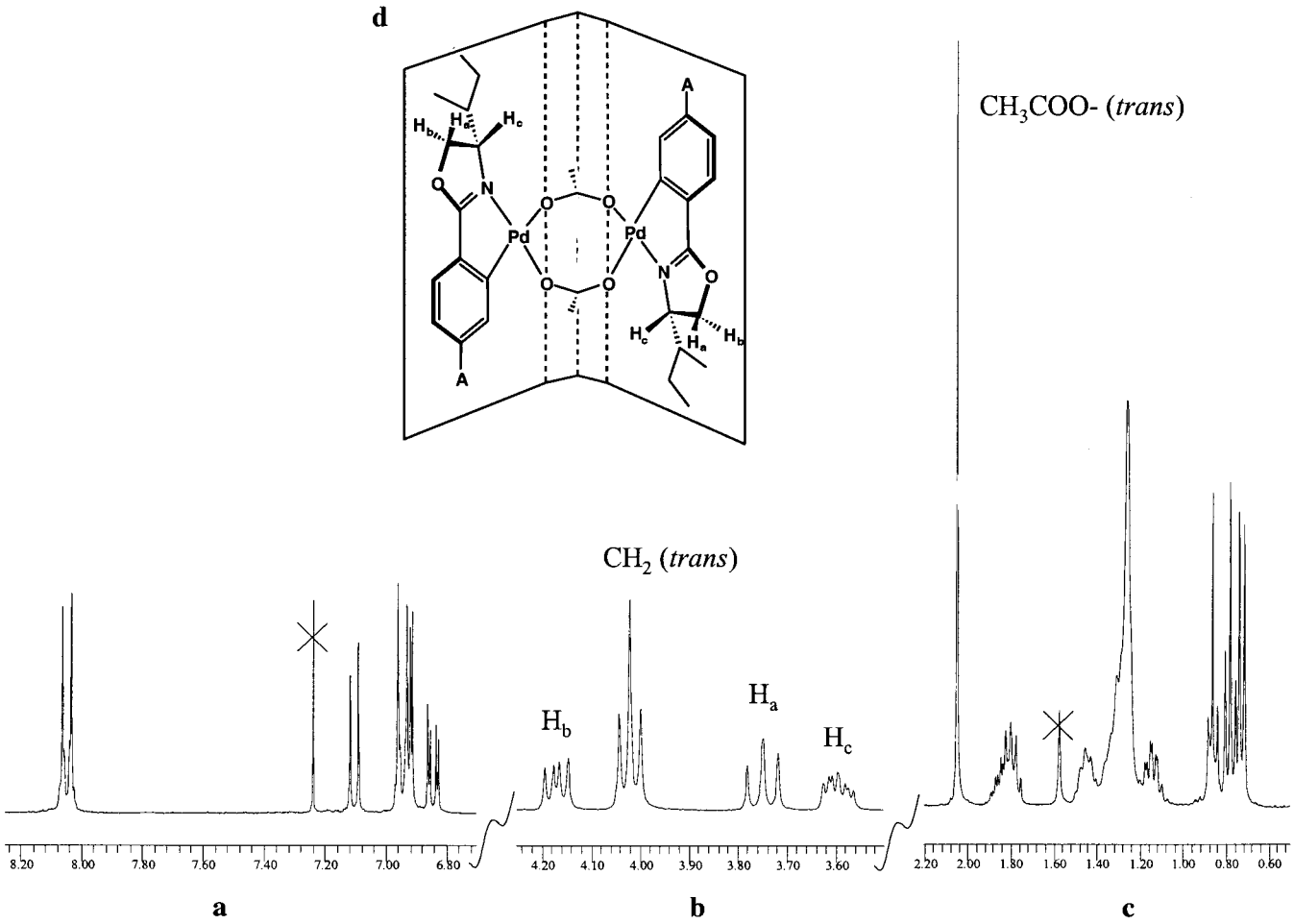

Figure 1. ^{1}H NMR spectrum of the planar complex **IV-Ileu-PdOAc**. Note that the scale is different for the different zones of the spectrum (a, b, and c). Only one set of peaks for each hydrogen involved in the coordination region is observed. This indicates the formation of a single diastereoisomer, the structure of which is represented in d.

palladium(II) complexes have been reported not to undergo interconversion in solution.[13] On the contrary, some oxazoline acetato-bridged palladium(II) complexes have revealed fluxional behavior in ^{1}H NMR experiments at various temperatures.[14] In our case, the presence of a stereogenic center (or two in the case of isoleucine derivatives) would be expected to give rise to a pair of diastereoisomers that should be distinguishable in the ^{1}H NMR spectrum, thus giving an NMR spectrum more complicated than the one actually observed. Examination of the signals corresponding to the protons near to the stereogenic center, i.e., H_a, H_b, and H_c (Figure 1b), at room temperature as well as at −55 °C, reveals that the diastereoselectivity upon complexation must be close to 100%. In fact, we only observed unique signals for all three protons ($\delta H_b = 4.16$ ppm, dd; $\delta H_a = 3.73$ ppm, dd; $\delta H_c = 3.55$ ppm, m) that correspond exclusively to one of the two possible diastereoisomers. It seems reasonable to believe that the configuration of the resulting complex will be determined by steric factors. Indeed, the N-coordinating atom belongs to a rigid system (the oxazoline ring) and, moreover, it has a bulky alkyl substituent (isopropyl -**Val**- or *sec*-butyl-**Ileu**- radicals) in the α position. This bulky group should be best located in the outer part of the nonplanar complex (Figure 1d). As a consequence, protons in the inner part of the molecule (i.e., H_a and H_c) are more shielded than that in the outer part (H_b) in comparison to their corresponding chemical shifts in the planar chloro-derived complex. Moreover, the rigidity of the oxazoline ring is clearly reflected by the difference in the coupling constants between H_b and H_c (J = 5.4 Hz), which are eclipsed, and H_a and H_c (J = 9.6 Hz), which are in a staggered relationship.

Mesomorphic Properties of the Pure Compounds. The thermal properties of the complexes were investigated by polarizing optical microscopy and differential scanning calorimetry. Results are given in Tables 1 and 2.

It is worth noting the predominance of the S_A mesophase, which is completely absent in the free ligands. Exclusively cholesteric mesophases were detected in these cases.[4]

The appearance of mesomorphic behavior is clearly dependent on the size of the A group. From the behavior of the three isoleucine derivatives (**I-Ileu-Cu**, **II-Ileu-Cu**, and **III-Ileu-Cu**), we can deduce that an increase in the polarizability of the ligand, by increasing the number of aromatic rings along the molecular axis, favors the arrangement of the molecules in mesophases along with a strong increment of clearing temperatures. Thus, the mononuclear copper(II) complexes (series **I**,

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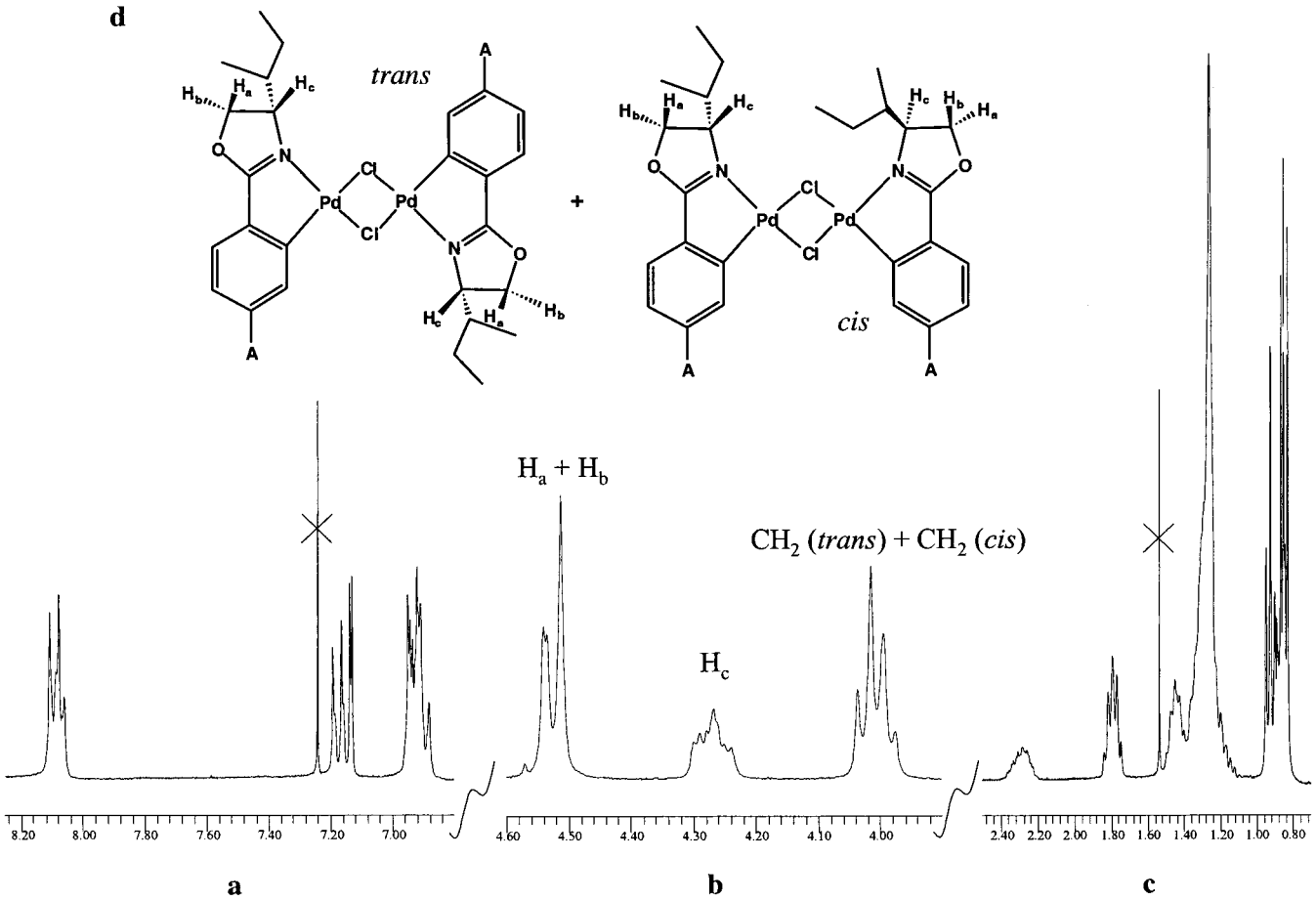


Figure 2. ^{1}H NMR spectrum of the planar complex **IV-Ileu-PdCl**. Note that the scale is different for the different zones of the spectrum (a, b, and c). Additional peaks appear in this spectrum by comparison with that of its acetato-bridged precursor (Figure 1). This result is explained by the formation of a mixture of trans and cis isomers whose structures are represented in d.

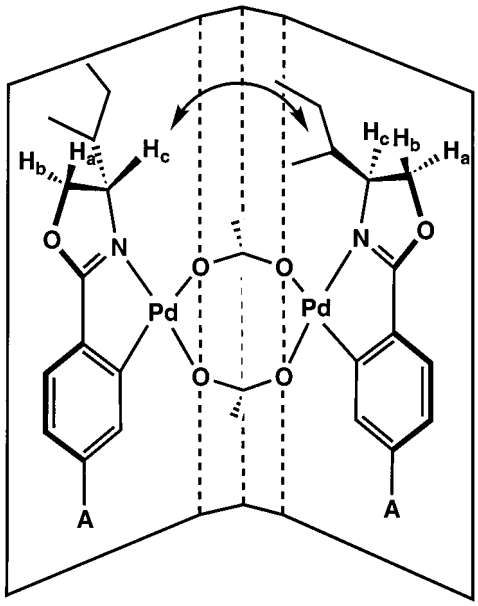
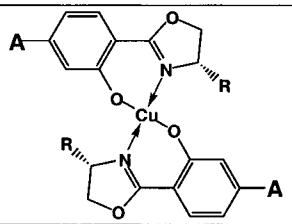


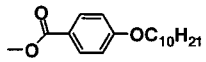
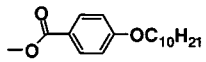
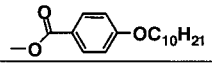
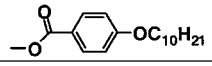
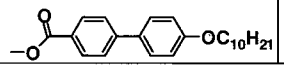
Figure 3. Structure of the cis diastereoisomer whose formation is impeded by steric factors due to a hydrogen H_c and a bulky alkyl group in the inner part of the nonplanar complex.

II, and **III**) are liquid crystalline only when the mesogenic unit contains at least four aromatic rings. Dimerization of the chiral oxazoline molecules by means of metal complexation promotes a layered ordering of the systems, which gives rise to the appearance of broad S_A ranges for complexes of series **II** and **III**. The flexible alkoxy chains in series **I** (**Val-Cu**, **Ileu-Cu**) cannot compete with the strong influence of the sterically bulky substituents, i.e., isopropyl and *sec*-butyl groups, on the rigid center of the complex. In contrast, these bulky groups allow the formation of a S_A mesophase in series **II** and **III** as has been commented above. Moreover, one can deduce a clear sterical influence of this alkyl group in S_A intervals by increasing the clearing temperatures as the length of the group is extended. As an exception, the isobutyl group of **II-Leu-Cu** destabilizes the S_A mesophase in contrast to its isoleucine isomer **II-Ileu-Cu**.

The free ligands (**I**, **II**, and **III**) can be viewed as calamitic structures with only one long terminal chain and these predominantly show monotropic nematic behavior. Indeed, the chiral oxazoline group acts as a bulky terminal moiety that makes it difficult for lateral interactions required for smectic ordering to occur. One exception to this trend occurs in the ligands derived from the biphenyl carboxylic acid where the core, which contains three aromatic rings, overcomes the effect of the terminal chiral group and favors lateral interactions within tilted layered organizations (S_C* phase). However, the antiparallel pairing of these ligands by means of metal complexation gives rise to planar molecules with a highly rigid central core, a situation that makes their space-filling requirements suitable for the formation of orthogonal layered molecular arrays (S_A phase).

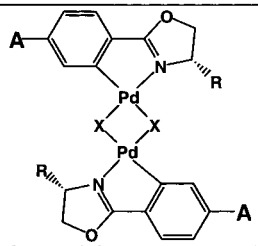
Table 1. Transition Temperatures and Enthalpies Corresponding to the Pure Copper(II) Complexes. All the Data Were Taken from the Second Heating Scan

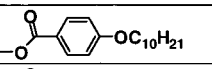
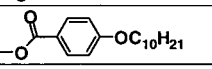
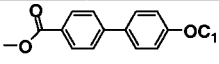
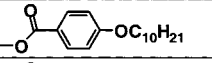
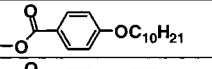
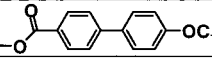


Name	A	R	temperatures, °C (enthalpies, KJ/mol)
I-Val-Cu	$-OC_{10}H_{21}$	$-CH(CH_3)_2$	g[a] –6 I
I-Ileu-Cu	$-OC_{10}H_{21}$	$-*CH(CH_3)CH_2CH_3$	C 92(34) I
II-Ala-Cu		$-CH_3$	C_1 81(10) C_2 135(31) S_A 169(0.7) I
II-Val-Cu		$-CH(CH_3)_2$	g[b] 75 S_A 175(0.5) I
II-Leu-Cu		$-CH_2CH(CH_3)_2$	g[b] 60 S_A 153(0.7) I
II-Ileu-Cu		$-*CH(CH_3)CH_2CH_3$	g[b] 77 S_A 190(0.5) I
III-Ileu-Cu		$-*CH(CH_3)CH_2CH_3$	g 52 S_A 92(-21)[c] C_1 128 C_2 140(24) S_A 287 (0.7) I(dec)

[a] This complex does not crystallize but shows a transition to a glassy state that retains the structure of the S_A phase. [b] All these compounds appear at room temperature as glasses that retain the structure of the S_A phase. The glass transition could not be accurately observed in DSC and has been estimated by optical microscopy. [c] The S_A phase undergoes cold crystallization on heating. The subsequent melting process occurs through two crystalline phases, and the S_A mesophase reappears at 140 °C.

Table 2. Transition Temperatures and Enthalpies Corresponding to the Pure Palladium(II) Complexes. All the Data Were Taken from the Second Heating Scan

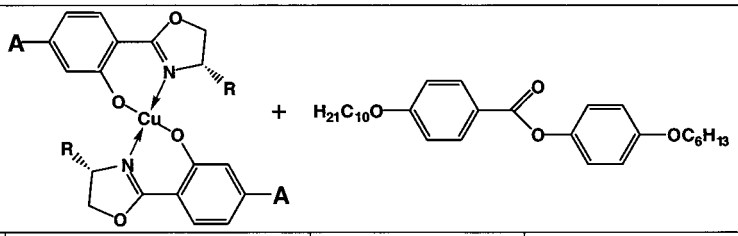


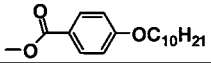
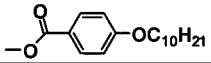
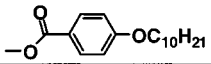
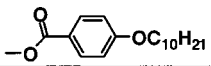
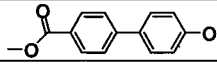
Name	A	R	X	temperatures, °C (enthalpies, KJ/mol)
IV-Val-PdOAc		$-CH(CH_3)_2$	$-OOCCH_3$	C 165(40) I
IV-Ileu-PdOAc		$-*CH(CH_3)CH_2CH_3$	$-OOCCH_3$	C 164(47) I
V-Ileu-PdOAc		$-*CH(CH_3)CH_2CH_3$	$-OOCCH_3$	g[a] 71 S_A 121(–15)[b] C_1 169(2.3) C_2 173(0.7) C_3 179(19) S_A 232 (1.7) I
IV-Val-PdCl		$-CH(CH_3)_2$	-Cl	g[c] 50 S_A 155(1.4) I
IV-Ileu-PdCl		$-*CH(CH_3)CH_2CH_3$	-Cl	g[a] 46 S_A 177(0.1) I
V-Ileu-PdCl		$-*CH(CH_3)CH_2CH_3$	-Cl	g[a] 71 S_A >250 dec

[a] All these compounds appear at room temperature as glasses that retain the structure of the S_A phase. The glass transition was observed by DSC as a step in the heating curve. [b] The S_A phase undergoes cold crystallization on heating. The subsequent melting process occurs through two crystalline phases, and the S_A mesophase reappears at 179 °C. This complex does not crystallize but shows a transition to a glassy state that retains the structure of the S_A phase. [c] This compound appears at room temperature as a glass that retains the structure of the S_A phase. The glass transition could not be accurately observed by DSC and was estimated by optical microscopy.

The organization of this mesophase can be described as a bilayer-like S_A phase induced by metal complexation and stabilized by interdigitation arising from the special shape of the complexes.[15] This stepped molecular shape, along with the marked increase in the molecular width, makes it difficult for the molecules to tilt within the

Table 3. Transition Temperatures Corresponding to the Binary Mixtures Prepared with the Copper(II) Complexes as Chiral Dopants. Data Correspond to the Cooling Scan



Name	A	R	temperatures, °C
M(I-Val-Cu)	$-OC_{10}H_{21}$	$-CH(CH_3)_2$	C_1 45 C_2 60 **Ch** 73 **I**
M(I-Ileu-Cu)	$-OC_{10}H_{21}$	$-{}^*CH(CH_3)CH_2CH_3$	C_1 38 C_2 57 C_3 68 **Ch** 99 **I**
M(II-Ala-Cu)		$-CH_3$	**C** 59 S_A 74 **Ch** 92 **I**
M(II-Val-Cu)		$-CH(CH_3)_2$	**C** 58 S_A 69 **Ch** 93 **I**
M(II-Leu-Cu)		$-CH_2CH(CH_3)_2$	**C** 59 **Ch** 89 **I**
M(II-Ileu-Cu)		$-{}^*CH(CH_3)CH_2CH_3$	**C** 59 **Ch** 95 **I**
M(III-Ileu-Cu)		$-{}^*CH(CH_3)CH_2CH_3$	**g**[a] 25 C_1 51 C_2 55 S_A 86 **Ch** 108 **I**

[a] The glassy state formed after cooling undergoes cold crystallization at 25 °C to give rise to a first crystalline phase C_1.

smectic layers, thus impeding the formation of the S_C* phase.

Similar observations were made for the dinuclear chloro-bridged palladium(II) complexes (series **IV** and **V**), with the three compounds containing four (**IV-Val-PdCl** and **IV-Ileu-PdCl**) and six (**V-Ileu-PdCl**) aromatic rings showing S_A behavior. However, the presence of four aromatic rings (series **IV**) is not sufficient to support the supramolecular organization required for a mesophase in the acetato-bridged palladium(II) complexes, which have an open-book shape (**IV-Val-PdOAc** and **IV-Ileu-PdOAc**). It appears that a longer aromatic core is needed in the ligands to promote the formation of a smectic A phase, which can only be observed for the biphenyl derivative (**V-Ileu-PdOAc**). The planar molecular shape of the chloro-bridged complexes promotes smectic ordering over wide temperature ranges, a situation in contrast to that in the open-book shaped acetato-bridged palladium complexes. The presence of a more polarizable biphenyl-containing mesogenic core enhances the intermolecular interactions of open-book shaped molecules, resulting in liquid-crystalline behavior. This is similar to the observations made for benzalazine-derived acetato-bridged complexes[16] in comparison to benzaldimine-derived analogues.[11]

Study of Binary Mixtures. The special characteristics of these complexes, which bear stereogenic centers in the most rigid part of the molecule, led us to view them as suitable chiral dopants inducing chiral mesophases in binary mixtures. We chose 6-hexyloxy 4′-decyloxybenzoate as the matrix (phase sequence C−62.5 °C−S_C−78.2 °C−S_A−84.5 °C−N−90.5 °C−I), given that it has already been successfully employed in FLC mixtures.[17] In a previous study, the free oxazoline ligands described here were found to behave as excellent chiral dopants for ferroelectric liquid crystalline mixtures using this matrix and gave rise to high spontaneous polarization values and fast electrooptical switching.[4]

All the mixtures studied contained 10 mol % of the chiral dopant. The mesomorphic behavior of these mixtures was studied by means of optical microscopy and differential scanning calorimetry. Data are gathered in Tables 3 and 4.

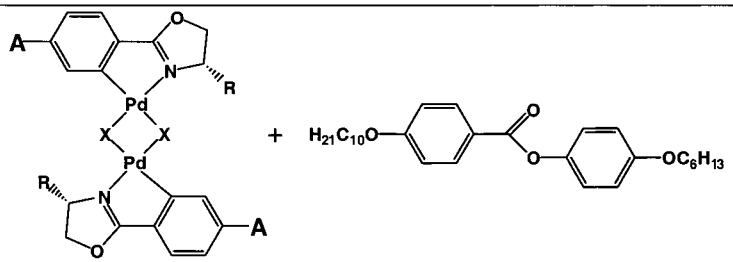
The phase sequence of the pure achiral matrix was not maintained in any of the mixtures. An overall predominance of less ordered mesophases, i.e., cholesteric and S_A, is observed. The most striking effect is the strong stabilization of nematic behavior to the detriment of layered arrangements, particularly the S_C mesophase present in the pure matrix. The special stepped shape of the chiral complex is quite different from the typical rodlike shape of the matrix molecules, despite the similarity between the core of the matrix and that of the ligands (Figure 4). This structural difference gives rise to a marked mismatch in size and shape between host and guest molecules. This effect must be responsible for a disruption in lateral interactions between dopant and matrix molecules. This disruption must be compounded by the steric effect of the

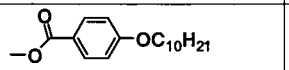
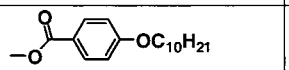
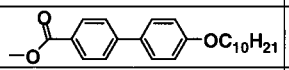
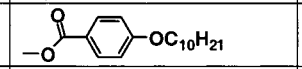
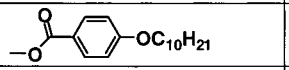
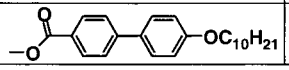
(15) (a) Levelut, A. M.; Ghedini, M.; Bartolino, R.; Nicoletta, F. P.; Rustichelli, F. *J. Phys. France* **1989**, *50*, 113−119. (b) Ghedini, M.; Morrone, S.; Gatteschi, D.; Zanchini, C. *Chem. Mater.* **1991**, *3*, 752−758. (c) Barberá, J.; Levelut, A. M.; Marcos, M.; Romero, P.; Serrano, J. L. *Liq. Cryst.* **1991**, *10*, 119−126.

(16) Espinet, P.; Pérez, J.; Marcos, M.; Ros, M. B.; Serrano, J. L.; Barberá, J.; Levelut, A. M. *Organometallics* **1990**, 2028−2033.

(17) Keller, P.; Cladis, P. E.; Finn, P. L.; Brand, H. R. *J. Phys.* **1985**, *46*, 2203.

Table 4. Transition Temperatures Corresponding to the Binary Mixtures Prepared with the Palladium(II) Complexes as Chiral Dopants. Data Correspond to the Cooling Scan



Name	A	R	X	temperatures, °C
M(IV-Val-PdOAc)		$-CH(CH_3)_2$	$-OOCCH_3$	**C_1** 19 **C_2** 59 **C_3** 72 **Ch** 83 **I** "Components are not completely miscible"[a]
M(IV-Ileu-PdOAc)		$-^*CH(CH_3)CH_2CH_3$	$-OOCCH_3$	**C_1** 21 **C_2** 45 **C_3** 59 **C_4** 75 **Ch** 85 **I** "Components are not completely miscible" [a]
M(V-Ileu-PdOAc)		$-^*CH(CH_3)CH_2CH_3$	$-OOCCH_3$	**g**[b] 28 **C_1** 58 **S_A** 81 **Ch** 104 **I**
M(IV-Val-PdCl)		$-CH(CH_3)_2$	-Cl	**C** 59 **Ch** 93 **I**
M(IV-Ileu-PdCl)		$-^*CH(CH_3)CH_2CH_3$	-Cl	**C** 58 **Ch** 96 **I**
M(V-Ileu-PdCl)		$-^*CH(CH_3)CH_2CH_3$	-Cl	**g**[b] 30 **C** 56 **S_A** 107 **Ch** 114 **I**

[a] These complexes did not show complete miscibility in the matrix. As a consequence, data correspond to mixtures with a percentage of the chiral component slightly below 10 mol %. [b] The glassy state formed after cooling undergoes cold crystallization at 25 °C to give rise to a crystalline phase (denoted C).

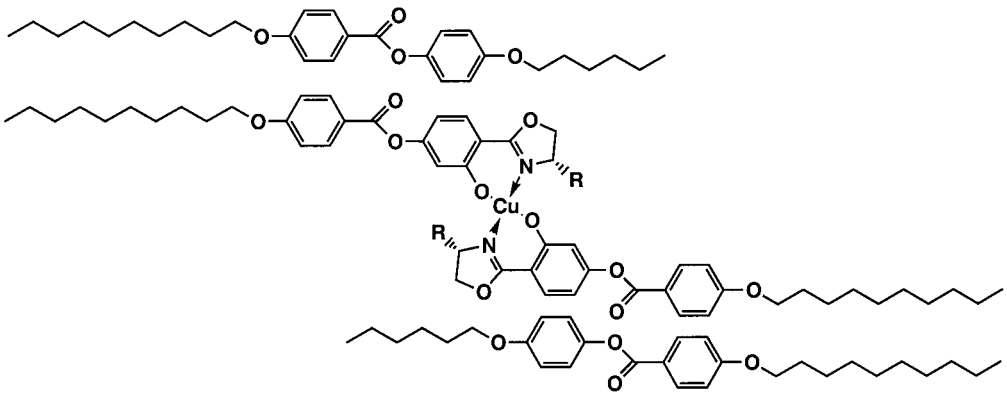


Figure 4. Mismatch between the liquid crystal host and the chiral dopant. The difference in shape and size must account for the predominance of less ordered nematic mesomorphism to the detriment of the layered mesophases present in the host.

alkyl groups in the stereogenic centers, which lie out of the coordination plane. The smectic A mesophase was only observed in mixtures with chiral dopants bearing four [copper(II) complexes] or six [copper(II) and palladium(II) complexes] aromatic rings. In the former case, the probability of forming the orthogonal layered organization is higher for the compounds with the smallest alkyl groups in the stereogenic centers (i.e., **II-Ala-Cu** and **II-Val-Cu** versus **II-Leu-Cu** and **II-Ileu-Cu**).

Hence, these chiral oxazoline complexes proved to be excellent at inducing broad ranges of cholesteric mesomorphism. Further studies on this subject are currently in progress.

Conclusions

Aryloxazolines derived from (*S*)-*β*-amino alcohols have been used as chiral building blocks for the synthesis of copper(II) and palladium(II) complexes with liquid-crystalline behavior. Most of them show S_A mesomorphism in their pure state, which may be favored by interactions between their highly rigid mesogenic nuclei. A special characteristic of these complexes is the confinement of stereogenic centers within a conformationally restricted ring in the rigid core of the molecule. This feature makes them suitable for the induction of chiral supramolecular organizations in the mesophase. Results have been especially important when complexes have been used as chiral dopants in a $N-S_A-S_C$ host. In this sense, all the complexes have revealed themselves as good inducers of broad ranges of chiral nematic behavior.

Another interesting consequence of the presence of stereogenic centers in a rigid coordination environment is the formation of a single diastereoisomer upon or-

thopalladation of the corresponding oxazoline ligands to give nonplanar acetato-bridged complexes. Indeed, only acetato-bridged complexes with trans configuration have been detected by ^{1}H NMR. The reason may lie in steric hindrance between the alkyl groups in the stereogenic centers of both oxazoline rings of the nonplanar complex.

Experimental Section

General Procedure for the Preparation of the Copper(II) Complexes. To a mixture of the oxazoline ligand (0.4 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.2 mmol) was added absolute ethanol (10 mL). The mixture was stirred for 5 min and CH_2Cl_2 (10 mL) was added to give a green solution. After 30 min the solvent was evaporated. The solid was dissolved in acetone (10 mL) and ethanol (10 mL) was added. The volume of the solution was reduced to 10 mL and the product precipitated at ambient temperature. The green solid was filtered off and washed with ethanol (10 mL).

I-Val-Cu. Yield: 90%. MS (FAB) *m*/*z* (%) = 1207 (51, $[2M - ligand]^+$), 846 (28, $[M + Cu]^+$), 785 (93, $[M]^+$), 422 (100, $[M - ligand]^+$). Anal. Calcd for $C_{44}H_{68}N_2O_6Cu$: C, 67.36; H, 8.74; N, 3.57. Found: C, 67.74; H, 9.08; N, 3.79.

I−Ileu−Cu. Yield: 92%. MS (FAB) *m*/*z* (%) = 1249 (17, $[2M - ligand]^+$), 874 (28, $[M + Cu]^+$), 812 (38, $[M]^+$), 438 (100, $[M - ligand]^+$). Anal. Calcd for $C_{46}H_{72}N_2O_6Cu$: C, 67.99; H, 8.93; N, 3.45. Found: C, 68.35; H, 9.23; N, 3.63.

III-Ileu-Cu. Yield: 85%. MS (FAB) *m*/*z* (%) = 1839 (91, $[2M - ligand]^+$), 1268 (100, $[M + Cu]^+$), 1205 (72, $[M]^+$). Anal. Calcd for $C_{72}H_{88}N_2O_{10}Cu$: C, 71.76; H, 7.36; N, 2.32. Found: C, 71.01; H, 7.60; N, 2.40.

II-Ala-Cu. Yield: 90%. MS (FAB) *m*/*z* (%) = 1484 (93, $[2M - ligand]^+$), 1030 (74, $[M + Cu]^+$), 967 (100, $[M]^+$). Anal. Calcd for $C_{58}H_{76}N_2O_{10}Cu$: C, 66.96; H, 7.08; N, 2.89. Found: C, 66.80; H, 7.48; N, 2.87.

II-Val-Cu. Yield: 95%. MS (FAB) *m*/*z* (%) = 1568 (99, $[2M - ligand]^+$), 1088 (90, $[M + Cu]^+$), 1024 (90, $[M]^+$). Anal. Calcd for $C_{54}H_{68}N_2O_{10}Cu$: C, 67.98; H, 7.48; N, 2.73. Found: C, 67.86; H, 7.93; N, 2.70.

II-Leu-Cu. Yield: 89%. MS (FAB) *m*/*z* (%) = 1609 (65, $[2M - ligand]^+$), 1114 (43, $[M + Cu]^+$), 1053 (55, $[M + 1]^+$). Anal. Calcd for $C_{60}H_{80}N_2O_{10}Cu$: C, 68.45; H, 7.66; N, 2.66. Found: C, 67.80; H, 8.46; N, 2.65.

II-Ileu-Cu. Yield: 90%. MS (FAB) *m*/*z* (%) = 1609 (47, $[2M - ligand]^+$), 1114 (43, $[M + Cu]^+$), 1052 (50, $[M]^+$). Anal. Calcd for $C_{60}H_{80}N_2O_{10}Cu$: C, 68.45; H, 7.66; N, 2.66. Found: C, 68.26; H, 8.17; N, 2.62.

General Procedure for the Synthesis of the Palladium(II) Complexes. (a) Acetato-Bridged Palladium(II) Complexes. The oxazoline ligand (0.3 mmol) was added to a hot solution of $Pd(OAc)_2$ (0.3 mmol) in acetic acid and the mixture was heated under reflux for 30 min. The yellow solution was allowed to cool and the product precipitated as yellow crystals, which were filtered off and washed with cold acetone.

(b) Chloro-Bridged Palladium(II) Complexes. To a stirred solution of the acetate-bridged complex (0.1 mmol) in CH_2Cl_2 was added a stoichiometric amount (3.45 mL, 0.058 N) of a solution of hydrogen chloride in methanol. The reaction mixture was stirred at ambient temperature for 12 h, the volume of the solution was reduced to 5 mL, and 30 mL acetone was added. The volume of the solution was again reduced to 10 mL and the product precipitated upon cooling at −10 °C. The product was filtered off and washed with cold acetone.

IV-Val-PdOAc. Yield: 69%. ^{1}H NMR ($CDCl_3$) 0.82 (m, 18 H), 1.26−1.83 (34 H), 2.05 (s, 6 H), 3.45 (m, 2 H), 3.70 (m, 2 H), 4.03 (t, 4 H, J = 6.2 Hz), 4.17 (m, 2 H), 6.82 (dd, 2 H, J = 2.1, 8.1 Hz), 6.91 (d, 2 H, J = 2.1 Hz), 7.11 (d, 2 H, J = 8.1 Hz), 6.95 (d, 4 H, J = 8.7 Hz), 8.06 (d, 4 H, J = 8.7 Hz). ^{13}C NMR ($CDCl_3$) 14.1, 15.4, 24.0, 18.5−31.9, 66.3, 68.4, 71.5, 114.3, 117.5, 121.3, 124.7, 125.8, 126.7, 132.2, 149.1, 151.6, 163.6, 164.9, 172.9, 181.1. MS (FAB) *m*/*z* (%) = 1260 (69, M^+), 1199 (99, $[M - O_2C_2H_5]^+$), 1141 (100, $[M - O_4C_4H_{10}]^+$). Anal. Calcd for $C_{62}H_{82}N_2O_{12}Pd_2$: C, 59.09; H, 6.56; N, 2.22. Found: C, 58.87; H, 6.85; N, 2.19.

IV-Val-PdCl. Yield: 73%. ^{1}H NMR ($CDCl_3$) 0.88 (m, 18 H), 1.26−2.48 (34 H), 4.02 (t, 4 H, J = 6.2 Hz), 4.17 (m, 2 H), 4.53 (m, 4 H), 6.92 (m, 6 H), 7.12 (d, 2 H, J = 2.0 Hz), 7.18 (d, 2 H, J = 8.2 Hz), 8.10 (d, 4 H, J = 8.6 Hz). ^{13}C NMR ($CDCl_3$) 14.1, 14.4, 18.5−31.9, 66.9, 68.3, 70.3, 114.3, 118.4, 121.4, 126.1, 126.6, 127.9, 132.3, 146.4, 151.6, 164.5, 163.6, 174.2. MS (FAB) *m*/*z* (%) = 1177 (27, $[M - Cl]^+$), 712 (100, $[M - ligand]^+$). Anal. Calcd for $C_{58}H_{76}Cl_2N_2O_8Pd_2$: C, 57.43; H, 6.32; N, 2.31. Found: C, 57.09; H, 6.77; N, 2.32.

IV-Ileu-PdOAc. Yield: 78%. ^{1}H NMR ($CDCl_3$) 0.79 (m, 18 H), 1.13−1.86 (m, 38 H), 2.05 (s, 6 H), 3.60 (m, 2 H), 3.76 (m, 2 H), 4.03 (t, 4 H, J = 6.3 Hz), 4.18 (m, 2 H), 6.85 (dd, 2 H, J = 2.1, 8.1 Hz), 6.95 (d, 4 H, J = 9.6 Hz), 6.92 (d, 2 H, J = 2.1 Hz), 7.11 (d, 2 H, J = 8.1 Hz), 8.05 (d, 4 H, J = 9.6 Hz). ^{13}C NMR ($CDCl_3$) 11.9, 12.8, 14.1, 24.0, 22.7−36.2, 64.3, 68.4, 70.9, 114.4, 117.7, 121.3, 124.6, 125.8, 128.7, 132.2, 149.2, 151.5, 163.6, 165.0, 172.9, 181.1. MS (FAB) *m*/*z* (%) = 1288 (61, M^+), 1227 (100, $[M - O_2C_2H_5]^+$), 1169 (92, $[M - O_4C_4H_{10}]^+$). Anal. Calcd for $C_{64}H_{86}N_2O_{12}Pd_2$: C, 59.67; H, 6.73; N, 2.17. Found: C, 59.36; H, 7.01; N, 2.14.

IV-Ileu-PdCl. Yield: 72%. ^{1}H NMR ($CDCl_3$) 0.83−0.95 (m, 18 H), 1.09−2.29 (38 H), 4.02 (t, 4 H, J = 6.5 Hz), 4.27 (m, 2 H), 4.52 (m, 4 H), 6.93 (m, 6 H), 7.13 (d, 2 H, J = 2.2 Hz), 7.16 (d, 2 H, J = 8.2 Hz), 8.09 (d, 4 H, J = 8.6 Hz). ^{13}C NMR ($CDCl_3$) 11.8, 12.1, 14.1, 22.7−36.1, 64.9, 65.7, 68.3, 70.4, 114.3, 118.4, 121.4, 126.2, 126.5, 127.9, 132.3, 146.6, 151.6, 163.5, 164, 174.1, 174.3. MS (FAB) *m*/*z* (%) = 1205 (22, M^+), 726 (100, $[M - ligand]^+$). Anal. Calcd for $C_{60}H_{80}Cl_2N_2O_8Pd_2$: C, 58.07; H, 6.50; N, 2.26. Found: C, 57.95; H, 6.78; N, 2.24.

V-Ileu-PdOAc. Yield: 70%. ^{1}H NMR ($CDCl_3$) 0.82 (m, 18 H), 1.15−1.85 (38 H), 2.07 (s, 6 H), 3.63 (m, 2 H), 3.78 (m, 2 H), 4.00 (t, 4 H, J = 6.3 Hz), 4.21 (m, 2 H), 6.89 (dd, 2 H, J = 1.8, 7.8 Hz), 6.96 (d, 2 H, J = 1.8 Hz), 6.99 (d, 4 H, J = 8.7 Hz), 7.14 (d, 2 H, J = 7.8 Hz), 7.58 (d, 4 H, J = 8.7 Hz), 7.68 (d, 4 H, J = 8.4 Hz), 8.16 (d, 4 H, J = 8.4 Hz). ^{13}C NMR ($CDCl_3$) 11.9, 12.8, 14.1, 24.1, 22.7−36.2, 64.3, 68.2, 71.0, 115.0, 117.6, 124.5, 125.8, 127.2, 128.9, 126.6, 128.4, 130.6, 131.9, 146.1, 149.3, 151.4, 159.6, 165.2, 172.9, 181.1. MS (FAB) *m*/*z* (%) = 1440 (60, M^+), 1381 (100, $[M - O_2C_2H_5]^+$), 1322 (95, $[M - O_4C_4H_{10}]^+$). Anal. Calcd for $C_{76}H_{94}N_2O_{12}Pd_2$: C, 63.37; H, 6.58; N, 1.94. Found: C, 63.06; H, 6.80; N, 1.96.

V-Ileu-PdCl. Yield: 48%. ^{1}H NMR ($CDCl_3$) 0.86−0.92 (m, 18 H), 1.26−2.29 (m, 38 H), 3.99 (t, 4 H, J = 6.3 Hz), 4.27 (m, 2 H), 4.52 (m, 4 H), 6.95 (m, 6 H), 7.20 (m, 4 H), 7.57 (d, 4 H, J = 8.4 Hz), 7.66 (d, 4 H, J = 8.1 Hz), 8.17 (d, 4 H, 4 H, J = 8.1 Hz). ^{13}C NMR ($CDCl_3$) 11.8, 12.1, 14.1, 22.7−36.1, 65.2, 65.7, 68.2, 70.4, 115.0, 118.4, 126.2, 127.4, 128.1, 130.8, 126.6, 128.4, 130.8, 131.9, 145.9, 146.7, 151.5, 159.6, 164.7, 174.1, 174.3. MS (FAB) *m*/*z* (%) = 1358 (19, $[M - Cl]^+$), 802 (100, $[M - ligand]^+$). Anal. Calcd for $C_{72}H_{88}Cl_2N_2O_8Pd_2$: C, 62.07; H, 6.37; N, 2.01. Found: C, 61.86; H, 6.56; N, 2.04.

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