

10% toluene in hexanes after the starting materials had been removed from the column with 100% hexanes. Crystals were grown from CH_2Cl_2 /hexanes in approximately 70% yield; mp 202–204 °C (dec); ^1H NMR (CDCl_3) δ 5.14 (10 H, s), 2.36 (3 H, s); IR (CHCl_3 solution) ν_{CO} 1983 (s), 1946 (m), 1801 (s) cm^{-1} . Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{AsO}_3\text{Ru}_2$: C, 33.21; H, 2.59; As, 14.80. Found: C, 32.93; H, 2.69; As, 14.59.

Preparation of $[\{\text{CpRu}(\text{CO})\}_2(\mu\text{-CO})(\mu\text{-AsC}_6\text{H}_5)\}$ (3). 2 (0.350 g, 0.59 mmol) and *cyclo*-(AsC_6H_5)₆ (0.54 g, 0.59 mmol) were combined in 100 mL of xylenes, and the reaction was heated to 110 °C overnight under nitrogen. The xylenes were removed from the reaction, and then the residue was placed on an alumina column and eluted with dichloromethane. One red-orange product was isolated off the column in good yield (80%) and identified as 4: mp 240–243 °C; IR (CH_2Cl_2) ν_{CO} = 1990 (s), 1953 (m), 1780 (s) cm^{-1} ; ^1H NMR (CDCl_3) δ 7.50–7.12 (m, 5 H), 5.30 (s, 10 H). Diffraction-grade crystals were grown from CH_2Cl_2 /hexanes. Anal. Calcd for $\text{C}_{19}\text{H}_{15}\text{AsO}_3\text{Ru}_2$: C, 40.15; H, 2.66; As, 13.18. Found: C, 39.89; H, 2.75; As, 13.01.

Crystallographic Structure Determinations. Crystallographic data are collected in Table I. For both structures, crystals were mounted on glass fibers, unit-cell parameters were obtained

from the angular settings of 25 reflections ($30^\circ \leq 2\theta \leq 35^\circ$), and empirical corrections for absorption were applied to the diffraction data. For 2, the centrosymmetric alternative *Pnma* was suggested by *E* statistics and verified by the presence of mirror-plane symmetry. The structures were solved by direct methods. All non-hydrogen atoms were anisotropically refined, and hydrogen atoms were incorporated as idealized contributions ($d(\text{CH}) = 0.96$ Å). Tables II and III contain the atomic coordinates for 2 and 3, and Tables IV and V contain selected bond distances and angles. All computations used SHELXTL (5.1) software (G. Sheldrick, Nicolet XRD, Madison, WI).

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Supplementary Material Available: Tables of bond distances, bond angles, anisotropic thermal parameters and hydrogen atom coordinates for 2 and 3 (6 pages); listings of observed and calculated structure factors for 2 and 3 (27 pages). Ordering information is given on any current masthead page.

Liquid Crystals Based on Ortho-Palladated Azines: Nonplanar Mesogens

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The synthesis and mesogenic properties of the complexes $[\text{Pd}(\text{C}_n\text{H}_{2n+1}\text{OC}_6\text{H}_3\text{CH}=\text{N}-\text{N}=\text{CHC}_6\text{H}_4\text{OC}_n\text{H}_{2n+1})\{\mu\text{-O}_2\text{CCH}_3\}_2]$ [I(*n*), *n* = 2, 6–10, 12, and 14] and $[\text{Pd}(\text{C}_{10}\text{H}_{21}\text{OC}_6\text{H}_3\text{CH}=\text{N}-\text{N}=\text{CHC}_6\text{H}_4\text{OC}_{10}\text{H}_{21})\{\mu\text{-X}\}_2]$ [X = Cl (II), Br (III), and SCN (IV)] are described. Not unexpectedly, II, III, and IV, which are planar dimers, show S_C mesophases. More interestingly the open-book-shaped dimers I(*n*) also exhibit N and/or S_C mesophases if the alkoxylic chains are sufficiently long (*n* ≥ 6). In spite of their unusual molecular shape, the mesophases resemble those produced by typical rodlike molecules.

Introduction

Organometallic and coordination compounds displaying liquid-crystalline behavior are currently of great interest as new mesogenic materials able to extend or improve the properties of the liquid-crystalline materials so far available, most of which are organic molecules. Linear (as in Ag^1) and square-planar (as in Pd^{II}) coordinations are capable of retaining beyond the melting point the ordered arrangements of individual molecules that give rise to mesogenic behavior, and some compounds containing these elements with liquid-crystal properties have been recently described.^{1–6}

We have reported^{7–9} some ortho-palladated compounds of imines $[\text{Pd}(p\text{-RC}_6\text{H}_3\text{C}(\text{Y})=\text{N}-\text{C}_6\text{H}_4\text{R}'\text{-}p)\{\mu\text{-X}\}_2]$ (R, R' = alkyl, alkoxy, and polar groups; Y = H and CH_3 ; X = Cl, Br, SCN, and OAc), many of which were mesogenic even when the free imines were not liquid crystals. It became apparent from these studies that a methyl sub-

Table I. Analytical Data, Molecular Weights (Calculated Values in Parentheses), and Yields

compd	N	C	H	MW	yield, %
I(2)	6.10 (6.08)	51.53 (52.13)	4.70 (4.81)	953 (921.6)	58
I(6)	5.04 (4.89)	58.31 (58.69)	5.99 (6.68)	1201 (1146.1)	37
I(7)	4.47 (4.66)	59.57 (59.95)	7.49 (7.04)	1175 (1202.2)	63
I(8)	4.65 (4.64)	64.10 (63.72)	7.85 (7.68)	1283 (1258.3)	52
I(9)	4.16 (4.26)	61.80 (62.14)	7.99 (7.67)	1391 (1314.4)	55
I(10)	4.16 (4.09)	62.99 (63.10)	7.70 (7.94)	1397 (1370.5)	50
I(12)	3.80 (3.78)	64.44 (64.81)	8.18 (8.43)	1539 (1482.7)	55
I(14)	3.36 (3.27)	62.53 (62.36)	8.21 (8.29)	1560 (1594.9)	43
II	4.34 (4.23)	61.75 (61.72)	7.37 (7.77)	1278 (1323.3)	85
III	4.07 (3.97)	58.14 (57.84)	7.06 (7.28)	1354 (1412.2)	87
IV	6.04 (6.14)	61.85 (61.44)	7.15 (7.51)	1404 (1368.5)	82

stituent in the azomethyne carbon or a bent bridge, such as acetate, diminished mesogenic behavior to such an ex-

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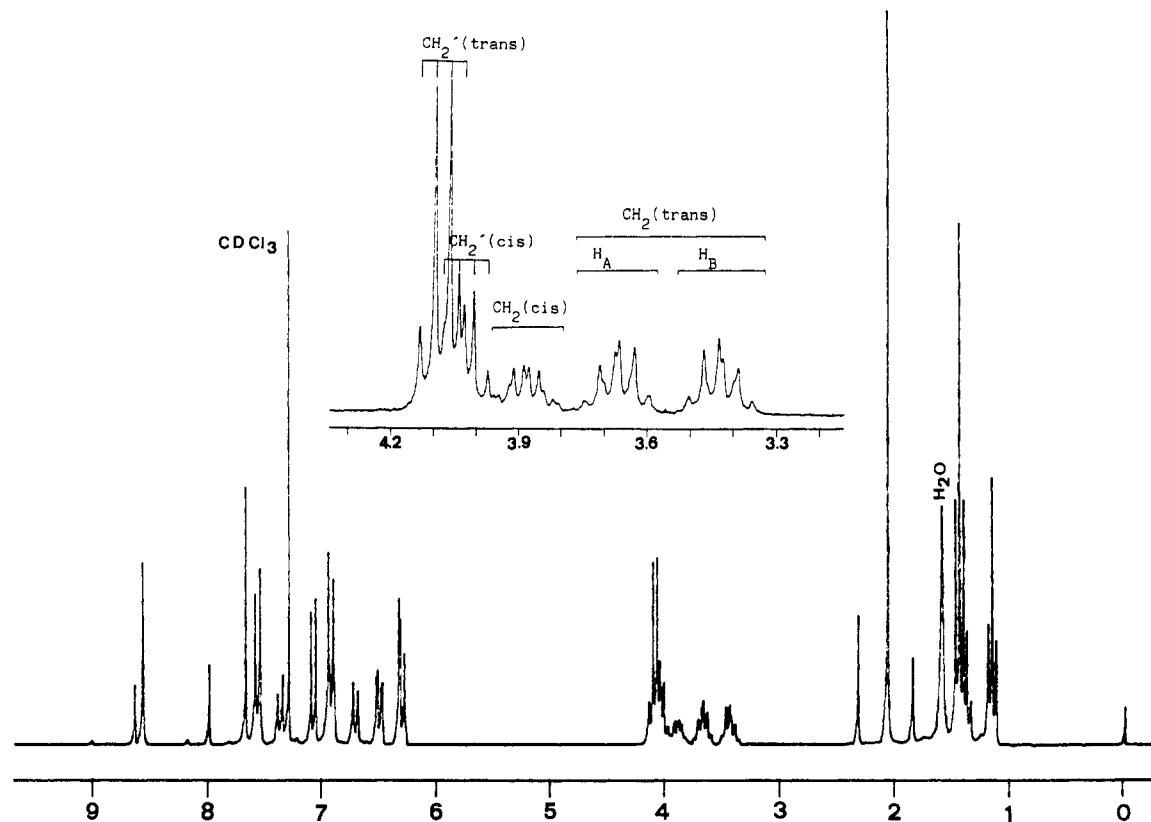


Figure 1. ^1H NMR spectra of compound I(2), $[\text{Pd}(\text{C}_2\text{H}_5\text{OC}_6\text{H}_3\text{CH}=\text{N}-\text{N}=\text{CHC}_6\text{H}_4\text{OC}_2\text{H}_5)(\mu\text{-O}_2\text{CCH}_3)_2]$.

tent that these derivatives either were not liquid crystals or were only monotropic.

In this paper we report the synthesis and properties of compounds derived from monocyclopalladation of azines ($p\text{-C}_n\text{H}_{2n+1}\text{OC}_6\text{H}_4\text{CH}=\text{N}-$) $_2$, which show a greatly improved range of mesogenic behavior.

Results and Discussion

Synthesis and Characterization of the Complexes.

Mono-ortho-palladation of the azines ($p\text{-C}_n\text{H}_{2n+1}\text{OC}_6\text{H}_4\text{CH}=\text{N}-$) $_2$ ($n = 2, 6-10, 12, 14$) is carried out by refluxing mixtures of $[\text{Pd}(\text{O}_2\text{CCH}_3)_2]_3$ and the corresponding azine (Pd:azine = 1:1) in anhydrous acetic acid, as recently reported for other azines.¹⁰ Refluxing times of 45 min give reasonable yields of the mono-ortho-palladated complexes (40–60% after recrystallization).

The microanalytical data (Table I) are consistent with the formulation of the products as ortho-palladated in only one ring. Molecular weight determinations on the complexes in CHCl_3 solution show that they are dimeric, as expected; molecular weight data are collected in Table I. IR data are of little structural value since several absorptions [$\nu(\text{C}=\text{N})$ ortho-palladated, $\nu(\text{C}=\text{N})$ free, $\nu(\text{C}=\text{C})$ rings, $\nu(\text{C}=\text{O})$ acetate] overlap in the range 1620–1530 cm^{-1} .

The ^1H NMR spectra are far more informative. Table II lists the parameters of I(2) and I(10) as representative of the series of acetato-bridged complexes (the rest of the I(n) complexes show little variation except for the different intensity of the signal at ca. δ 1.30), and Figure 1 shows the spectrum of I(2). The azomethine hydrogens give rise to two pairs of signals (intensity ratio ca. 3:1), which means that the products are ortho-palladated in only one ring (pairs of signals) and that the two possible isomers, trans and cis, are present (in ca. 3:1 ratio) as previously observed for related complexes.^{10,11}

One CH_3CO_2^- signal (trans isomer) and two other CH_3CO_2^- signals (cis isomer) are consistently observed.

All the I(n) complexes prepared were composed of this mixture of trans and cis isomers. It was calculated from the relative intensities of the azomethine protons that all the mixtures contained between 72% and 76% of the trans isomer; three independent preparations of I(10) gave a composition of the final mixture within this range, and the same mixture was produced when I(10) was converted into II with HCl and II (which has no isomers) was converted back to I(10) as described in the Experimental Section (see Scheme I).

In the trans isomer, the two hydrogens in the first methylene groups of the alkoxy chains (only these are distinctly observable) couple to each other, thus proving to be chemically inequivalent. These methylene groups appear in the range δ 3.3–4.2, and the expansion of their signals is shown in Figure 1. The two multiplets under the square bracket of CH_2 (trans) in the Figure 1 collapse to an AB system ($J = 8.9$ Hz) on irradiation at δ 1.17, showing that the hydrogens in these methylene groups are diastereotopic. A similar effect is observed in the multiplet under the square bracket of CH_2 (cis) in Figure 1; on irradiation at δ 1.46 the signal collapses to a degenerated AB

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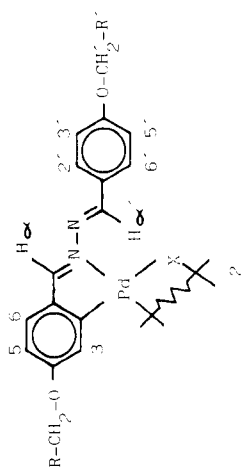
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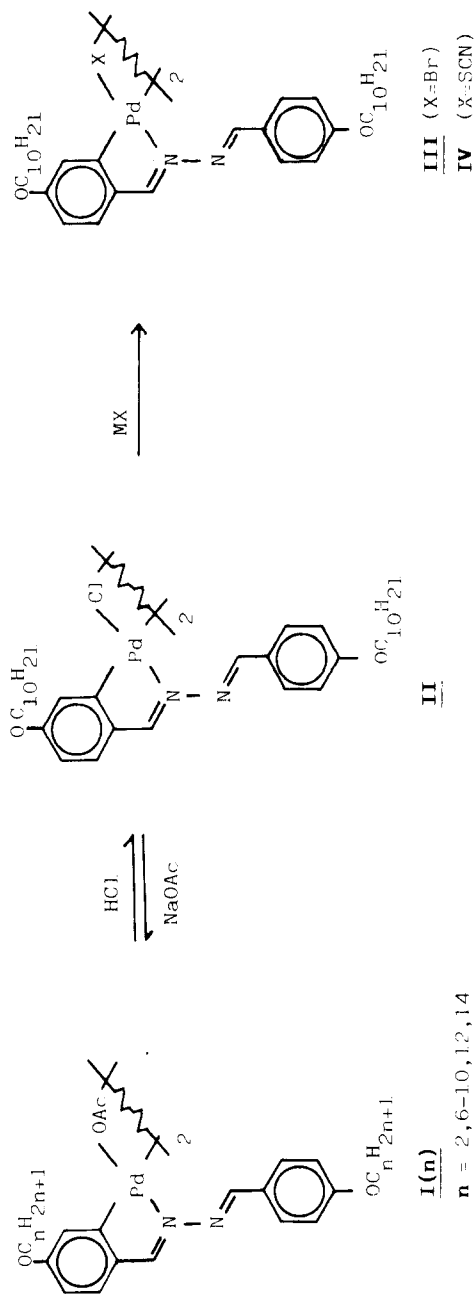
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Table II. The 200-MHz Spectra of I(2), I(10), II, III, and IV Complexes in CDCl₃^a

compd	X	δ/ppm and multiplicities ^{c,e}											J/Hz/s			
		R'	R	H6	H5	H3	H2', 6'	H3', 5'	Hα	Hα'	CH ₂	CH ₂ '	X(CH ₃ COO) ⁻	J _{H5-H6}	J _{H5-H3}	J _{Hβ-H3'}
I(2)- <i>trans</i>	AcO-	CH ₃	7.05 (d)	6.47 (dd)	6.30 (d)	7.53 (d)	6.89 (d)	7.64 (s)	8.53 (s)	3.75-3.55 (m), 3.55-3.35 (m) ^f	4.08 (q) ^f	2.07 (s)	2.07 (s)	8.4	2.4	8.8
I(2)- <i>cis</i>	AcO-	CH ₃	-	-	-	7.34 (d)	6.68 (d)	7.96 (s)	8.60 (s)	3.95-3.80 (m) ^f	4.03 (q) ^f	[2.33 (s), 1.85 (s)]	-	-	-	8.8
I(10)- <i>trans</i>	AcO-	C ₉ ^b	7.03 (d)	6.49 (dd)	6.30 (d)	7.54 (d)	6.89 (d)	7.64 (s)	8.55 (s)	[3.66-3.50 (m), 3.38-3.23 (m)]	3.99 (t)	2.09 (s)	8.3	2.3	8.9	
I(10)- <i>cis</i>	AcO-	C ₉	-	-	-	7.35 (d)	6.71 (d)	7.95 (s)	8.60 (s)	3.95-3.70 (m)	-	[2.34 (s), -]	-	-	-	9.0
II	Cl	C ₉	7.19 (d)	6.60 (dd)	6.99 (d)	7.72 (br) ^g	6.87 (br)	8.14 (s)	9.01 (s)	[3.99 (t) ^h , 4.05 (t) ^h]	-	-	8.4	2.0	-	-
III	Br	C ₉	7.20 (d)	6.59 (dd)	7.16 (d)	7.73 (br) ^g	6.89 (br)	8.13 (s)	8.97 (s)	[4.05 (t) ^h , 4.10-3.90 (m) ^g]	-	-	8.3	2.2	-	-
IV- <i>trans</i>	SCN	C ₉	7.23 (d)	6.58 (dd)	6.52 (d)	7.81 (d)	7.00 (d)	8.22 (s)	8.86 (s)	-	-	-	8.4	2.1	8.6	
IV- <i>cis</i>	SCN	C ₉	6.65 (d)	6.40 (dd)	-	7.96 (d)	6.99 (d)	7.50 (s)	9.52 (s)	3.73 (t)	-	-	8.4	- ^m	8.8	

^a Assignments confirmed by double-resonance experiments and by comparison with the imine complexes⁸ and ligands²² previously described. ^b C₉ = *n*-nonyl group. ^c s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. ^d - *cis* signals overlapped by *trans* signals. ^e R and R' protons of compounds I(10), II, III, IV appeared in the range δ 0.8-1.9. Compound I(2) (*trans* isomer) CH₃ δ 1.16 (t), CH₂' δ 1.45 (t); *cis* isomer CH₃ δ 1.38 (t), CH₂' (-). ^f Coupling constants from first-order analysis. ^g Compounds I(2) *trans* isomer *J*_{CH₂-CH₃'} = 7.0 Hz, *cis* isomer *J*_{CH₂-CH₃'} = 6.9 Hz. Compound I(10) *trans* isomer *J*_{CH₂-R} = 6.6 Hz. ^h An AB system appears by irradiation at δ 1.17, δ 3.59 (d, 1 H, *J* = 8.9 Hz, H_A), 3.35 (d, 1 H, *J* = 8.9 Hz, H_B). ⁱ These signals are modified by irradiation at δ 1.46; quartets at δ 4.08 and δ 4.03 collapsed to singlets. A multiplet at δ 3.95-3.80 appears as a degenerated AB system. ^j Hump signals. Unresolved doublet. ^k Distorted triplets. ^l Two overlapped triplets. ^m *J* value not determined.}}

Scheme I



I(n)

n = 2, 6-10, 12, 14

III (X=Br)

IV (X=SCN)

Table III. Optical, Thermal,^a Thermodynamic,^b and Thermogravimetric (TG) Data of Complexes I(n) to IV

complex	X	C	→	C	→	S	→	SC	→	N	→	I	TG
I(2)	AcO ⁻		209.2 (11.1)										222.5
I(6)	AcO ⁻		170.8 (85.0)								159.3 ^c		212.5
I(7)	AcO ⁻		96.2	(43.9)	114.6				152.4 (0.3)		164.7 (1.2)		215.3
I(8)	AcO ⁻		126.4 (1.2)		135.3 (58.4)		141.6	(6.9)	145.4		153.7 (2.8)		243.0
I(9)	AcO ⁻		106.3	(83.3)	115.1				152.9 (9.6)				235.6
I(10)	AcO ⁻		131.8 (139.7)						151.1 (10.8)				230.0
I(12)	AcO ⁻		74.6 (8.0)		99.0 (80.9)				147.5 (7.2)				218.0
I(14)	AcO ⁻		101.8 (49.3)		109.3 (53.9)				141.1 (67.0)				207.0
II	Cl		102.0 (35.0)						226.0				222.5
III	Br		118.0 (67.1)						249.0				264.0
IV	SCN		113.8 (2.4)		123.8 (95.8)				218.6 (30.6)				255.0

^aTemperature, °C. ^bParentetical data under the temperatures correspond to ΔH in kJ/mol. ^cMonotropic transition.

system. The methylene groups in the non-ortho-metalated ring (CH₂'(trans) and CH₂'(cis)), which give the two overlapped quartets (trans and cis isomers overlapping) collapse to singlets on irradiation at δ 1.46, showing that the hydrogens CH₂' (Table II) in practice have the same chemical shift although they are, in theory, diastereotopic.

As we have reported elsewhere,⁸ this means that the open-book structure of these C,N-ortho-palladated aceto-bridged dimers (see those found crystallographically for [(MeC₆H₃C₇H₄NS)Pd]₂(μ -O₂CMe)₂ and [(MeC₆H₃C₇H₄NO)Pd]₂(μ -O₂CMe)₂)¹² does not undergo inversion under the conditions of observation, contrary to the fluxionality observed in related complexes with η^3 -allyl in place of C,N-ortho-metalated ligands¹³⁻¹⁵ (which also have an open-book structure in the solid state).^{16,17} Consequently the trans isomer must be chiral, and the products are really a mixture of 25% of the cis isomer and 75% of a racemic mixture of the two enantiomers of the trans isomer.

The ¹H NMR spectra of the halo-bridged complexes II and III are straightforward since only the trans isomer is present. Moreover, the planar structure of the dimers (see the structure found crystallographically for *trans*-[Pt₂(μ -Cl)₂(C₆H₃N=NC₆H₄)₂]¹⁸ produces equivalence of the hydrogens in the methylene groups, giving rise to a distorted "triplet" by coupling to the rest of the chain. A notable feature is the broadening of the aromatic hydrogens of the non-ortho-metalated ring, which could not be resolved by heating (+60 °C) or cooling (-60 °C). We have no explanation for this broadening, which seems to be associated with planar halo-bridged dimers.

Finally, in the spectrum of the thiocyanate-bridged complex IV, where isomerism is more likely to take place, only two isomers (probably cis and trans isomers) were detected (ca. 60% and 40%). The fact that the product

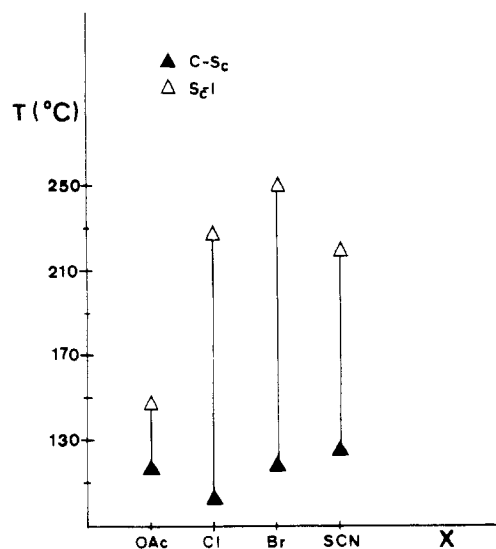


Figure 2. Transition temperatures of the complexes [Pd-(C₁₀H₂₁OC₆H₃CH=N-N=CHC₆H₄OC₁₀H₂₁)(μ -X)]₂.

is a mixture of isomers seemingly has a positive effect on its properties as mesogenic material.

Mesogenic Behavior. All the complexes synthesized, with the exception of I(2), are mesogens. The compounds are stable in air within the temperature ranges of the measurements, although they begin to decompose after long periods at high temperatures. The transition temperatures, enthalpy data, and thermogravimetric data of the complexes are summarized in Table III.

Most of the complexes exhibit crystalline polymorphism, which was detected by DSC but not by optical microscopy. The mesophases shown by the complexes were identified as S_C and N mesophases by their optical textures, which are similar to those observed for classical rodlike organic compounds^{19,20} except for their higher viscosities.

The nematic mesophase showed the marbled texture on heating and the schlieren texture on cooling. The smectic C mesophase is clearly identified on the cooling process

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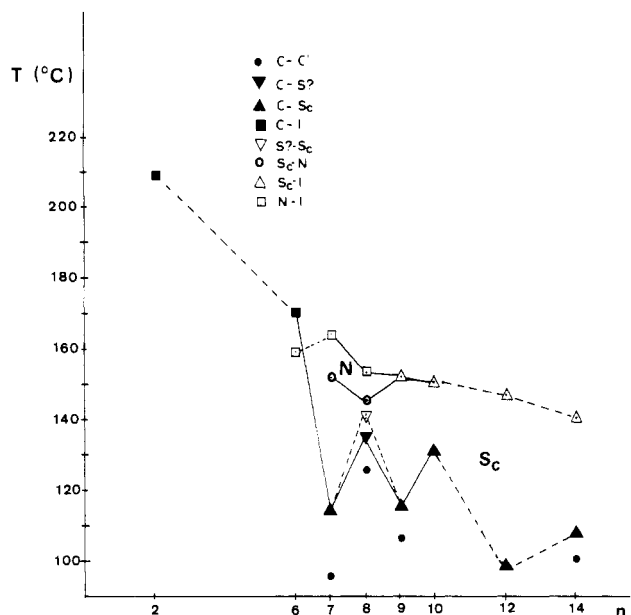


Figure 3. Transition temperatures as a function of the alkoxy chain length for the complexes $[\text{Pd}(\text{C}_n\text{H}_{2n+1}\text{OC}_6\text{H}_4\text{CH}=\text{N}-\text{N}=\text{CHC}_6\text{H}_4\text{OC}_n\text{H}_{2n+1})(\mu\text{-O}_2\text{CCH}_3)_2]$.

by their typical schlieren and focalconic textures. These textures flash when the sample is subjected to mechanical stress, and as a result a homogeneous texture appears. Formation of bâtonnets was observed when the smectic C phase appears from the isotropic liquid.

Figure 2 represents the mesogenic properties of the four complexes derived from 4,4'-bis(decyloxy)benzalazine and shows the influence of the central bridge X (X = OAc, Cl, Br, and SCN). The four complexes give rise to S_C mesophases. The appearance of an enantiotropic mesophase for the acetato-bridged complex is notable since this bridging group had proved to diminish mesogenic behavior in related complexes derived from imines.^{7,9} Two factors may contribute to this improvement of mesogenic behavior, namely: (i) the extra C=N link in the azines, which may allow a better molecular arrangement (and consequently an increase in molecular interactions) by conferring greater mobility to the non-ortho-palladated moiety, and (ii) the existence of a mixture of cis and trans isomers (the imine-derived complexes were pure trans isomers), which, in addition to decreasing the melting temperatures, may cause the appearance of mesophases.

The Cl-, Br-, and SCN-bridged complexes show wider mesophase ranges, greater thermal stability (see Table III), and lower melting points than the OAc-bridged complex.

The influence of the terminal chain length of the ligands on the mesogenic properties of the acetato-bridged complexes $I(n)$ ($n = 2, 6-10, 12,$ and 14) can be seen in Figure 3. The central nonplanar structure of the complexes is expected to disfavor molecular arrangement, and mesomorphism appears only when the increase in the anisotropy of polarizability due to the terminal chains is sufficient.

Thus, the shortest chain ($n = 2$) does not give rise to mesogenic behavior: for $n = 6$ a monotropic nematic phase appears; for $n = 7$ and 8 smectic C and nematic phases are formed; for $n = 9, 10, 12,$ and 14 only a smectic C phase is found. There is a decrease in the transition temperature as the length of the terminal chain increases, and a slight even-odd effect is observed in N-I transitions for complexes $n = 6-9$.

The structure of these dimers can be schematically represented as an open book with the methyl groups of the

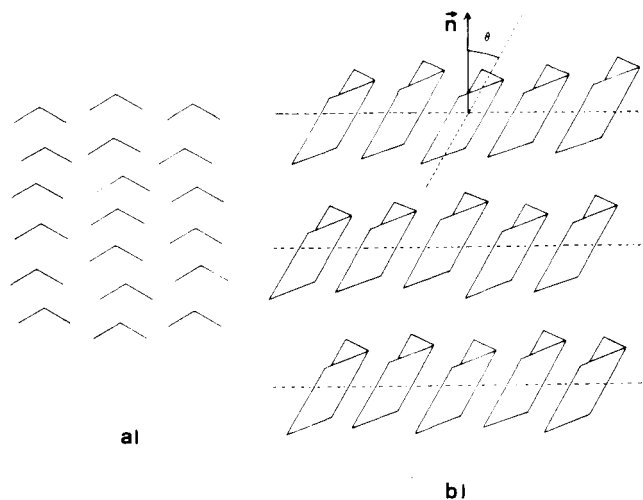


Figure 4. Schematic representation of a section (a) parallel and (b) perpendicular to a layer of an S_C phase of $I(n)$.

acetates in the spine of the book and the main axis of the azine ligands arranged parallel to this spine. The open-book shape of the molecules makes it difficult for the molecules in the mesophase to move freely, and consequently the more ordered smectic arrangements appear frequently and predominate over the more mobile nematic phases.

Although we do not yet have structural information from X-ray studies, from the assumption of the parallel arrangement of the methyl of the acetate group with the main axis of the azine ligand, we suppose that the smectic mesophase has a layer structure as a calamitic S_C phase, but in each layer the molecules are associated like columns (Figure 4 shows a schematic representation of a section parallel (a) and perpendicular (b) to a layer). And we deduce from the optical observations that the distribution of the books in the nematic phase is closer to a calamitic nematic phase than to a discotic nematic one. Preliminary X-ray studies of the mesophases are in agreement with this.

Experimental Section

Synthesis. The synthesis of ligands HL was described in a previous paper.²¹

Synthesis of the Complexes. $\text{Pd}_2(\mu\text{-OAc})_2\text{L}_2$. A suspension of 0.15 g (0.223 mmol) of $\text{Pd}_3(\text{O}_2\text{CCH}_3)_6$ and a stoichiometric amount of the corresponding azine (0.668 mmol; 1:1 Pd:azine) in anhydrous acetic acid (30 mL) was refluxed for 45 min and then removed from the heat and cooled to room temperature. The precipitate was filtered, washed with acetic acid, extracted in warm CHCl_3 (50 mL), and filtered to remove traces of palladium. Evaporation of the CHCl_3 solution to dryness gave a yellow-orange solid, which was stirred with 30 mL of warm CH_2Cl_2 to extract an orange impurity (with a characteristic ^1H NMR singlet at δ 8.47 (CDCl_3)) and filtered. Typically, repetition of this CH_2Cl_2 extraction twice left a yellow-lemmon pure compound (checked by ^1H NMR) only sparingly soluble in CH_2Cl_2 , corresponding to $I(2)$ - $I(14)$ in 40-60% yields.

$\text{Pd}_2(\mu\text{-Cl})_2\text{L}_2$. To a stirred solution of $I(10)$ (0.2 g, 0.146 mmol) in CHCl_3 (30 mL) was added dropwise a methanolic solution of HCl (630 μL , 0.464 N). After 1 h of stirring, the solution was evaporated to dryness, and the residue was stirred with acetone (10 mL), filtered, washed with 10 mL of acetone, and dried to give yellow II in 85% yield.

$\text{Pd}_2(\mu\text{-Br})_2\text{L}_2$. A suspension of $I(10)$ (0.13 g, 0.196 mmol) and KBr (0.3 g) in acetone (30 mL) was refluxed for 12 h and then

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evaporated to dryness. The residue was extracted with CHCl_3 (30 mL), and the insoluble potassium salts were filtered off. The filtrate was evaporated to dryness, and the residue stirred with acetone (10 mL) to give complex III as a yellow solid (87% yield).

$\text{Pd}_2(\mu\text{-SCN})_2\text{L}_2$. A suspension of I(10) (0.13 g, 0.196 mmol) and KSCN (0.3 g) in CHCl_3 :acetone (2:1, 40 mL) was stirred at room temperature for 24 h. The yellow suspension was filtered, washed with water to remove the potassium salts and then with acetone, and dried to give an 82% yield of IV as a yellow solid.

Techniques. NMR spectra were recorded on a Varian XL-200 (^1H , 200 MHz) spectrometer. IR spectra were obtained on a Perkin-Elmer 599 spectrometer. Microanalyses were performed with a Perkin-Elmer 240 B microanalyzer. Molecular weights were measured in CHCl_3 solution with a Knauer vapor pressure osmometer (isopiestic method).

The textures of the mesophases were studied with a Meiji polarizing microscope equipped with a Mettler FP82 hot stage and FP80 central processor. Transition temperatures were measured by differential scanning calorimetry with a Perkin-Elmer

DSC-2 operated at a scanning rate of 5 K/min on heating. The apparatus was calibrated with indium (429.6 K, 28.4 J/g) and tin (505.06 K, 60.46 J/g) as standards.

The thermogravimetric analysis were obtained on a Perkin-Elmer TGS-2 equipped with a System 4 microprocessor controller at a heating rate of 10 °C/min under nitrogen.

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Registry No. *trans*-I(2), 124919-60-4; *trans*-I(6), 124942-34-3; *trans*-I(7), 124919-61-5; *trans*-I(8), 124919-62-6; *trans*-I(9), 124919-63-7; *trans*-I(10), 124919-64-8; *trans*-I(12), 124919-65-9; *trans*-I(14), 124919-66-0; *cis*-I(2), 124942-35-4; *cis*-I(6), 124942-36-5; *cis*-I(7), 124942-37-6; *cis*-I(8), 124942-38-7; *cis*-I(9), 124942-39-8; *cis*-I(10), 121756-13-6; *cis*-I(12), 124942-40-1; *cis*-I(14), 124942-41-2; II, 124919-67-1; III, 124919-68-2; *trans*-IV, 124919-69-3; *cis*-IV, 124942-42-3.

Iron-Promoted Nitrene-Extrusion Reactions in 7-Azanorbornadiene Derivatives

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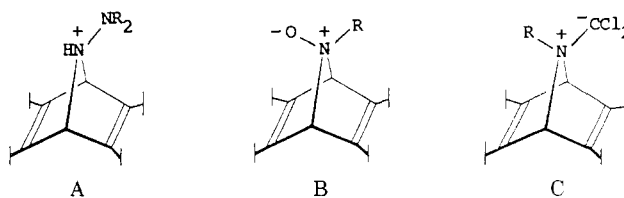
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Nitrene-extrusion reactions are found to proceed in the thermolysis of a series of 7-azanorbornadiene derivatives (ANB) with diiron nonacarbonyl. Several intermediates of the structure $(\text{ANB})\text{Fe}(\text{CO})_3$ are isolated, and their geometries are identified by spectroscopic analyses. The nitrene-extrusion reactions proceed in excellent yields for the iron complexes, in which electron-withdrawing substituents appear at the C-2, C-3, and N-7 positions of ANB. However, when some of these substituents are removed, the efficiency of nitrene extrusion is reduced. The rates of reactions are measured and found to be related directly to the electronic nature of the substituents. The Fe-N bond distance also changes with respect to the N-7 substituents, as evidenced by the single-crystal X-ray diffraction analyses of (2,3-dicarbomethoxy-7-(methylsulfonyl)-ANB) $\text{Fe}(\text{CO})_3$ and (2,3-dicarbomethoxy-7-phenyl-ANB) $\text{Fe}(\text{CO})_3$. The benzo-fused ANB derivatives react in an analogous manner, whereas the 7-azanorbornene derivatives do not undergo the processes of deamination.

Nitrene-extrusion reactions in 7-azanorbornadiene (ANB) derivatives are of potential usefulness in organic synthesis for the preparation of aromatic products.^{2,3} However, due to the lack of effective deamination reagents, these reactions have seldom been utilized in practical syntheses.⁴ Recently it was found that certain ANB derivatives react with diiron nonacarbonyl to produce a series of complex adducts that, upon heating, undergo deamination reactions in high yields.⁵ However, a prerequisite for these reactions is the existence of an electron-withdrawing substituent at the N-7 position. This condition accommodates perfectly the shortcomings of present deamination methods. Classical deamination methods generally require the presence of an electron-releasing group attached to the nitrogen,⁶ yet such a requirement

is unfavorable for pyrroles undergoing highly efficient Diels-Alder type cycloaddition reactions.^{7,8} Moreover, classical deamination methods have to proceed through certain reactive intermediates such as the structures A-C.^{2,6}



The yields, therefore, are limited due to the necessity of multistep treatments. In this report we provide, for the

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