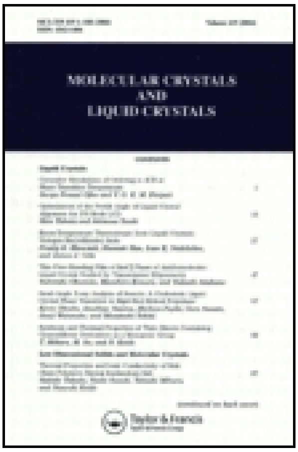

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Organometallic Ferroelectric Liquid Crystals. III. Syntheses and Liquid Crystal Properties of ortho-Palladated Binuclear Complexes of Azine, Imine and Azo Derivatives

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Organometallic Ferroelectric Liquid Crystals. III. Syntheses and Liquid Crystal Properties of ortho-Palladated Binuclear Complexes of Azine, Imine and Azo Derivatives

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In this paper, we report the syntheses of a series of title complexes from the reaction of azine, imine or azo ligands with $Pd(OAc)_2$ and with different bridging groups. Moreover we have investigated the mesomorphic properties of these complexes using DSC and polarizing microscopy. The results show that the mesophase temperature ranges of complexes are wider than that of corresponding organic ligands. The role of the central organic ligands, the bridging ligands between two metallic nuclei, and terminal carbon number on the mesomorphic behavior was also determined. When the bridging ligands contain an optically active group, the complexes appear to exhibit chiral smectic C phase (S_C^*).

Keywords: FLC, organometallic, synthesis

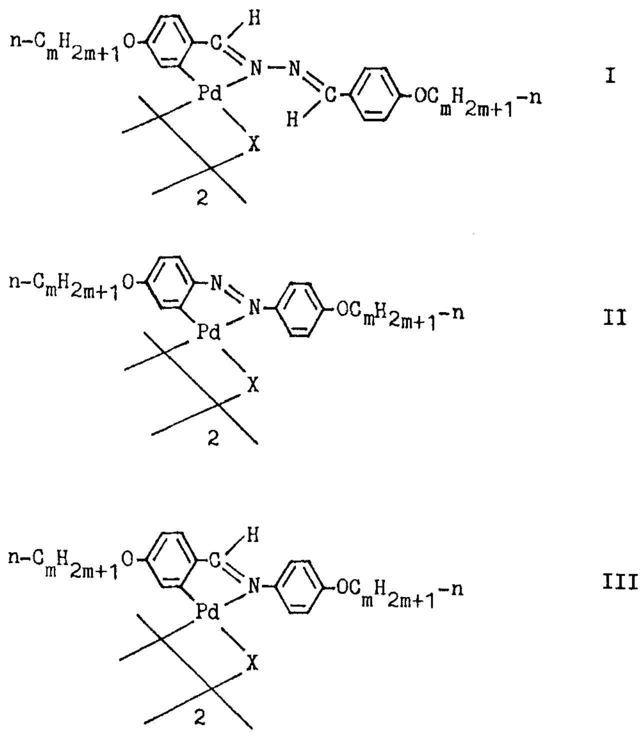
Ferroelectric liquid crystals (FLCs) are attractive for devices, because they permit direct interaction of the liquid crystal with an electric field, optical field, and magnetic field and may be turned-on turned-off by reversing the polarity of the field. As a result, FLCs are currently major area of interest in mesogenic material science both in basic and applied research.[1–3] A recent development in FLC is the appearance of organometallic ferroelectric liquid crystals (OMFLCs), which appropriately have both characterization of metallic complexes and organic FLCs. For OMFLC based on rodlike organometallic molecules with chiral centers in the group bridging between two metal atoms or at main chain, three novel aspects may be noted: (1) unprecedented molecular shape; (2) a new way of introducing chirality; and (3) the presence of metallic atoms in the molecule. In this paper, we report the effect of central bridging group of organic fragment, the bridging ligands between two metallic nuclei, and number of carbon atoms in the side chains on the mesomorphic properties of organometallic ferroelectric liquid crystals. We have discovered that their mesomorphic performances are better than the corresponding organic mesogens.

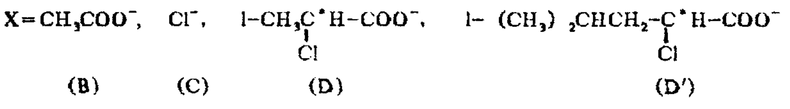
RESULTS AND DISCUSSION

We synthesized three series of ortho-palladated dimers $(Pd(C,N)(\mu - X))_2$ which are azine, azo and imine derivatives with structures I, II, III, respectively (Figure 1).

The molecular structures of organometallic complexes have been characterized by elemental analysis, IR and NMR.

Effect of Central Metal on the Mesomorphic Properties of Organometallic Mesogens. The phase behavior determined by DSC data and polarizing microscopic results are shown in Table I.





$$X = CH_3COO^-,\quad Cl^-,\quad l\text{-}CH_3\underset{\displaystyle Cl}{C^*}H\text{-}COO^-,\quad l\text{-}(CH_3)_2CHCH_2\text{-}\underset{\displaystyle Cl}{C^*}H\text{-}COO^-$$

(B) (C) (D) (D′)

FIGURE 1 Structures of ortho-palladated binuclear complexes.

TABLE I

Phase transition of organic and organometallic mesogens

Compounds	Phase transition	Temp.(°C)	ΔH(KJ / mol)
LI:	C_1---C_2	98.3	26.50
	C_2---C_3	109.0	38.50
	C_3---S_C	121.0	62.00
	S_C---I	128.0	20.50
IB-C14:$(PdL^1(\mu\text{-}CH_3COO))_2$	C---S_C	109.0	146.10
	S_C---I	143.0	13.60
IC-C14:$(PdL^1(\mu\text{-}Cl))_2$	C---S_C	114.0	20.60
	S_c---I	220.0	
ID-C14:$(PdL^1(\mu\text{-}S(-)\text{-}CH_3\underset{\overset{\mid}{Cl}}{C}{}^*HCOO))_2$	C---S_C^*	70.6	76.00
	S_C^*---S_A	99.0	27.60
	S_A---I	127.0	10.70
ID'-C14:$(PdL^1(\mu\text{-}S(-)\text{-}(CH_3)_2CHCH_2\underset{\overset{\mid}{Cl}}{C}{}^*HCOO))_2$	C---S_C^*	45.0	12.5
	S_C^*--I	57.6	1.96
LII:	C---I	112.4	75.00
	I---S	(107.7)	−14.60
	S---C	(105.6)	−63.70
IIB-C14:$(PdL^2(\mu\text{-}CH_3COO))_2$	C---S_C	92.1	87.00
	S_C---I	104.5	14.30
IIC-C14:$(PdL^2(\mu\text{-}Cl))_2$	C---S_B	150.0	21.00
	S_B---I	180.0	
IID-C14:$(PdL^2(\mu\text{-}S(-)\text{-}CH_3\underset{\overset{\mid}{Cl}}{C}{}^*HCOO))_2$	C---S_C^*	67.1	102.70
	S_C^*---S_A	84.0	49.00
	S_A---I	91.0	7.10
LIII:	C---I	113.0	96.10
IIIB-C14	C---I	179.9	47.42
IIIC-C14:$(PdL^3(\mu\text{-}Cl))_2$	C---S_C	123.0	60.00
	S_C---I	240.0	
IIID-C14:$(PdL^3(\mu\text{-}S(-)\text{-}CH_3\underset{\overset{\mid}{Cl}}{C}{}^*HCOO))_2$	C---S_C^*	106.0	16.10
	S_C^*---I	146.8	7.47

LI = L^1 = $n\text{-}C_{14}H_{29}O\text{-}C_6H_4\text{-}CH = N\text{-}N = CH\text{-}C_6H_4\text{-}OC_{14}H_{29}\text{-}n$
LII = L^2 = $n\text{-}C_{14}H_{29}O\text{-}C_6H_4\text{-}N = N\text{-}C_6H_4\text{-}OC_{14}H_{29}\text{-}n$
LIII = L^3 = $n\text{-}C_{14}H_{29}O\text{-}C_6H_4\text{-}CH = N\text{-}C_6H_4\text{-}OC_{14}H_{29}\text{-}n$

If the mesomorphism and phase transition temperatures of organic molecules are compared with those of the corresponding organometallic complexes, we find that the mesogenic temperature ranges of the organometallic complexes are not only wider, but the phase transition temperatures are also lower and the mesogenic performances are better than those of corresponding organic mesogens. For example, the organic molecule (LIII) is non-mesomorphism, whereas IIIC-C_{14} and IIID-C_{14} possess enantiotropic smectic phases. Similarly, IIB-C_{14} and IIC-C_{14} display better mesomorphic behavior than LII, and the palladated complexes of LI exhibit a wider smectic phase than the organic mesogen LI. Two factors may be attributed to this improvement of mesomorphic behavior: (i) the formation of five membered metallocycles enhance the rigidity of complexes; and (ii) the large and polarizable electron density of Pd^{2+} in the organometallic mesogens increases the intermolecular action, these aspects lead to organized arrangements between molecules and facilitate the formation of liquid crystal phases.

Effect of Central Bridging Groups on the Mesomorphism. We defined the ligands LI, LII, LIII, groups linking two conjugated systems, —CH=N—N=CH—, —N=N—, and —CH=N—, respectively. It is noticed from Figure 2 that these central bridging groups participate in the formation of five-membered metallocycles. Therefore, we predicted that they will have an important effect on the mesomorphism of the FLCs.

It was well known that the ortho-palladated binuclear azine complexes exhibit trans- and cis-isomers, when the central part containing two metallic atoms has a non-planar structure. The corresponding azo and imine complexes display only a trans-isomer, however, they exhibit D- and L-enantioisomers. Whether the isomers are geometrical or optical, the presence of isomers will effect the mesomorphism of the organometallic complexes.

We investigated the effect of the azine, azo, and imine bridging groups by comparing a homologous series keeping the chiral bridging group and sidechain length constant. As shown in Figure 2 the isotropic transition temperatures of the organometallic complexes decreased according to the order azine < imine < azo. The temperature range of mesophase azo < imine < azine order. Thus, the ortho-

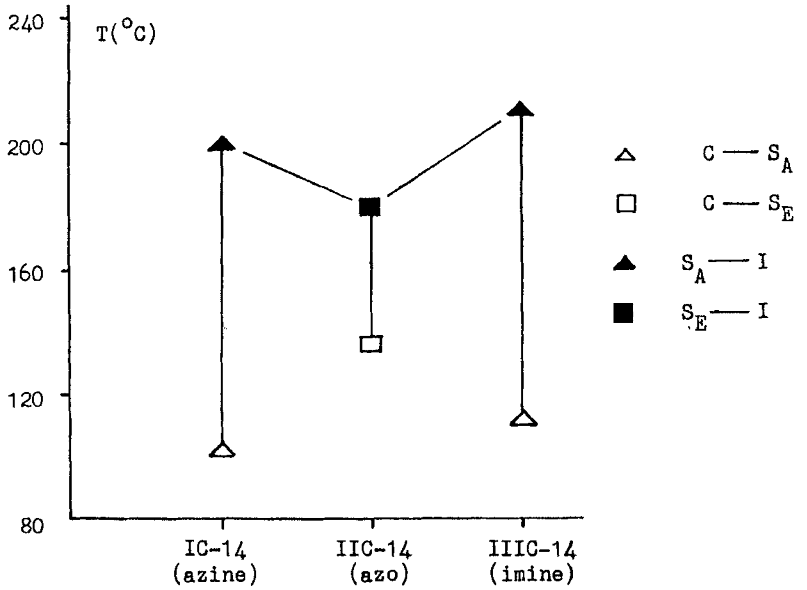
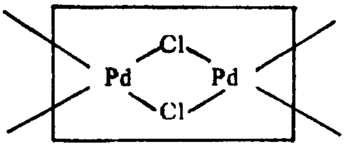


FIGURE 2 Effect of central bridging of organic ligands on the mesomorphism of organometallic complexes.

palladated binuclear azine complexes have lower crystal to mesophase transition and wider mesophase ranges. It is likely that their better mesogenic properties are related firstly with the presence of trans- and cis-isomers, and secondly with the presence of free —C═N— group. Owing to the —C═N— group which is conjugated with other benzene ring, the molecular rigidity and planarity were enhanced, the intramolecular interactions were enhanced, and the ordered arrangement of molecules increased. The combination of these features produces a reduction of phase transition temperatures and an enhancement of clearing point temperatures.

Effect of Bridging Ligand between Two Metallic Nuclei on the Mesogenic Properties of Organometallic Complexes. It was known from Table I that the phase transition temperatures of azine, azo and imine complexes decrease according to Cl^-, AcO^-, $L\text{—}CH_3\text{—}\underset{\underset{Cl}{|}}{C^*H}\text{—}COO^-$, $L\text{—}(CH_3)_2CHCH_2\underset{\underset{Cl}{|}}{C^*H}\text{—}COO^-$. When bridged ligand is Cl^- ion, the central bimetallic core of complexes exhibits a planar structure as shown:



This structural characterization promotes intermolecular order. Therefore, their melting points and clearing points are higher. For other complexes, because of steric hindrance and directional bonding of the bridging ligands, the central bimetallic core of complexes have a "half-open book" structure, and molecular rigidity of complexes is decreased. Owing to the steric hindrance of bridging ligands increased according to above order, the intermolecular interaction and the molecular rigidity is decreased according to the same order. Therefore, the molecular order is decreased, the clearing point decreased successively, and the range of phase transition temperature also decreased successively.

Effect of Terminal Carbon Number on the Mesogenic Properties. The experimental results are shown in Table II and Figures 3, 4, and 5. In Figure 3 it is shown that the phase transitions of ID series of complexes are C---S_C^*---S_A---I, except when the terminal carbon number N is 7, 16, which exhibit a C---S_C^*---I phase sequence. However, they all have a chiral smectic C phase (S_C^*), and their clearing point transitions follow an odd-even dependence on the terminal carbon number.

It was known from Figure 4 that the IIIB series of complexes display only monotropic mesomorphism when the terminal carbon number is 8, 9 or 12, while other complexes of this series were non-mesomorphism.

It can also seen from Figure 5 that the mesomorphism of IIIC series of complexes are more complicated. When the terminal carbon number is 8 or 10, these complexes appear to be non-mesomorphism. However when N = 12, the complex

TABLE II

Phase transition and enthalpy of organometallic mesogens

Complexes	Terminal carbon number	Phase transition	Temp.(^{0}C)	ΔH(KJ / mol)
ID	C6	C---S_C^*	134.0	23.37
		S_C^*---S_A	141.8	7.37
		S_A---I	148.3	0.82
	C7	C---S_C^*	141.6	32.27
		S_C^*---I	150.2	1.20
	C8	C---S_C^*	78.9	18.00
		S_C^*---S_A	117.3	9.34
		S_A---I	133.4	2.07
	C9	C---S_C^*	80.3	36.43
		S_C^*---S_A	170.0	16.44
		S_A---I	187.8	28.72
	C10	C---S_C^*	121.0	24.29
		S_C^*---S_A	133.0	
		S_A---I	144.8	4.12
	C11	C---S_C^*	126.0	32.63
		S_C^*---S_A	140.0	
		S_A---I	145.9	5.65
	C12	C---S_C^*	107.1	27.00
		S_C^*---S_A	119.4	10.16
		S_A---I	140.7	4.95
	C14	C---S_C^*	70.9	36.82
		S_C^*---S_A	99.0	15.07
		S_A---I	127.0	5.80
	C16	C---S_C^*	71.3	85.84
		S_C^*---I	114.0	5.12
IIIB	C6	C---I	212.6	64.70
	C7	C---I	204.7	50.63
	C8	C---I	203.7	55.49
	C9	C---I	199.4	52.93
		I---S_C	(137.5)	
		S_C---C	(90.0)	
	C10	C---I	192.7	39.23
		I---S_C	(125.0)	−15.46
		S_C---C	(91.7)	−26.46
	C11	C---I	185.6	49.42
		I---S_C	(128.6)	−18.89
		S_C---C	(85.7)	−37.72
	C14	C---I	179.9	47.42
IIIC	C6	C---S_C	159.4	18.39
		S_C---I	239.0	11.40
	C7	C---S_C	142.2	17.43
		S_C---I	231.6	8.80
	C8	C---I	201.6	49.12
	C9	C---S_C	124.4	17.00
		S_C---I	225.2	7.33
	C10	C---I	127.5	13.08
	C12	C---I	117.8	48.53
		I---S_A	(171.5)	−5.68
		S_A---S_C	(151.8)	−17.14
		S_C---C	(109.9)	−6.42
	C14	C---S_C	123.0	57.61
		S_C---I	240.0	

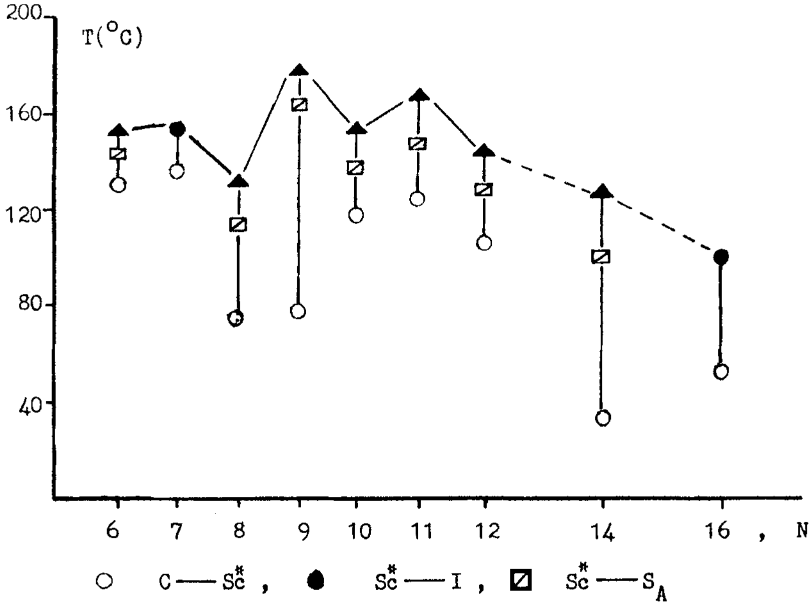


FIGURE 3 Effect of terminal carbon number (*N*) on the mesomorphism of ID complexes.

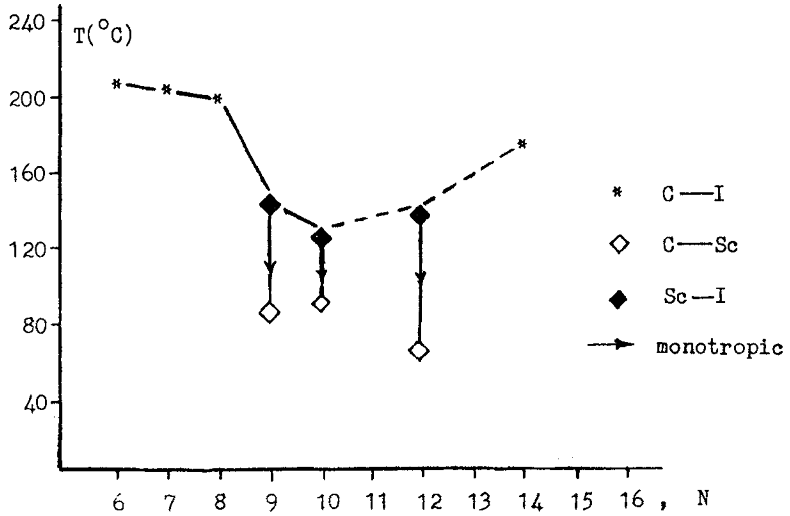


FIGURE 4 Effect of terminal carbon number (*N*) on the mesomorphism of IIIB complexes.

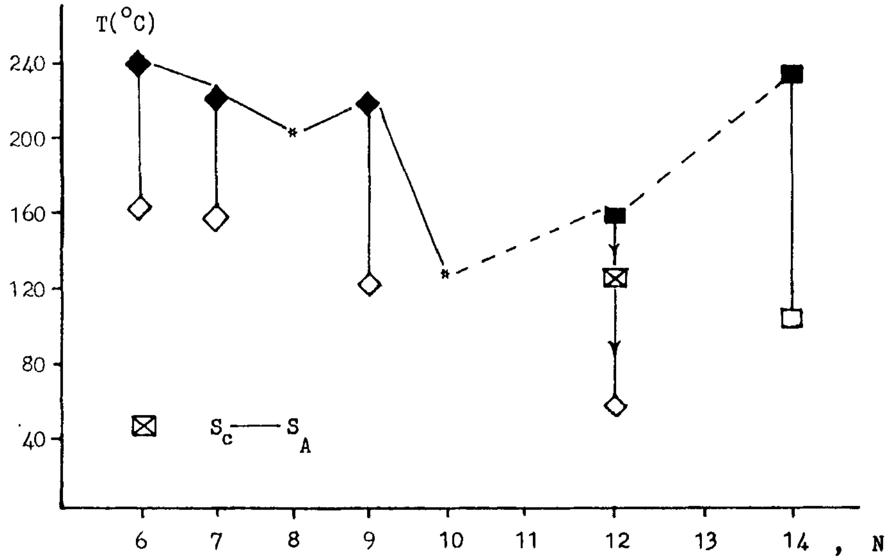


FIGURE 5 Effect of terminal carbon number (*N*) on the mesomorphism of IIIC complexes.

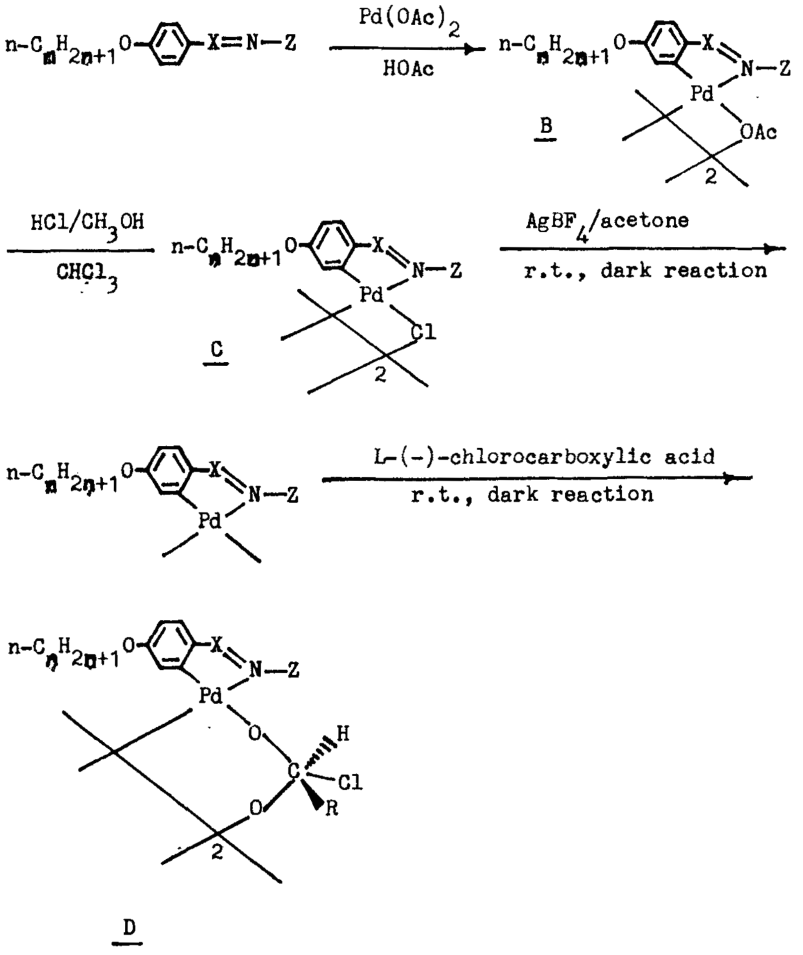
displays only monotropic mesomorphism. Other derivatives appeared to exhibit C---S_C---I enantiotropic mesomorphism.

Generally speaking, the effect of terminal carbon number on the mesomorphism of three series of complexes is importantly different, and is related to the central bridging group, the bridging ligand between two metallic nuclei, the rigidity of organometallic molecule, and the planarity of the structure of the molecule.

EXPERIMENTAL SECTION

General Procedures. The ^1H NMR spectra were recorded on 300 MHz Brucker AC-P300 spectrometer, using $CDCl_3$ as solvent and TMS as internal standard. The IR spectra (nujol) were performed on NICOLET FT-MX-1E spectrometer. Elemental analyses were obtained from CARLO ERBA-1106 microanalyzer. The thermotropic behaviors were determined by DSC using Perkin-Elmer 7 series analysis system. The textures of mesophases were observed under ORTHLUX-IIPOL-BK polarizing microscope.

The azine, azo and imine long-chain ligands were synthesized by similar methods previously described. The aceto-bridging binuclear complexes were first obtained through ortho-palladated reaction of above ligand with palladium acetate.[4-7] Secondly, the corresponding chloro-bridging complexes were prepared by ligand exchange reaction. Finally, the chloro-bridges were splitted by using $AgBF_4$, and the chloric ions were isolated from the reaction system as AgCl form, at this moment obtain binuclear organometallic complexes containing optical active groups, when L-(–)-chlorocarboxylic acid were added into the resulting solution. The synthetical route is shown in Scheme I.



I: $X=CH$, $Z=n\text{-}C_nH_{2n+1}OC_6H_4CHN$;
II: $X=N$, $Z=n\text{-}C_nH_{2n+1}OC_6H_4$
III: $X=CH$, $Z=n\text{-}C_nH_{2n+1}OC_6H_4$:

SCHEME I Syntheses of organometallic mesogens.

Aceto-bridging ortho-palladated dimers: A mixture of $Pd(Ac)_2$ and azine (azo or imine) ligand (Pd/ligand = 1:1) in acetic acid was refluxed until the appearance of palladium black, cooled, filtered and washed the residue with acetic acid. The crude product was soluted in $CHCl_3$ and filtered to remove non-soluble impurities, the filtrate was concentrated and poured into alcohol to separate out the product, which was filtered off, washed with alcohol and dried.

Chloro-bridging ortho-palladated dimers: To the solution of aceto-bridged dimers in $CHCl_3$ was dropwise added 0.7026 mol/L methanol solution of HCl (Cl/Pd = 1:1), the mixture was stirred for 1 h, concentrated, precipitated the product by

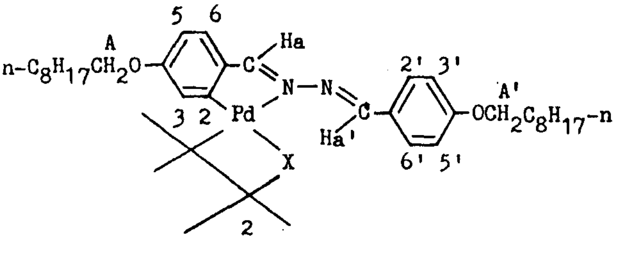
TABLE III

Elemental analyses data of organometallic complexes

Complexes	C%		H%		N%		Color
	Found	Cald.	Found	Cald.	Fond	Cald.	
IB-C6	57.51	58.69	6.58	6.68	4.77	4.89	yellow
IB-C7	59.25	59.95	7.19	6.99	4.50	4.60	yellow
IB-C8	59.92	61.12	7.34	7.32	4.30	4.45	yellow
IB-C9	62.54	62.06	7.77	7.76	4.20	4.26	yellow
IB-C10	62.86	63.10	8.03	7.94	4.03	4.09	yellow
IB-C11	64.08	63.99	8.30	8.13	3.93	3.93	yellow
IB-C12	63.71	64.85	8.32	8.37	3.68	3.78	yellow
IB-C14	66.27	66.27	9.02	8.78	3.47	3.51	yellow
IB-C16	66.80	67.59	9.27	9.15	3.25	3.28	yellow
IC-C6	56.44	56.87	6.57	6.43	4.94	5.14	yellow
IC-C7	57.81	58.73	6.91	6.81	4.76	4.89	yellow
IC-C8	59.86	59.54	6.84	7.11	4.43	4.63	yellow
IC-C9	59.89	60.56	7.42	7.62	4.22	4.41	yellow
IC-C10	60.89	61.72	7.65	7.77	4.06	4.23	yellow
IC-C11	63.15	62.73	8.18	8.04	4.06	4.06	yellow
IC-C12	63.18	63.63	8.44	8.23	3.84	3.90	yellow
IC-C14	65.22	65.18	8.92	8.73	3.61	3.62	yellow
IC-C16	65.58	66.61	9.26	9.05	3.32	3.38	yellow
ID-C6	55.87	56.07	6.41	6.28	4.36	4.51	yellow
ID-C7	56.16	57.27	6.91	6.77	4.08	4.30	yellow
ID-C8	58.41	58.53	6.53	6.94	3.86	4.13	yellow
ID-C9	58.98	59.62	7.22	7.24	3.78	3.97	yellow
ID-C10	60.31	60.57	7.82	7.50	3.77	3.82	yellow
ID-C11	61.93	61.53	7.99	7.75	3.69	3.68	yellow
ID-C12	60.15	62.39	8.05	7.98	3.22	3.53	yellow
ID-C14	63.66	63.89	8.48	8.46	3.15	3.31	yellow
ID-C16	64.21	65.25	8.94	8.83	2.92	3.10	yellow
ID′-C14	65.09	64.85	8.93	8.84	3.07	3.14	yellow
IIB-C14	65.60	65.44	9.21	8.83	3.64	3.63	dark red
IIC-C14	64.08	64.25	8.87	8.70	3.71	3.74	red
IID-C14	62.41	62.99	8.58	8.42	3.32	3.42	red
IIIB-C6	59.22	59.40	7.09	6.83	2.52	2.57	yellow green
IIIB-C7	60.27	60.68	7.08	7.20	2.35	2.44	yellow green
IIIB-C8	61.86	61.84	7.68	7.53	2.32	2.33	yellow green
IIIB-C9	62.65	62.90	8.16	7.84	2.16	2.22	yellow green
IIIB-C10	63.41	63.87	8.05	8.12	2.04	2.13	yellow green
IIIB-C12	65.15	65.58	8.28	8.61	1.92	1.96	yellow green
IIIB-C14	67.04	67.04	9.25	8.97	1.83	1.82	yellow green
IIIC-C6	57.47	57.47	6.88	6.51	2.79	2.68	yellow
IIIC-C7	58.32	58.91	6.64	6.91	2.44	2.54	yellow
IIIC-C8	60.20	60.21	7.32	7.21	2.26	2.39	yellow
IIIC-C9	60.83	61.39	7.30	7.64	2.24	2.31	yellow
IIIC-C10	62.57	62.46	8.13	7.89	2.02	2.21	yellow
IIIC-C12	64.02	64.34	9.21	8.46	1.99	2.03	yellow
IIIC-C14	65.18	65.95	8.93	8.84	1.78	1.87	yellow

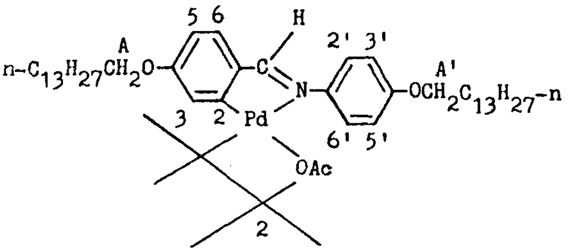
TABLE IV

NMR spectra of representative title complexes



$X = CH_3COO^-$, IB-C9

$CH_3\overset{*}{C}HCOO^-$, ID-C9 ($\underset{Cl}{|}$)



IIIB-C14

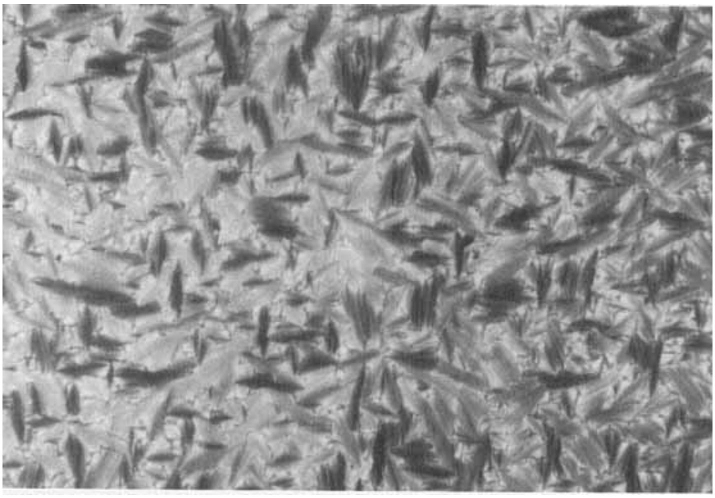
Compd.	.^{1}H Chemical Shift, ppm										Coupling Constant,Hz		
	H_6	H_5	H_3	$H_{2',6'}$	$H_{3',5'}$	H_a	$H_{a'}$	A	A'	X	H_5–H_6	H_5–H_3	$H_{2'}$–$H_{3'}$
IB–C9	7.04 (d)	6.42 (dd)	6.29 (d)	7.52 (d)	6.87 (d)	7.63 (s)	8.53 (s)	3.98 (t)	3.96 (t)	2.08 (s)	9.0	3.0	9.0
ID–C9	7.07 (d)	6.47 (dd)	6.27 (d)	7.54 (d)	6.88 (d)	7.71 (s)	8.42 (s)	4.00 (t)	3.97 (t)	4.41 (s)	9.0	3.0	9.0
IIIB–C14	7.08 (d)	6.47 (dd)	6.39 (d)	7.12 (d)	6.69 (d)	7.50 (s)		3.87 (t)	3.75 (t)	2.03 (s)	9.0	3.0	9.0

addition of acetone, filtered off, washed with acetone and dried in vacuo, the products are pure enough for further reaction.

Syntheses of ID, IID and IIID complexes: To the suspension of 1 mmol chloro-bridging ortho-palladated dimers in 40 mL acetone, 1 mmol $AgBF_4$ was added, the mixture was refluxed in dark for 12 h, filtered the white precipitate off. To the filtrate, 1 mmol L-(–)-chlorocarboxylic acid was added. The resulting solution was stirred for 24 h in dark under room temperature, filtered, concentrated, a yellow precipitate was isolated from the concentrated solution by added alcohol, filtered, washed the residue with alcohol, dried in vacuo.

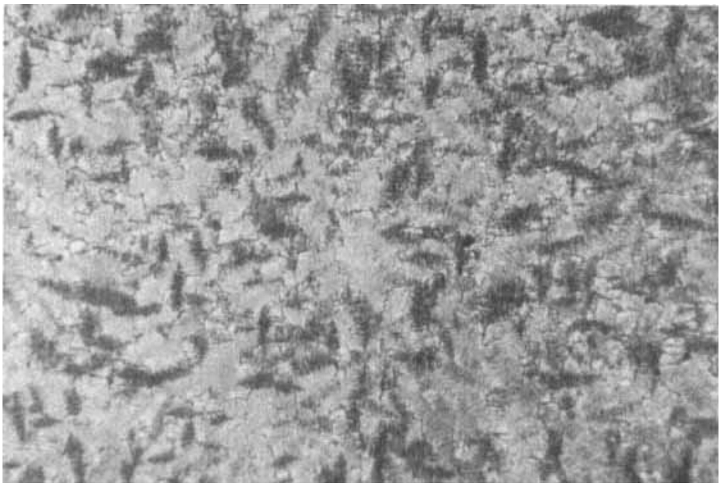
The elemental analyses data of these organometallic complexes are summarized in Table III.

NMR and mesogenic textures of the representative title complexes are shown in Table IV and Figure 6, respectively.



(a)

IIID-C14: S_A, fan-shaped texture, crossed polarizers. 118°C, on cooling run. ×220.

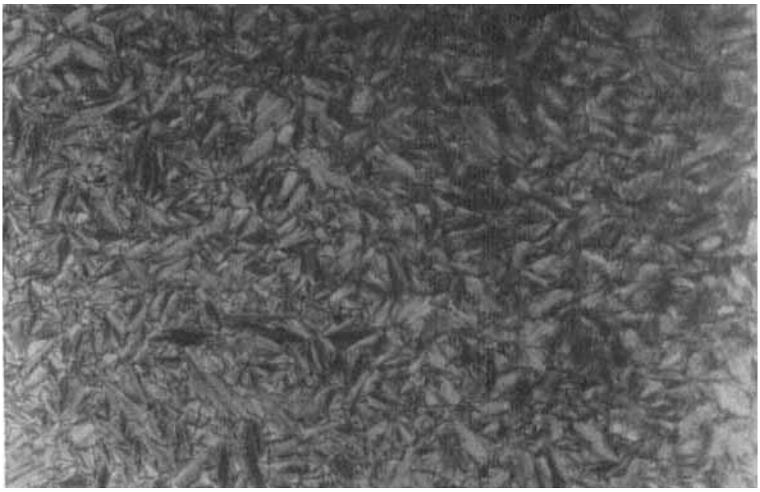


(b)

IIID-C14: S_C^*, fan-shaped texture with equidistant liners. Crossed polarizers, 58°C, on cooling run. ×220.

FIGURE 6 Typical textures of organometallic mesogens (a–c). See Color Plate XIV.

Table IV shows that the ^1H chemical shifts of two benzene rings are different and the chemical shift of one ring is shifted into higher field, this result suggests that this benzene ring is deshielded with a net transference of electron density from benzene ring into central metal palladium, thus conforming that the ortho-palladation reaction between benzene ring and palladium has occurred.



(c)

IIC-C14: S_A phase, 55°C, on cooling run, ×220.

FIGURE 6 *Continued*. See Color Plate XIV.

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References

1. P. Espinet, J. Etxebarra, M. Macos, J. Perez, A. Remon and J. L. Serrano, *Angew. Chem. Int. Ed. Engl.*, **28**, 1065 (1989).
2. A.-M. Giroud Godquin and P. M. Maitlis, *ibid.*, **30**, 375 (1991).
3. H. B. E. Lawrene, Avail. Univ. Microfilms Int., Order No. BRD-93071 (1990).
4. P. M. Maitlis, D. W. Bruce, R. Dhillon, D. A. Dunmur, F. P. Fanizzi, S. E. Hunt, R. Le Lagadec, E. Lalinde, R. Orr, J. P. Rourke, N. J. S. Salt, J. P. Stacey and P. Styring, *New J. Chem.*, **14**, 549 (1990).
5. P. Espinet, J. Perrez, M. Marcos, M. B. Ros, J. L. Serrano and J. Barbera, *Organometallics*, **9**, 2928 (1990).
6. T. Sierr, E. Melendez and J. L. Serrano, *Chem. Mater.*, **3**, 157 (1991).
7. Hoshino Naomi, Hasegewa Hiroyuki and Matsunaga Yoshio, *Liq. Cryst.*, **9**(2), 267 (1991).