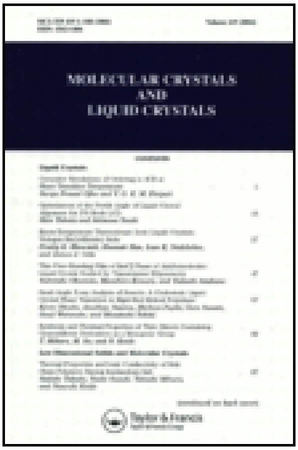

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LIQUID CRYSTALLINE ASSEMBLY OF CALAMATIC MESOGENS AND ROD-COIL MOLECULE BY Pd AND Ru COMPLEXATION

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Abstract A series of cyanobiphenyl palladium complexed liquid crystals was synthesized. The Pd complexation of cyanobiphenyl mesogen results the enhancement of thermal stability and more ordered mesophase. π-Complexation of Cp*Ru(Cp*=C_5Me_5) moiety to the mesogenic group of rod-coil molecule shows the suppression of phase transition temperature without the change of the mesophase.

INTRODUCTION

Metallomesogens, liquid crystalline materials containning transition metals, are attracting special attention and rapidly expanding research area because the transition metal center opens up a new geometric shapes, unique optical, magnetic and electrical properities of the organic liquid crystals.[1] Since many transition metal ion have unpaired electrons, transition metallomesogens will provide a good opportunity of paramagnetism which is one of very useful physical properties to apply electronic devices. It is well known that nitriles can bind readily to a variety of transition metals.[2] In this contribution, we report the synthesis and thermal behavior of Pd complexed mesogen through the N atom of nitrile mesogen and π-complexation of Cp*Ru(Cp*=C_5Me_5) moiety to the mesogenic group of rod-coil molecule containing poly(ethylene oxide).

EXPERIMENTAL

All reactions were carried out under an atmosphere of Ar at room temperature using standard Schlenk techniques. The following compounds were prepared by reported methods: Cp*Ru(CH_3CN)$_3$(OTf),[3] $PdCl_2(PhCN)_2$.[4] The details of the synthesis and characterization of the cyanobiphenyl mesogens[5] and the rod-coil molecules[6] were reported in elsewhere. The ^{1}H-NMR spectra were obtained from $CDCl_3$ solution on a Bruker DPX 250 spectrometer. Infrared spectra were obtained on a Nicolet Impact 400 FT-IR spectrometer using KBr pellet. A Perkin Elmer DSC-7 differential scanning calorimeter, equipped with a 1020 thermal analysis controller was used to determine the thermal transitions which were reported as the maxima and minima of their endothermic or exothermic peaks, respectively. A Nikon Optiphot 2-pol optical polarized microscope (magnification: x100) equipped with a Mettler FP 82 hot stage and a Mettler FP 90 central processor was used to observe the thermal transitions and to analyze the anisotropic textures.

Preparation of $[PdCl_2L_2]$ $\{L=NC\text{-}C_6H_4C_6H_4\text{-}O\text{-}(CH_2)n\text{-}O\text{-}2.5\text{-}Me_2C_6H_3,\ NC\text{-}n,\ n=6.8.11\}$

A series of palladium complexed cyanobiphenyl mesogen were synthesized with 40-50 % yields using the similar procedure that is described below for $[PdCl_2L_2]$ (L=NC-11). To a CH_2Cl_2 solution(3ml) of $PdCl_2(PhCN)_2$ (M.W.=383, 19mg, 0.05mmol) was added cyanobiphenyl mesogen(L=NC-11, M.W.=470, 50mg, 0.11mmol) The resulting solution was stirred at room temperature for 12h. After removing the solvent under vacuum, the crude product was recrystallized from CH_2Cl_2/hexane at -20 °C to give creamy yellow product(15mg, 47%). ^{1}H NMR($CDCl_3$, δ, ppm); 1.24-1.87(m, 18H, $\text{-O-}CH_2\text{-}\underline{(CH_2)_9}\text{–}CH_2\text{-O-}$),2.20(s, 3H, -o-$CH_3$), 2.34(s, 3H, -m-$CH_3$), 3.96(t, 2H, J=6.4Hz), $\text{-O-}\underline{CH_2}\text{-}(CH_2)_{10}\text{-}$), 4.03(t, 2H, J=6.5Hz,$\text{-O-}(CH_2)_{10}\text{-}\underline{CH_2}\text{-}$), 6.67-7.84(m, 11H, Ar-H); IR(υC≡N)=2286cm^{-1}.

Complexation of π-Cp*Ru with ethyl 4'-(4'-oxy-4-biphenylcarbonyloxy)-4-biphenylcarboxylate with 16 ethylene oxide units

To a CH_2Cl_2 solution(5ml) of $[Cp^*Ru(CH_3CN)_3](OTf)$ (20mg, MW=508, 0.039mmol) was added rod-coil molecule(MW=1170, 50mg, 0.043mmol). The reaction mixture was stirred at room temperature for 10h. After removing the solvent under vacuum, the crude product was recrystallized from CH_2Cl_2/hexane at -20 °C to give yellow brown waxy solid(38mg, 62% yield). ^{1}H NMR($CDCl_3$, δ, ppm); 1.36(t, 3H, $CH_2\underline{CH_3}$, J=7.3Hz), 1.78(s, $C_5\underline{(CH_3)_5}$, 15H), 3.32(s, 3H, $\underline{CH_3}O$), 3.45-3.75(m, 60H, $O\underline{CH_2}$), 3.83(t, 2H, $\underline{CH_2}CH_2$Ophenyl, J=5.0Hz), 4.13(t, 2H, $CH_2\underline{CH_2}$Ophenyl, J=5.0Hz), 4.35(q, 2H, CH_2CH_3, J=7.1Hz), 6.16-6.71(m, 4H, π-Cp*Rucomplexed Ar-H), 6.96(d, 2H, ortho to CH_2O, J=9.0Hz), 7.2-8.3(m, 12H, Ar-H).

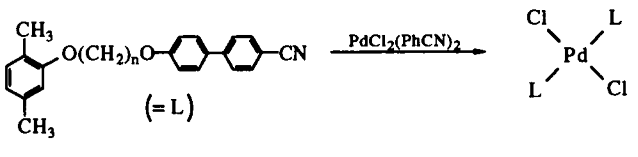
RESULTS AND DISCUSSION

Palladium Complex with Cyanobiphenyl Mesogen

Scheme 1 outlines the synthesis of cyanobiphenyl mesogenic ligand and its corresponding Pd complex. Figure 1 shows the FT-IR spectra of the mesogenic ligand NC-11 and the complex CN-11-Pd which are representative examples for NC-n and NC-n-Pd. As expected, the NC stretching band at 2222 cm^{-1} exhibited by the mesogenic ligand shifts completely to 2286 cm^{-1} upon Pd complexation. This result indicates that the Pd complex is absence of free mesogenic ligand. The phase behavior of the mesogenic ligands and the Pd complexes was investigated by a combination techniques of DSC and thermal optical polarized microscopy and is summarized in Table 1.

NC-11 is crystalline on heating, however a smectic A as well as nematic mesophase is exhibited on cooling scan. Therefore, the ligand NC-11 displays only monotropic mesophases. A representative texture of the nematic phase of NC-11 is shown in Figure 2(a). In contrast, the Pd complex of NC-11 displays an

Scheme 1



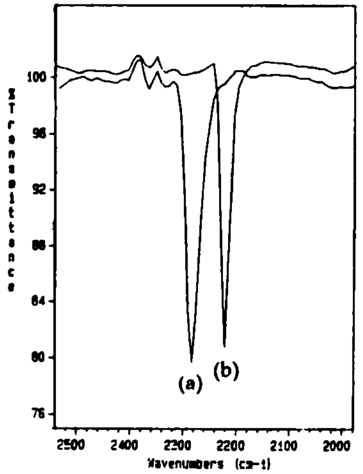


Fig.1 IR spectra of cyanobiphenyl and its Pd complex
(a) Pd-complexed cyanobiphenyl $\nu_{(C\equiv N)}$ = 2286cm^{-1}
(b) Free cyanobiphenyl $\nu_{(C\equiv N)}$ = 2222cm^{-1}

Table 1. Characterization of the Mesogenic Ligand and the Pd, Ru Complexes (s_A=smectic A phase, n=nematic phase, i=isotropic phase). Data on first line are from first heating and cooling scans. Data on second line are from second heating scan.

Compound	phase transitions (°C)	
	heating	cooling
NC-6	k 115.5 i	i 51.4 n -10.8 k
NC-6-Pd	k 130.2 n 140 decomp. k 121.2 n 140 decomp.	n 67.2
NC-8	k 85.5 i	i 47.9 n -15.1 k
NC-8-Pd	k 103.8 n 130 decomp. k 81.1 n 130 decomp.	n 48.1 k
NC-11	k 47.7 i	i 36.9 n 31.2 sA -28.1 k
NC-11-Pd	k 45.1 s_A 97.7 i k 29.0 s_A 95.8 i	i 94.7 s_A
Rod-Coil	k55.7 k20.3 s_B123.0	i 119.4 s_B 116.0 k 11.5
Rod-Coil-Ru	k44.0 s_B 108.2 i	i 100.1 s_B

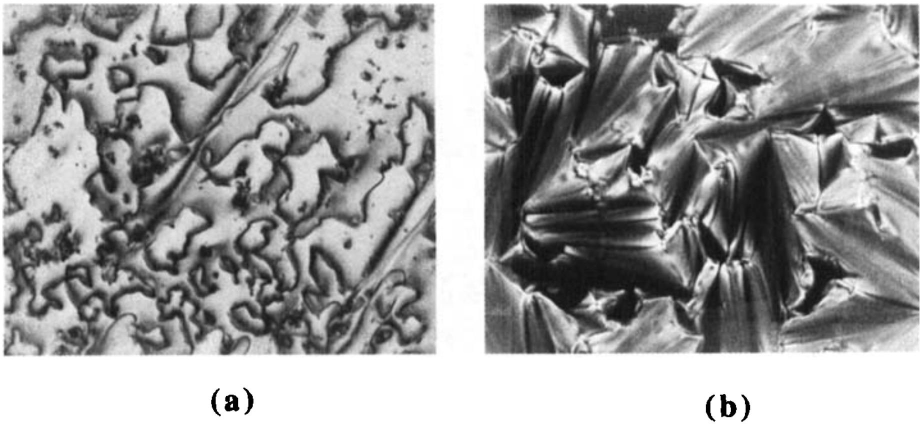

(a) (b)

Fig. 2 Representative optical polarized micrographys (x100) of the texture exhibited by; (a) neumatic mesophase of CN-11 (b) smetic A mesophase of CN-11-Pd
See Color Plate II.

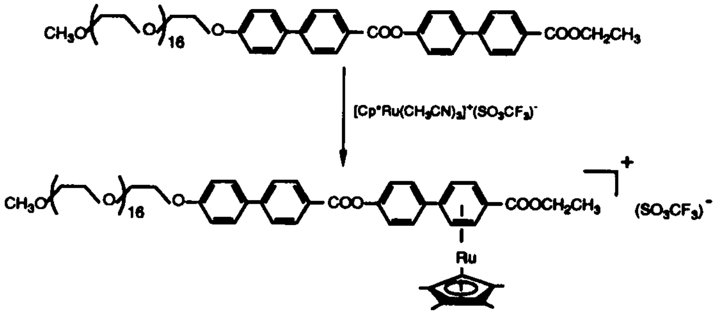
enantiotropic smectic A phase with an isotropization transition temperature (Ti) much higher than that of its corresponding mesogenic ligand. Transition from isotropic liquid at 94.7 °C can be seen by the rapid formation of batonnets which merge into a focal conic fan like texture with pseudoisotropic areas indicating a smectic A phase as shown in Figure 2(b). This result suggests that complexation of mesogenic ligand with transition metal gives rise to thermodynamically stable and more ordered liquid crystalline phase which is most probably due to enhanced rigidity of the system through metal complexation. This trend agrees well with the result available in the previous literature.[7]

The mesogenic ligand NC-8 melts into isotropic liquid at 85.5 °C. Cooling from isotropic liquid, a nematic mesophase is induced at 47.9 °C, which is followed by a crystallization at -15.1 °C. The complex of NC-8 with Pd metal, however, melts into a nematic phase followed by decomposition at 140 °C. Cooling from 135 °C which is lower than decomposition temperature, the nematic phase remains until crystallization occurs at 47.1 °C (Table 1). Although the complex is decomposed above 140 °C, it exhibits an enantiotropic nematic mesophase. The mesogenic ligand NC-6 and its corresponding Pd complex show similar mesomorphic behavior to that of NC-8 system except that crystalline melting transition shows at higher temperature as shown in Table 1.

Ruthenium Complex with Rod-Coil Molecule

The synthesis of Ru complex which is π-complex is outlined in Scheme 2. The ^{1}H NMR spectrum(experimental section) shows a new multiplet at 6.16-6.71 ppm which is about 1 ppm upfield shifted with respect to free phenyl protons. In well characterized organometallic complexes, upfield shifts are observed upon π-coordination of arenes to the metal centers.[3,8] The mesomorphic behavior of the rod-coil ligand and the Ru complex was determined by a combination of techniques consisting of DSC and thermal optical microscopy. The phase transition temperatures and the associated enthalpy changes of the ligand and complex are presented in Table 1. As summarized in Table 1, the rod-coil ligand shows a microphase phase separated morphology and exhibits an enatiotropic smectic B mesophase. Upon complexation with ruthenium metal, a crystalline melting transition corresponding to microphase

Scheme 2



separated coil segments disappears and another crystalline melting transition corresponding to rod segments is suppressed upto 30 °C, however an isotropization transition temperature decreases only slightly compared to those of the crystalline melting transitions (Table 1). Cooling from isotropic liquid of the complex, lancet texture was formed indicating of smectic B phase. This result suggests that π-complexation of the rod-coil molecule with ruthenium metal can regulate the transition temperature and transition temperature range of the mesophase without the change of the nature of mesophase.

CONCLUSION

The ligand NC-11 exhibits a monotropic nematic mesophase as its highest temperature mesophase, however the corresponding complex with palladium metal induces an enantiotropic smectic A phase with broader mesophase temperature range. Both ligands NC-8 and NC-6 display a monotropic nematic phase and their corresponding Pd complexes exhibit an enantiotropic nematic phase enhanced thermal stability. This demonstrates that the complexation of cyanobiphenyl mesogenic ligand with palladium metal gives rise to enhanced thermal stability of mesophase and/or more ordered mesophase. The ruthenium complexation of rod-coil molecule which is typical π-complexation shows to be tailor made phase transition temperature without the change of the nature of the mesophase.

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