

Note

# Synthesis and Liquid Crystal Behaviors of 2 *A*-Dioxo-3-pentyl 4-decyloxy Cinnamate Rhodium(I) Complexes

HAN, Jie<sup>a</sup> (韩杰)    ZHANG, Liang-Fu<sup>\*a</sup> (张良辅)    WAN, Wen<sup>a</sup> (万文)

<sup>a</sup> Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, Sichuan 610041, China

<sup>b</sup> Department of Chemistry, Nankai University, Tianjin 300071, China

The title complexes have been synthesized by the reaction of  $[\text{RhCl}(\text{CO})_2]_2$  or  $[\text{RhCl}(\text{COD})]_2$  (COD = 1 *5*-cyclooctadiene) with the organic ligand 2 *A*-dioxo-3-pentyl 4-decyloxy cinnamate 2. The complex 3 based on dicarbonylrhodium(I) shows nematic phase, while the complex 4 containing rhodium(I) bound to a COD ligand is a nonmesogen. The relationship between molecular structures and liquid crystal behavior has also been discussed by means of computer-aided molecular modeling.

**Keywords** liquid crystal,  $\beta$ -diketonate, rhodium(I) complex, synthesis

## Introduction

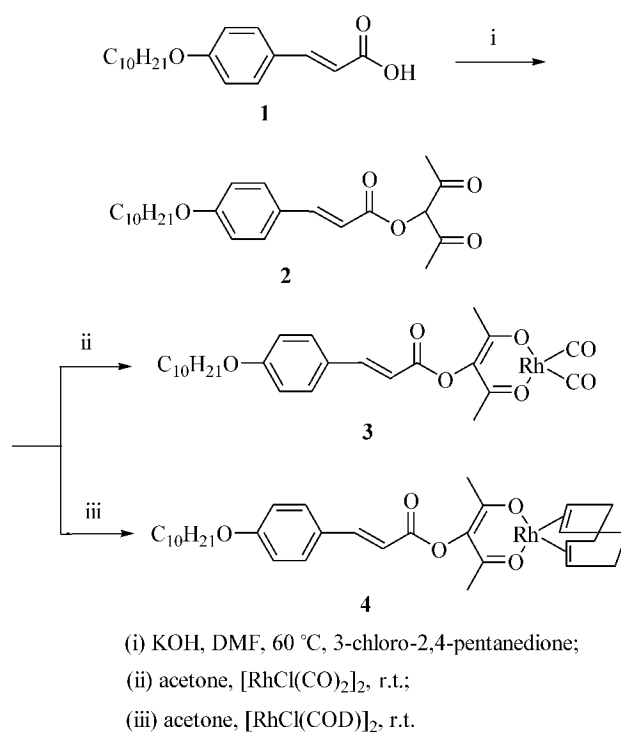
The synthesis and investigation of the physical properties of the new organometallic liquid crystals based on the  $\beta$ -diketonate are important for researching the relationship between molecular structures and mesophases. So far, the metal atom of mesogenic  $\beta$ -diketonate complexes is most situated at the center of the molecules,<sup>1</sup> such molecules have always central symmetry, which will be disadvantageous to further enhancement of electro-optic response. Only a few of metallomesogens with terminal metal atom have been reported to date. Our results<sup>2</sup> and the reports by Esteruelos *et al.*<sup>3</sup> show that this kind of organometallic complexes have great dipole moments, which are beneficial to the formation of the mesomorphism. In order to explore the effect of the terminal group on the liquid crystal behavior, the new  $\gamma$ -substituted  $\beta$ -diketonate, 2 *A*-dioxo-3-pentyl 4-decyloxy cinnamate and its rhodium(I) complexes have been synthesized in this paper, among which the rod-like type organometallic complexes containing the terminal rhodium(I) bound to a COD ligand have never been reported previously. The synthetic route of the title complexes is shown in Scheme 1.

## Results and discussion

### Synthesis and characterization

The ligand 2 has been prepared by reaction of 4-

Scheme 1



alkoxycinnamic acid 1 with 3-chloro-2 *A*-pentanedione in dry DMF as shown in Scheme 1. The complexes 3 and 4 have been obtained in good yield from the reaction of the ligand 2 with  $[\text{RhCl}(\text{CO})_2]_2$  or  $[\text{RhCl}(\text{COD})]_2$  under the excess of barium carbonate in acetone.

The structures of the compounds 2, 3 and 4 have been confirmed by IR, <sup>1</sup>H NMR, MS and elemental analysis data.

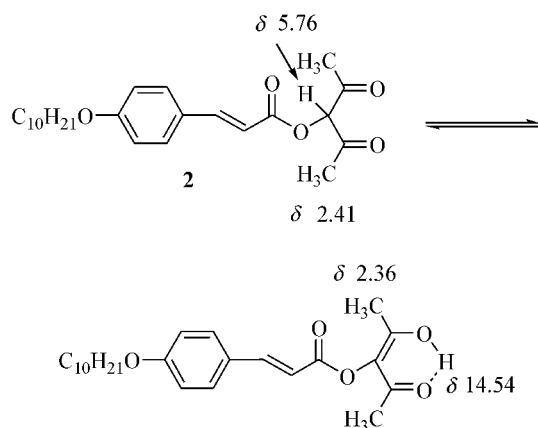
The infrared spectrum of the ligand 2 shows a strong absorption peak at *ca.* 1710  $\text{cm}^{-1}$ , which is assigned to the  $\nu_{\text{C}=\text{O}}$  and  $\nu_{\text{COO}}$ . In contrast, the absorption peak at *ca.* 1716  $\text{cm}^{-1}$  in the infrared spectra of the complexes becomes weaker than that of the free ligand, which implies that the two carbonyl groups have chelated with the metal ion. The infrared spectrum of the complex 3 shows absorption at *ca.* 2081 and 2009  $\text{cm}^{-1}$ , which are the character-

\* E-mail: liangfuzhang@hotmail.com; Tel.: +86-28-85229122

istic of the carbon monoxide stretching region.<sup>4</sup> The absorption band at *ca.* 1580 cm<sup>-1</sup> in the infrared spectra of the complexes **3** and **4** accounts for the formation of the six-membered metal chelate ring.<sup>5</sup>

From the <sup>1</sup>H NMR data of the ligand **2**, it is found that the ligand **2** exists in both of the ketone form and the enol form (Scheme 2). The <sup>1</sup>H NMR spectrum for **2** shows a signal at  $\delta$  14.54 due to the enolic proton, a signal at  $\delta$  2.36 for the CH<sub>3</sub> protons in the enol form, and the signals at  $\delta$  5.76 and  $\delta$  2.41 are assigned to the CH and CH<sub>3</sub> protons in the keto form, respectively. As to the complexes **3** and **4**, the corresponding CH<sub>3</sub> protons show only a signal at *ca.*  $\delta$  2.14, which also accounts for the formation of the metalloheterocyclic complexes.

#### Scheme 2



#### Mesogenic behavior

The phase transition and enthalpy of the ligand **2** and complexes **3** and **4** are summarized in Table 1.

**Table 1** Phase transition and transition enthalpies (kJ·mol<sup>-1</sup>) of compounds **2**, **3** and **4**

Compound	Transition <sup>a</sup>	Temperature (°C)	$\Delta H$ (kJ·mol <sup>-1</sup> )
<b>2</b>	C—I	34	18.33
<b>3</b>	C—N	94	13.19
	N—I	102	2.70
<b>4</b>	C—I	78	20.38

<sup>a</sup> C : crystals ; N : nematic phase ; I : isotropic liquid.

From Table 1, it can be seen: (i) The free ligand **2** does not exhibit mesogenic behavior; (ii) In comparison with the non-mesogenic free ligand **2**, the complex **3** is an enantiotropic mesogen and shows a typical texture of nematic phase (Fig. 1) which has been affirmed on the basis of the optical texture,<sup>6</sup> while the complex **4** has no mesomorphism. The results observed may be explained using geometrical structure and electronic factor of the molecules. The “rigid core” of the free ligand **2** is clearly small, which can not satisfy the structural demand to form the liquid crystal state. Two factors may be attributed to

the appearance of the mesomorphic behavior for the complex **3**: (i) the chelating ring of the  $\beta$ -diketone complexes is not only six-membered conjugation structure, but also planar structure because of its aromaticity, which may enhance the rigidity and extend the conjugated system of the complexes; and (ii) the terminal carbon monoxides in the complexes are strong ligands which can be easily coordinated with the metal rhodium(I) by the d- $\pi$  and  $\pi$ - $\pi^*$  interaction, both interactions tend to reduce the strength of the C $\equiv$ O bond and extend the conjugation of the “rigid core” of the organometallic molecules, which can be confirmed experimentally by comparing the vibrational spectra of free and coordinated CO, the free molecule has a stretching frequency  $\nu_{\text{CO}}$  2143 cm<sup>-1</sup>,<sup>7</sup> whereas the coordinated CO in the complex **3** has stretching frequencies at 2081 and 2009 cm<sup>-1</sup>, which implies that the CO ligand accepts  $\pi$ -back donation from metal ion and may give rise to a large anisotropy of polarizability. Both of the factors (i) and (ii) lead the complex **3** to have not only good conjugation structure, but also great dipole moments and facilitate the formation of liquid crystal phases. The reason why the complex **4** has no mesomorphism may be the voluminous terminal COD ligand, which strongly impedes the ordered intermolecular arrangement necessary for mesophase formation.



**Fig. 1** Texture of the complex **3** under cross polarizers, 65 °C, cooling, N,  $\times$  250.

In order to get further insight into the relationship between the molecular structures and the mesogenic properties, the geometries of the compounds **2** and **3** were fully optimized by the Gaussian 98 program.<sup>8</sup> Because the studied molecules are rather big, a small basis set, LanL2MB<sup>9</sup> was used, but the optimized configuration with this basis set are reliable.<sup>10</sup> The length and the anisotropy of polarizability of the compounds were also computed further. The results are summarized in Table 2 and Figs. 2 and 3.

**Table 2** The length and the anisotropy of polarizability of the compounds **2** and **3**

Compound	Length (nm)	Length-to-breadth ratio	Anisotropy of polarizability (a. u.) <sup>a</sup>
<b>2</b>	2.379	4.60	122.67
<b>3</b>	2.788	4.87	182.06

<sup>a</sup> 1 a. u. = 2.541765 Debye.

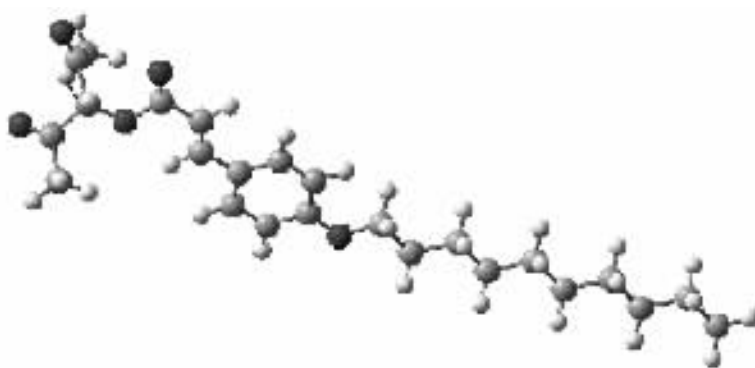


Fig. 2 Configuration of the ligand 2.

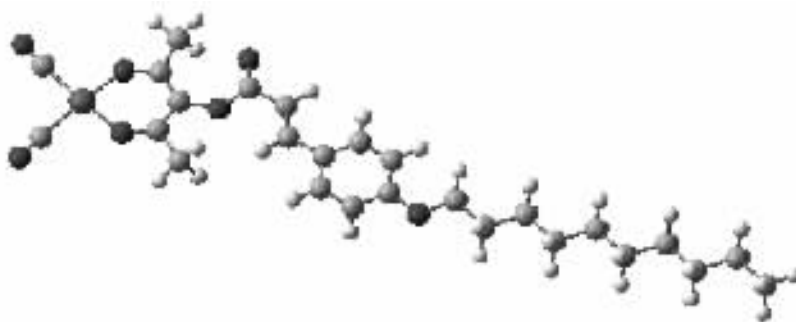


Fig. 3 Configuration of the complex 3.

From Table 2, it is found that the complex 3 is longer than the ligand 2. From Table 2 and Figs. 2, 3, the following results are found: (i) the length and the length-to-breadth ratio of the complex 3 are bigger than those of the ligand 2, which may be explained by the coordination of terminal carbonyl ligands and the formation of the six membered metalloheterocyclic structure. (ii) the anisotropy of polarizability of the complex 3 is much larger than that of the ligand 2, the large anisotropy of polarizability is beneficial to the intermolecular ordered arrangement and the formation of the mesomorphism; (iii) the complex 3 has a symmetrical plane and belongs to point group  $C_s$ , while the ligand 2 has no symmetry, which also causes that the complex 3 has a larger conjugation to form the "rigid core" than the ligand 2. In summary, the above results are advantageous to the formation of the liquid crystal state for the complex 3, which are consistent with the experimental facts.

## Experimental

The compounds were characterized by IR,  $^1\text{H}$  NMR, MS spectra and elemental analyses. The IR spectra (KBr) were performed on a NICOLET FT-MX-IE spectrometer. The  $^1\text{H}$  NMR spectra were recorded on a 300 MHz Bruker AC-P300 spectrometer, using  $\text{CDCl}_3$  as solvent and TMS as internal standard. MS spectra were carried out on a Finnigan MAT4510 spectrometer. Elemental analyses were obtained from CARLOERBA-1106 microanalyzer.

The optical textures of the mesophases were observed

under ORTHLUX-II POLBK Polarizing optical microscope with a hot stage. The transition temperatures and enthalpies were measured with a Perkin-Elmer DSC-7 instrument operated at a scanning rate of  $5\text{ }^\circ\text{C}/\text{min}$ .

### Synthesis of 2 *A*-dioxo-3-pentyl 4-decyloxy cinnamate (2)

To a suspension of  $1^{11}$  (3.04 g, 10 mmol) in dry DMF (30 mL) was added KOH (62 mg, 11 mmol), the mixture was stirred at  $60\text{ }^\circ\text{C}$  for 3 h, then 3-chloro-2,4-pentanedione (1.25 mL, 11 mmol) was added to the above mixture and stirred over night at  $40\text{--}50\text{ }^\circ\text{C}$ . After it was cooled to ambient temperature, 100 mL of water was added to the reaction mixture and the mixture was extracted three times with chloroform. The combined extracts were washed with water for three times and then dried over sodium sulfate. The solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel using ethyl acetate:petroleum ether (60–90  $^\circ\text{C}$ ) (1:2) as eluant. The products were recrystallized from ethanol to give compound 2 (2.1 g, 69%) as white solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 14.54, 5.76 (s, 1H), 7.90 (d,  $J = 16\text{ Hz}$ , 1H, C=C—H), 7.58 (d,  $J = 8.8\text{ Hz}$ , 2H, ArH), 6.97 (d,  $J = 8.8\text{ Hz}$ , 2H, ArH), 6.50 (d,  $J = 16\text{ Hz}$ , 1H, C=C—H), 4.06 (t,  $J = 6.6\text{ Hz}$ , 2H,  $\text{ArOCH}_2$ ), 2.41, 2.36 (s, 6H,  $2\text{CH}_3$ ), 1.90–1.36 [m, 16H, ( $\text{CH}_2$ ) $_8$ ], 0.93 (t,  $J = 6.4\text{ Hz}$ , 3H,  $\text{CH}_3$ ); IR (KBr)  $\nu$ : 2926, 2854, 1720, 1631, 1602, 1511, 1254, 1148, 829  $\text{cm}^{-1}$ ; MS (70 eV)  $m/z$  (%): 402 ( $\text{M}^+$ , 17), 287 (100). Anal. calcd for  $\text{C}_{24}\text{H}_{34}\text{O}_5$ : C

71.64, H 8.45; found C 71.58, H 8.57.

### Synthesis of complexes 3 and 4

A mixture of acetone solution of **2** (40.2 mg, 0.1 mmol) and  $[\text{RhCl}(\text{CO})_2]_2$  (19.5 mg, 0.05 mmol) or  $[\text{RhCl}(\text{COD})]_2$  (25.0 mg, 0.05 mmol) with excess of solid barium carbonate was stirred under argon atmosphere at room temperature for 2 h. After filtration and distillation, the remainder mixture was purified by silica gel using chloroform as eluant and recrystallized from ethanol.

**3** Yellow solid, yield 74%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 7.96 (d,  $J = 16$  Hz, 1H, C = C—H), 7.65 (d,  $J = 8.3$  Hz, 2H, ArH), 6.90 (d,  $J = 8.3$  Hz, 2H, ArH), 6.50 (d,  $J = 16$  Hz, 1H, C = C—H), 4.10 (t, 2H,  $J = 6.6$  Hz,  $\text{ArOCH}_2$ ), 2.14 (s, 6H, 2 $\text{CH}_3$ ), 1.86—1.20 [m, 16H, ( $\text{CH}_2$ )<sub>8</sub>], 0.92 (t,  $J = 6.4$  Hz, 3H,  $\text{CH}_3$ ); IR (KBr)  $\nu$ : 2923, 2852, 2081, 2009, 1723, 1631, 1601, 1580, 1509, 1473, 1253, 1139, 827  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{26}\text{H}_{33}\text{O}_7\text{Rh}$ : C 55.71, H 5.89; found C 55.43, H 6.12.

**4** Yellow solid, yield 67%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 7.78 (d,  $J = 16$  Hz, 1H, C = C—H), 7.50 (d,  $J = 8.4$  Hz, 2H, ArH), 6.70 (d,  $J = 8.4$  Hz, 2H, ArH), 6.43 (d,  $J = 16$  Hz, 1H, C = C—H), 4.40—3.96 (m, 6H,  $\text{ArOCH}_2$  and cod), 2.30 (m, 8H, cod), 2.02 (s, 6H, 2 $\text{CH}_3$ ), 1.90—1.20 [m, 16H, ( $\text{CH}_2$ )<sub>8</sub>], 0.94 (t,  $J = 6.4$  Hz, 3H,  $\text{CH}_3$ ); IR (KBr)  $\nu$ : 2925, 2853, 1724, 1631, 1603, 1578, 1512, 1468, 1373, 1249, 1133, 829  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_4\text{H}_5\text{O}_5\text{Rh}$ : C 66.67, H 7.92; found C 66.42, H 8.16.

### References

- (a) Trzaska, S. T.; Zheng, H.; Swager, T. M. *Chem. Mater.* **1999**, *11*, 130.
- (b) Zheng, H.; Lai, C. K.; Swager, T. M. *Chem. Mater.* **1995**, *7*, 2067.
- (c) Ohta, K.; Muroki, H.; Takagi, A. *Mol. Cryst. Liq. Cryst.* **1986**, *141*, 19.
- (a) Wan, W.; Guan, W.-J.; Zhang, L.-F. *J. Organomet. Chem.* **1998**, *557*, 157.

- (b) Wan, W.; Zhao, K.-Q.; Zhang, L.-F. *Acta Chim. Sinica* **1998**, *56*, 278 (in Chinese).
- (c) Han, J.; Zhang, L.-F.; Wan, W. *J. Organomet. Chem.* **2003**, *672*, 86.
- Esteruelos, M. A.; Sola, E.; Oro, L. A. *J. Organomet. Chem.* **1990**, *103*, 157.
- Gallay, J.; Montauzou, D. D.; Poilblanc, R. *J. Organomet. Chem.* **1972**, *38*, 179.
- Singh, P. R.; Sahai, R. *Indian J. Chem.* **1970**, *8*, 178.
- Demus, D.; Richter, L. *Textures of Liquid Crystals*, Verlag Chemie, Weinheim, New York, **1978**, pp. 27—94.
- Henrici-olive, G.; Olive, S. *Coordination and Catalysis*, Verlag Chemie, Weinheim, New York, **1977**, pp. 119—111.
- Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, O.; Morokums, K.; Malick, D. K.; Rabuck, A. D.; Roghachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A. 7, Gaussian, Inc., Pittsburgh PA, **1998**.
- Hay, P. T.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270.
- Xu, G.-X.; Li, Y.-M.; Wang, D.-M. *Quantum Chemistry*, 1st ed., Science Press, Beijing, **1985**, p. 818.
- (a) Neubent, M. E.; Maurer, L. *J. Mol. Cryst. Liq. Cryst.* **1978**, *45*, 207.
- (b) Rodwick, L.; Paul, M. D. *J. Am. Chem. Soc.* **1974**, *96*, 1797.
- Chatt, J.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 3178.
- Mccleverty, J. A.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 211.

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