Calamitic organometallic liquid crystals with terminal metal. Syntheses and liquid crystal properties of dicarbonylrhodium(I) β-diketonate complexes

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Abstract

A series of novel organometallic complexes based on γ-substituted β-diketone ligands with terminal metal Rh(I) have been prepared by reaction of the ligands with $[Rh(CO)_2(\mu\text{-Cl})]_2$. The mesomorphism of the ligands and complexes has been investigated using DSC and polarizing microscope. It is found that non-mesogenic ligands with $n = 7, 8, 9, 10, 11$ can form liquid crystalline phase by direct coordination to metal. The effect of the terminal carbon number on the mesomorphism has also been discussed. © 1998 Elsevier Science S.A. All rights reserved.

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Rod-like molecules containing rigid core have traditionally been regarded as the most suitable geometry to give rise to mesogenic behavior [1]. The synthesis of organometallic liquid crystals containing transition-metal atom as rigid core is currently in progress [2–4] owing to the special combination of liquid-crystalline properties with their unusual electro-optic and magnetic properties, which can offer several potential applications.

So far, the metal atom of organometallic liquid crystals is most situated at the center of the molecules [5–7]. Such molecules have always central symmetry, which will be disadvantageous to further enhancement of electro-optic response. It is well known that 1,3-disubstituted β-diketonate complexes of Cu(II) and Ni(II) give rise mostly to discotic liquid crystals, which often show the structures of central symmetry. However, the mesomorphism of rod-like γ-substituted β-diketonate complexes with terminal metal atom has never been reported, whose structure is non-centrosymmetrical.

Then we report here the results of the synthesis and liquid-crystalline properties of a new family of terminal metalloheterocyclic complexes: dicarbonylrhodium(I) β-diketonate complexes.

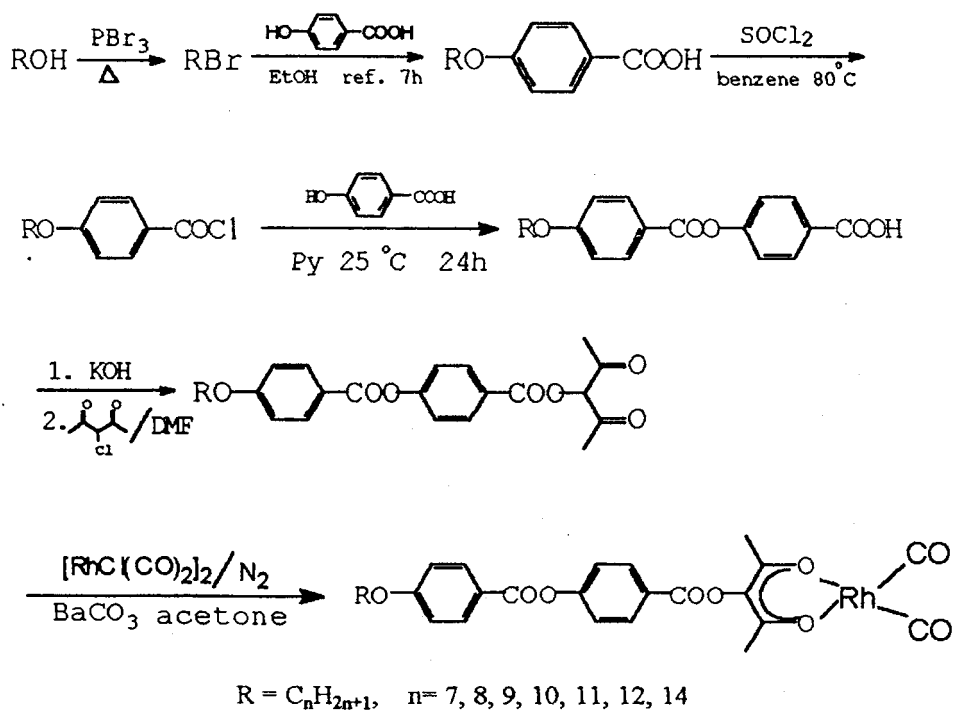The synthetic route of the title complexes is outlined in Scheme 1.

Owing to the d–π and π–π* interaction between metal and carbon monoxides, we can expect that these complexes have not only good conjugation structure, but also have great dipole moments.

1. Results and discussion

1.1. Synthesis and characterization

The ligands were prepared by reaction of 4-(4′-alkoxybenzoxy)benzoate with 3-chloro-2,4-pentane-dione in dry DMF as shown in Scheme 1. The complexes were obtained with good yields from the reaction of the ligands with μ-dichlorotetracarbonyl dirhodium under the excess of barium carbonate in acetone.

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$$\text{ROH} \xrightarrow[\Delta]{\text{PBr}_3} \text{RBr} \xrightarrow[\text{EtOH ref. 7h}]{\text{HO}-\langle\ \rangle-\text{COOH}} \text{RO}-\langle\ \rangle-\text{COOH} \xrightarrow[\text{benzene 80°C}]{\text{SOCl}_2}$$

$$\text{RO}-\langle\ \rangle-\text{COCl} \xrightarrow[\text{Py 25°C 24h}]{\text{HO}-\langle\ \rangle-\text{COOH}} \text{RO}-\langle\ \rangle-\text{COO}-\langle\ \rangle-\text{COOH}$$

$$\xrightarrow[\text{2. } \underset{\text{Cl}}{\text{acetylacetone}}/\text{DMF}]{\text{1. KOH}} \text{RO}-\langle\ \rangle-\text{COO}-\langle\ \rangle-\text{COO-CH}(\text{COCH}_3)_2$$

$$\xrightarrow[\text{BaCO}_3 \text{ acetone}]{[\text{RhCl(CO)}_2]_2/\text{N}_2} \text{RO}-\langle\ \rangle-\text{COO}-\langle\ \rangle-\text{COO-} \cdots \text{Rh(CO)}_2$$

$$R = C_nH_{2n+1}, \quad n = 7, 8, 9, 10, 11, 12, 14$$

Scheme 1.

The elemental analyses, IR, and ¹H-NMR of the complexes are consistent with the above proposed structures.

The free ligands of γ-substituted acetylacetone have two stretching vibration frequencies at 1720 and 1740 cm⁻¹, which are respectively assigned to the $v_{(C=O)}$ and $v_{(COO)}$. While, the stretching vibration frequencies of the carbonyl group in the corresponding complexes are lowered to 1590–1580 cm⁻¹ except for the stretching vibration band of ester group still around 1740 cm⁻¹, It is shown that the carbonyl and C=C bond in the conjugated chelated ring possess double bond and single bond characters respectively, accounting for the large frequency shifts of C=C bond and carbonyl group absorption after the chelation of ligand with metal [8,9]. We also find that there is no appreciable shift with phenyl group(< 4 cm⁻¹) between the ligands and the complexes. The infrared spectra of the β-diketonate complexes appear absorption 2030 and 2005 cm⁻¹, which are the characteristic of the carbon monoxide stretching region.

According to the ¹H-NMR data of the ligands and the complexes, it is found that the proton chemical shift values and coupling constants of complexes are a little lower than those of the free ligands. We think that the results are presumably due to the electronic delocalization in the organometallic complexes. One is the aid of the interaction of metal atom with CO ligands through the d–π and π–π* action. The other is the effect of the great electronic field on the β-diketonate quasi-aromatic ring. Those results lead to the shielding effect of β-diketonate on the proton.

¹H-NMR studies of the complex and ligand with $n = 10$ are shown in Table 1.

The stability of the complexes was studied by thermogravimetric analysis and none of the complexes appeared weight loss until 230°C.

1.2. Mesogenic behavior

All of the described complexes can form liquid crystals. The complexes and the ligands show mesogenic behaviors which obey the rules observed in classical rod-like organometallomesogens and organic compounds: the longer the terminal chain, the lower the melting points and the wider the liquid-crystalline phase. The transition temperature and enthalpies were determined by DSC and the structure of the mesomorphism of the ligands and complexes has been affirmed on the basis of the optical textures.

1.2.1. The ligand

The ligands with $n = 7, 8, 9, 10, 11$ have no mesomorphism. While, the ligands with $n = 12, 14$ show enantiotropic mesophase. The transition temperatures and enthalpies are shown in Table 2. The transition temperatures of ligands versus the terminal alkoxyl group are displayed in Fig. 1.

One of the textures observed with a polarizing microscope, between crossed polarizers, is shown in Fig. 2.

Table 1
The ^{1}H-NMR spectra of ligand and complex with $n = 10$ in CDCl$_3$

	δ (ppm) (multiplicities)				a	b	c	J (Hz)	
	H$_1$, H$_1'$	H$_2$, H$_2'$	H$_3$, H$_3'$	H$_4$, H$_4'$				H$_{12}$	H$_{14}$
Ligand	6.95(d)	8.12 (d)	7.35(d)	8.22(d)	4.05(t)	2.08(s)	5.70(s)	8.0	8.4
Complex	6.90(d)	8.08 (d)	7.38(d)	8.20(d)	3.98(t)	2.05(s)		7.8	8.8

1.2.2. The complex

The mesophases of the complexes are identified by their polarizing optical textures as smectic C phase. It is found that the transition temperature ranges of complexes with $n = 7, 8, 9, 10, 11$ become wider with the increase of the terminal carbon number. However, these complexes show high transition temperature and a narrow mesophase range. Interestingly, the complex with $n = 14$ gives a much lower melting point at 89°C and shows a wider mesophase range to 42°C. We are surprised to find that the complex with $n = 12$ only gives monotropic mesomorphism phase. It is found that the clearing point temperatures of the complexes become lower with the increase of the terminal carbon number

and all the complexes have higher transition temperatures than the corresponding ligands. It can be observed that the clearing point temperatures of the complexes obey an odd–even effect.

In comparison with the non-mesogenic free ligands ($n = 7, 8, 9, 10, 11$), it is found that all of the corresponding rhodium complexes show liquid-crystalline phases. To the best of our knowledge, the mesogenic complexes previously described contained a liquid crystal ligand or, alternatively, involved significant structural changes upon coordination of the organic ligand. Our results and recent reports [10,11] show that the new organometallic liquid crystals can be obtained by direct coordination of a single molecule of non mesogenic ligand to metal. These materials represent further exam-

Table 2
Optical, thermal and thermodynamic data for the ligands

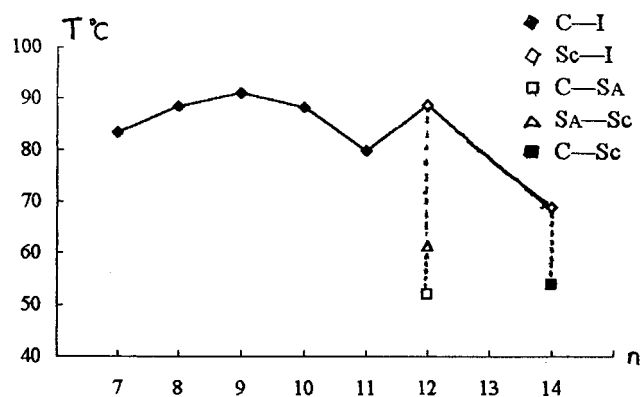| n	Transition	Temp[a], °C	ΔH^a, (kJ mol^{-1})
7	C–I	83.4	18.08
8	C–I	88.4	32.29
9	C–I	91.0	21.71
10	C–I	88.3	27.21
11	C–I	79.8	18.74
12	C–SA	51.9	7.02
	S*–Sc	61.3	1.11
	Sc–I	88.7	18.65
14	C–Sc	53.9	22.32
	Sc–I	68.8	8.02

[a] DSC data from first scan.
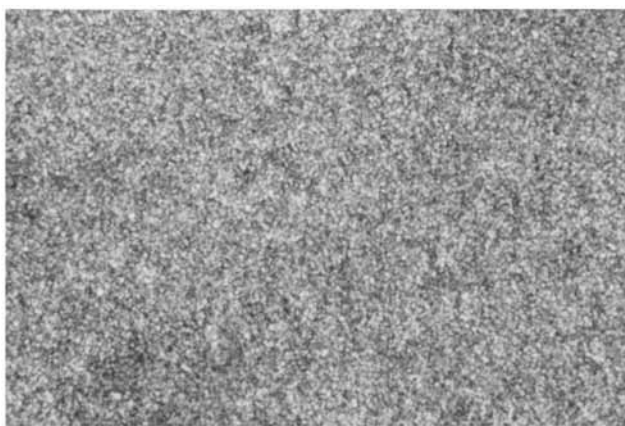

Fig. 1. Transition temperatures as a function of the alkoxy chain length for the ligands.

Fig. 2. Texture of the ligand ($n = 14$) under cross polarizers. 60°C, on cooling run. $\times 220$ Sc phase.

Fig. 3. Transition temperatures as a function of the alkoxy chain length for the complexes.

ples of mesomorphic complexes derived from non-mesogenic ligands.

The transition temperatures and enthalpies of the complexes determined by DSC are summarized in Table 3. The transition temperatures of complexes versus the terminal alkoxyl group are displayed in Fig. 3.

One of the textures observed with a polarizing optical microscope is shown in Fig. 4.

Table 3
Optical, thermal and thermodynamic data for the complexes

n	Transition[a],	Temp[b], °C	ΔH[b], (KJ mol^{-1})
7	C–C′	151.0	6.95
	C′–Sc	166.3	4.64
	Sc–I	169.8	0.72
8	C–Sc	158.7	25.87
	–Sc–I	170.5	1.85
9	C–C′	149.2	2.47
	C′–Sc	156.2	10.94
	Sc–I	171.6	6.49
10	C–C′	143.2	3.28
	C′–Sc	149.7	3.41
	Sc–I	164.7	1.74
11	C–C′	143.6	5.33
	C′–Sc	152.9	6.44
	Sc–I	166.9	3.20
12	C–I	148.0	44.83
	I–N	141.0[c]	
	N–C	126.5[c]	
14	C–C′	59.80	1.67
	C′–Sc	88.93	11.00
	Sc–I	130.56	20.04

[a] C,C′, crystalline phase; 1, isotropic liquid.
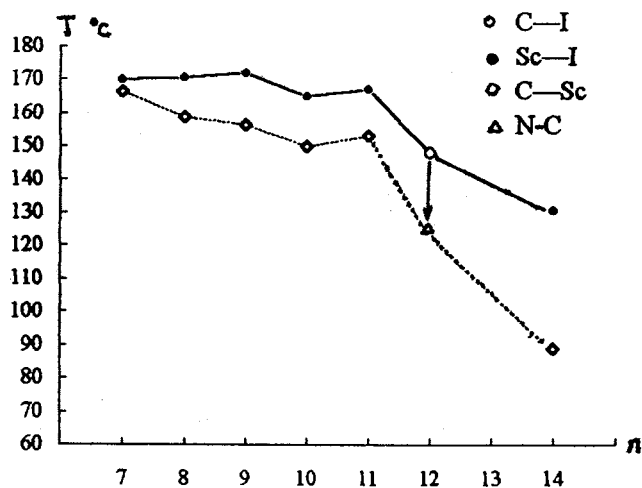[b] DSC data from first scan.
[c] Optical microscopy data.

2. Experimental section

2.1. Techniques

The ^{1}H-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-IE spectrometer. Elemental analyses were obtained from CARLO ERBA-1106 microanalyzer. The thermotropic behaviors were determined by DSC using Perkin–Elmer 7 series analysis system operated at a scanning rate of 10°C min^{-1}. The apparatus was calibrated with indium (156.6°C, 28.4 J g^{-1}) and tin (231.1°C 60.5 J g^{-1}). The textures of mesophase were observed under ORTH-LUX-II POLBK Polarizing optical microscope with a hot stage (self made) and TDA temperature controller.
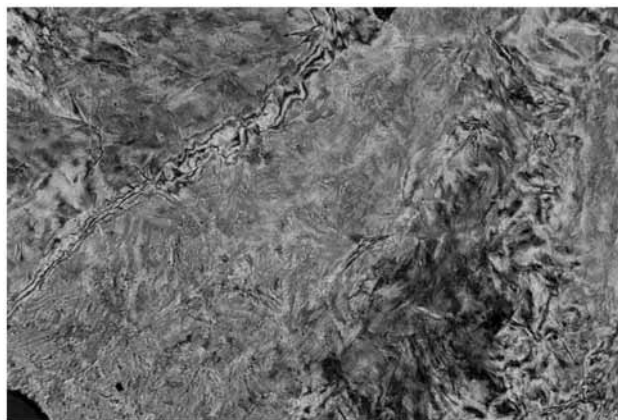

Fig. 4. Texture of the complex ($n = 12$) under cross polarizers. 130°C, on cooling run. $\times 220$, nematic phase.

Table 4
The elemental analyses (percent) of the ligands and the complexes (calculated values in parenthesis) and yields

Compounds	n	C (%)	H (%)	Yields (%)
Ligand	7	68.88 (68.72)	6.71 (6.61)	58
	8	69.43 (69.23)	6.90 (6.84)	63
	9	69.57 (69.71)	7.24 (7.05)	47
	10	70.28 (70.16)	7.43 (7.26)	50
	11	70.58 (70.59)	7.31 (7.45)	54
	12	70.78 (70.99)	7.70 (7.63)	59
	14	71.52 (71.74)	7.93 (7.97)	51
Complex	7	54.80 (54.90)	4.80 (4.74)	82
	8	55.79 (55.59)	4.96 (4.95)	87
	9	56.21 (56.25)	5.27 (5.16)	83
	10	56.79 (56.88)	5.51 (535)	78
	11	57.23 (57.48)	5.76 (5.54)	89
	12	57.89 (58.06)	5.98 (5.72)	91
	14	59.30 (59.15)	6.23 (6.06)	88

2.2. Synthesis

2.2.1. Synthesis of the ligands

The ligands were prepared in good yields by reaction of potassium 4-*n*-alkoxybenzoxybenzoate [12,13] with 3-chloro-2,4-pentanedione [14] in dry DMF at 40–50°C stirring overnight to give red solution [15]. After cooled, 250 ml water was added to the reaction mixture and the mixture was extracted several times with chloroform. The combined extracts were dried with sodium sulfate and distilled. The residue was chromatographed on silica gel using ethyl acetate: petroleum ether (60–90°C) (1:2) as eluant. The products were purified by recrystallization from ethanol, yields 50–60%.

2.2.2. Synthesis of the complexes

A mixture of acetone solutions of ligand (1 mmol) and μ-dichlorotetracarbonyl dirhodium [Rh(CO)$_2$Cl]$_2$ [16] (0.5 mmol) with excess of solid barium carbonate was stirred under N$_2$ at room temperature for 30 min [17]. After filtered and distilled, the reminder mixture was chromatographed on silica gel using chloroform as eluent. The products were purified by recrystallization from ethanol, yield about 85%.

The elemental analyses and yields of the ligands and the complexes are summarized in Table 4. All the compounds were characterized by IR and ^{1}H-NMR techniques without significant difference within the same series

3. Conclusion

A new series of calamitic organometallomesogens of β-diketonate complexes with terminal metal Rh(I) have been synthesized and characterized. Interestingly, the results reported in the paper show that non-mesogenic rod-like ligands of β-diketone can form liquid crystalline phases by direct coordination to metal Rh(I).

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