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Synthesis and Liquid-Crystal Properties of Di(arylethynyl)bis(triethylphosphine)platinum(II)

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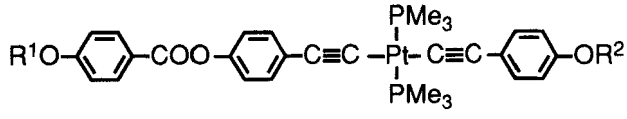
The title complexes containing platinum-carbon σ-bonds and triethylphosphine ligands were synthesized and their thermal properties were examined. The complexes composed of a four-ring system showed enantiotropic nematic phases, though they have a very large lateral group. Direction of the ester group of the complexes strongly influenced the thermal stability of mesophases.

INTRODUCTION

There is currently considerable interest in metallomesogens owing to their unique optical, magnetic and electronic properties based on transition metals. Among metallomesogens reported thus far,[1] little attention has been focused on organometallic mesogens especially possessing a σ-bond between carbon and transition metal. This is because many organotransition metal complexes having a σ carbon-metal bond are, in general, thermally unstable and sensitive to moisture and air. To our knowledge, cyclopalladated complexes with several types of ligands[2] and some metal carbonyl complexes[3] have been shown to form thermotropic liquid crystals. We have reported previously that *trans*-di(arylethynyl)bis(trimethylphosphine)platinum(II) complex **1**, which is the constituent unit of rod-like metal-poly(yne) polymers forming lyotropic liquid crystals,[4] exhibits thermotropic liquid-crystal properties.[5]

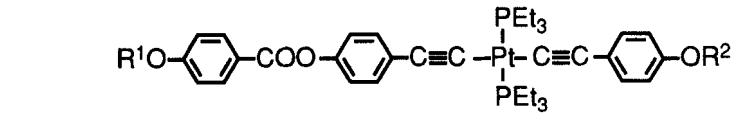


(**1**)

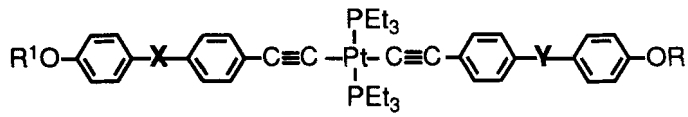
The platinum arylethynyl **1** provides a rare example of organometallic mesogens and the first example of thermotropic liquid-crystalline molecules containing a tertiary phosphine which is a good stabilizing ligand for organometallic complexes.

It is well known that the bulkiness of lateral groups strikingly influences the stability of mesophases.[6] For an investigation about the net effect of lateral groups

on mesophases, the present platinum complexes are of good choice because the bulkiness of lateral groups can be easily varied, without any changes in the main chain structure of molecules, by replacing the trimethylphosphine ligand with larger trialkylphosphines like triethylphosphine. We report here the preparation and mesogenic behavior of *trans*-di(arylethynyl)bis(triethylphosphine)platinum(II) complexes **2**–**5** which bear a larger lateral ligand, triethylphosphine, than trimethylphosphine in complex **1**.



(**2**) $R^1=C_nH_{2n+1}$, $R^2=C_mH_{2m+1}$



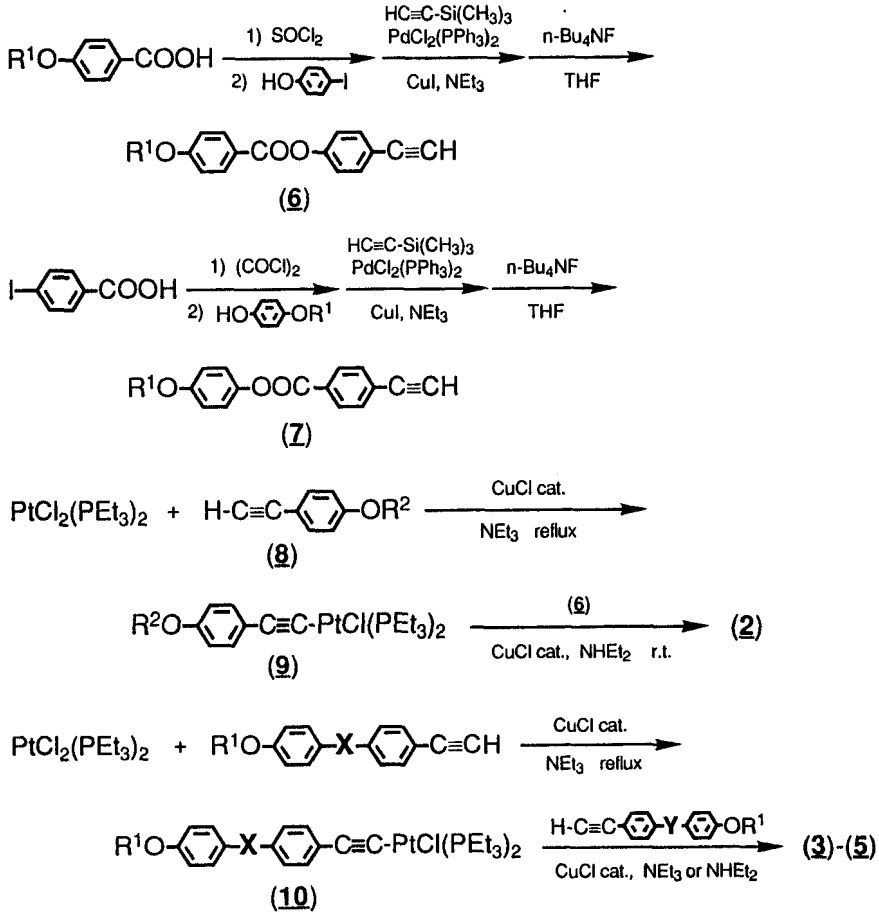
(**3**): X=-COO-, Y=-OOC- (**4**): X=-OOC-, Y=-COO-
(**5**): X=-COO-, Y=-COO-

RESULTS AND DISCUSSION

Synthesis and Characterization

The synthetic routes to complexes **2**–**5** are shown in Scheme 1.
Most of the complexes **2**–**5** were synthesized by dehydrohalogenation between terminal acetylenes and metal halides using a copper(I) halide catalyst.[5,7] Terminal acetylene compounds **6** and **7** were prepared starting from benzoic acid derivatives. Esterification with phenols was carried out using thionyl chloride for alkoxybenzoic acids and oxalyl chloride for iodobenzoic acid. Though compound **6** displayed mesogenic properties depending upon the chain length of terminal alkyl groups, compound **7** showed no mesogenic properties.

The complexes **3**–**5** have isomeric structures in respect of a different direction of the ester groups. Isomers **3** and **4**, having symmetrical structures, were prepared from the reaction of dichlorobis(triethylphosphine)platinum with two moles of ligands **6** and **7**, respectively, in the presence of copper(I) chloride as a catalyst in triethylamine under reflux conditions. Isomer **5** of an unsymmetrical structure was successfully obtained from the reaction of **10**, which was synthesized from dichlorobis(triethylphosphine)platinum with one equimolar ligand **6**, with one equimolar ligand **7** in the presence of a copper(I) chloride catalyst in diethylamine at room temperature. The target complexes **2**–**5** were purified by column chromatography on alumina and recrystallization, and obtained as yellow crystalline solids. The identification was made by elemental analysis, IR and ^{1}H-NMR spectra, which were consistent with the proposed structure. Square planar complexes of Pt(II)



SCHEME I

have two possible configurations: *cis* and *trans*. The *trans*-configuration of complexes **2**–**5** has been confirmed by the NMR method. For example, the $^{31}P\{^1H\}$NMR spectrum of complex **2c** exhibited only one signal at 17.2 ppm (down-field from an external triphenylphosphine reference) with attendant satellites due to the coupling (J_{Pt-P} = 2370 Hz) with ^{195}Pt nuclei (I = 1/2, natural abandance 34%), indicating the two phosphorus ligands to be magnetically equivalent to each other. Detailed spectral data are collected in the Experimental Section.

Thermal Property

The thermal properties and phase sequences of **2**–**5** are summarized in Tables I–III. All the complexes showed only a nematic phase. The identification of mesophases has been made on the basis of optical textures, namely, a typical nematic droplet on cooling from the isotropic liquid and marble texture. Generally the

TABLE I

Transition temperatures (°C) and thermal data ($\Delta H/kJmol^{-1}$) for complex **2**

	n	m	C		N		I	TG(°C)
2a	3	8	•	105 [38.8]	(•	81 [1.9])	•	247
2b	5	8	•	106 [52.2]	(•	72 [1.8])	•	231
2c	8	8	•	93 [41.9]	(•	62 [2.0])	•	248
2d	10	8	•	92 [48.8]	(•	56 [2.0])	•	242
2e	3	5	•	113 [41.7]	(•	95 [2.4])	•	255
2f	5	5	•	108 [38.3]	(•	86 [2.1])	•	252

TABLE II

Transition temperatures (°C) and thermal data ($\Delta H/kJmol^{-1}$) for complex **3**

	n	C		N		I	TG(°C)
3a	3	•	191 [30.5]	•	220[1)]	•	240
3b	5	•	158 [21.6]	•	199 [2.0]	•	250
3c	6	•	150 [48.4]	•	185 [2.9]	•	227
3d	7	•	144 [63.8]	•	169 [3.2]	•	238
3e	8	•	134 [27.2]	•	156 [2.7]	•	247
3f	10	•	123 [50.4]	•	136 [2.6]	•	248
3g	12	•	119[2)] [66.0][3)]	•	122[2)]	•	248

1) Optical microscopic data. 2) Heating rate at 2 °C/min.
3) Combined enthalpies.

melting and clearing temperatures of metallomesogens are raised over those for corresponding organic mesogenes owing to the incorporation of a metal.[2,3,8] Complex **2** formed an *N* phase in a lower temperature range compared with the analogous complex of type **1**, and the thermal stabilities of *N* phases are relatively low and all of complexes **2** exhibited monotropic transitions. This result may be due to the larger lateral ligand, triethylphosphine, of complex **2** than the lateral trimethylphosphine ligand of complex **1**. Large lateral groups result in a decrease of structural anisotropy (a decrease in the length : width ratio) in the molecules. Judging from the CPK molecular model, though the length of molecules **1** and **2** must be equal, the width of molecule **2** is about 1.2 times longer than that of molecule **1**. The temperatures of nematic-to-crystal transition could not be determined with

TABLE III

Transition temperatures (°C) and thermal data (ΔH/kJmol^{-1}) for complexes 4 and 5

	n	C		N		I	TG(°C)
4 a	5	•	181 [45.4]	(•	172 [2.0])	•	259
4 b	6	•	147 [63.4]	•	169 [3.7]	•	245
4 c	7	•	124 [67.4]	•	147 [2.6]	•	248
4 d	8	•	124 [63.5]	•	142 [1.8]	•	248
5 a	5	•	126 [40.0]	•	190 [2.7]	•	230
5 b	6	•	125 [37.4]	•	182 [3.1]	•	243
5 c	7	•	105 [28.1]	•	163 [3.2]	•	224
5 d	8	•	114 [64.9]	•	156 [2.9]	•	247

the exception of **2a** (74°C), because of the absense of definite peaks in the DSC measurement and a broad temperature range under the observation with a polarising microscope.

An increase of structural anisotropy effectively stabilized mesophases. This is the case for four-ring system complexes **3**–**5**, which form more stable *N* phases than complex **2**. With respect to a length of terminal alkyl chains, however, complexes with longer chains showed lower nematic-to-isotropic transition temperatures and resulted in a narrower temperature range of mesophases. Complexes, even with long alkyl chains, formed relatively stable *N* phases, but no *S* phases were observed for all of complexes **3**–**5**. Replacement of triethylphosphine with tri-n-butylphosphine in complex **3e** resulted in no formation of any mesophases (m.p. 87°C).

It is believed that a phenyl benzoate mesogen shows an efficient intermolecular interaction owing to the dipole moment of the ester group across the molecular axis, and is widely adopted for the construction of liquid crystalline materials. Some reports have revealed that the direction of an ester group in an organic liquid crystalline molecule influences the thermal stability of mesophases.[9] In order to investigate the effect of ester groups in metallomesogens, we have synthesized three types of complexes **3**–**5** which have a different structure in respect of the direction of ester groups. Among them complex **3** formed the most stable mesophases. This result shows the same trend of the effect by the direction of ester groups reported previously. Complex **5** showed a substantial reduction in the crystal-to-nematic transition, compared with the analogues **3** and **4**. This may be attributable to the less efficient packing in the crystal for the unsymmetrical structure of complex **5**. The nematic-to-isotropic transition temperatures for complex **5** fell between those of the symmetrical isomers. As a result, complex **5** exhibited the widest mesomorphic range in the three structural isomers.

EXPERIMENTAL

Elemental microanalyses were done by the Material Analysis Center, ISIR, Osaka University. IR spectra were obtained with a Hitachi 295 infrared spectrophotometer. ^{1}H NMR spectra were recorded with a Brucker WM-360 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard, and ^{31}P NMR spectra with a JEOL FX-100 instrument at 40.3 MHz in CD_2Cl_2 with PPh_3 as an external standard. Textures were observed using an Olympus BH-2 polarizing microscope in conjunction with a Mettler FP52 heating stage and an FP5 control unit, and phase transition temperatures and enthalpies were determined using a Shimazu DSC-50 differential scanning calorimeter. The apparatus was calibrated with standard samples of indium (156.6°C, 28.44 J/g) and tin (232.1°C, 60.5 J/g). The rate of heating or cooling was fixed to 5°C/min under an argon atmosphere unless otherwise stated. Thermogravimetric analyses were performed on a Shimazu TGA-50 thermogravimetric analyzer at a heating rate of 5°C/min under an argon atmosphere.

Dichlorobis(triethylphosphine)platinum was prepared from potassium tetrachloroplatinate and triethylphosphine by a literature method.[10]

Synthesis of Complex 3e (n = 8)

A mixture of dichlorobis(triethylphosphine)platinum(II) (352 mg, 0.7 mmol) and 4-octyloxyphenylacetylene (569 mg, 1.4 mmol) in a mixture of triethylamine (30 ml) and toluene (30 ml) was allowed to react in the presence of copper(I) chloride as a catalyst at 90°C for 5 h under a nitrogen atmosphere. After concentration of the solution, the resultant product was purified by column chromatography on alumina, followed by recrystallization from dichloromethane-hexane (1:2). A yellow crystalline product was obtained: yield 720 mg (83%). ^{1}H NMR ($CDCl_3$) δ = 0.90 (6H, t, J = 7 Hz, CH_3), 1.19–1.40 (38H, m, alkyl, $P(CH_2C\underline{H}_3)_3$), 1.82(4H, tt, J = 7 Hz, $OCH_2C\underline{H}_2$), 2.14–2.22(12H, m, $P(C\underline{H}_2CH_3)_3$), 4.04(4H, t, J = 7 Hz, OCH_2), 6.96(4H, d, J = 9 Hz, Ar), 7.04(4H, d, J = 9 Hz, Ar), 7.31(4H, d, J = 8 Hz, Ar), 8.13(4H, d, J = 9 Hz, Ar); ^{31}P NMR (CD_2Cl_2) δ = 17.3 ppm (J_{P-Pt} = 2360 Hz); IR(KBr) 2100(C≡C), 1730, 1710(C=O), 1600, 1500(Ar), 1250(C—O) cm^{-1}; Anal. Calcd for $C_{58}H_{80}O_6P_2Pt$: C, 61.63; H, 7.13; P, 5.48%. Found: C, 61.82; H, 6.89; P, 5.30%.

Yields and microanalytical results of analogues are collected in Table V.

Other complexes were prepared in a similar manner to that reported previously.[5]

Physical data of **2c**: ^{1}H NMR ($CDCl_3$) δ = 0.87–0.90(6H, m, CH_3), 1.18–1.48(38H, m, alkyl, $P(CH_2C\underline{H}_3)_3$), 1.74–1.84(12H, m, $P(C\underline{H}_2CH_3)_3$), 3.92(2H, t, J = 7 Hz, OCH_2), 4.04(2H, t, J = 7 Hz, OCH_2), 6.75(2H, d, J = 9 Hz, Ar), 6.96(2H, d, J = 9 Hz, Ar), 7.03(2H, d, J = 9 Hz, Ar), 7.20(2H, d, J = 9 Hz, Ar), 7.30(2H, d, J = 9 Hz, Ar), 8.13(2H, d, J = 9Hz, Ar): ^{31}P NMR (CD_2Cl_2) δ = 17.2 ppm(J_{P-Pt} = 2370 Hz); IR(nujol) 2100(C≡C), 1730(C=O), 1600, 1500(Ar), 1250(C—O) cm^{-1}; Anal. Calcd for $C_{51}H_{76}O_4P_2Pt$: C, 60.64; H, 7.58; P, 6.13%. Found: C, 60.96; H, 7.71; P, 6.63%.

Yields and microanalytical results of analogues are collected in Table IV.

TABLE IV

Microanalytical data for complex 2

complex				Calcd(%)			Found(%)		
	m	n	Yield(%)	C	H	P	C	H	P
2a	3	8	77	58.77	7.08	6.59	59.05	7.15	6.42
2b	5	8	68	59.55	7.29	6.40	59.72	7.24	6.39
2c	8	8	64	60.64	7.58	6.13	60.96	7.71	6.03
2d	10	8	76	61.31	7.77	5.97	61.49	7.80	5.91
2e	3	5	78	57.51	6.73	6.90	57.55	6.69	6.77
2f	5	5	80	58.36	6.96	6.68	58.69	6.99	6.63

TABLE V

Microanalytical data for complex 3, 4 and 5

			Calcd(%)			Found(%)		
	n	Yield(%)	C	H	P	C	H	P
3a	3	50	58.23	6.11	6.26	57.96	6.50	6.22
3b	5	77	59.70	6.55	5.92	59.39	6.37	5.71
3c	6	67	60.38	6.76	5.77	60.49	6.63	5.48
3d	7	70	61.02	6.95	5.62	61.27	7.17	5.66
3e	8	89	61.63	7.13	5.48	61.82	6.89	5.30
3f	10	76	62.77	7.48	5.22	63.00	7.52	5.11
3g	12	83	63.80	7.79	4.99	63.57	7.57	4.74
4a	5	75	59.70	6.55	5.92	59.93	6.34	5.98
4b	6	76	60.38	6.76	5.77	60.11	6.98	5.71
4c	7	74	61.02	6.95	5.62	60.74	7.00	5.53
4d	8	81	61.63	7.13	5.48	61.77	6.91	5.32
5a	5	88	59.70	6.55	5.92	59.74	6.34	6.02
5b	6	79	60.38	6.76	5.77	60.19	7.04	5.74
5c	7	65	61.02	6.95	5.62	60.82	6.99	5.41
5d	8	78	61.63	7.13	5.48	61.51	6.95	5.22

Physical data of **4d**: ^{1}H NMR ($CDCl_3$) δ = 0.87–0.91(6H, m, CH_3), 1.20–1.46(38H, m, alkyl, $P(CH_2\underline{CH_3})_3$), 1.79(4H, tt, J = 7 Hz, $OCH_2\underline{CH_2}$), 2.17–2.21(12H, m, $P(\underline{CH_2}CH_3)_3$), 3.96(4H, t, J = 7 Hz, OCH_2), 6.92(4H, d, J = 9 Hz, Ar), 7.10(4H, d, J = 9 Hz, Ar), 7.35(4H, d, J = 9 Hz, Ar), 8.03(4H, d, J = 9 Hz, Ar); ^{31}P NMR (CD_2Cl_2) δ = 17.7 ppm (J_{P-Pt} = 2340 Hz); IR(KBr) 2100(C≡C), 1730(C=O), 1600, 1500(Ar), 1250(C—O) cm^{-1}; Anal. Calcd for $C_{58}H_{80}O_6P_2Pt$: C, 61.63; H, 7.13; P, 5.48%. Found: C, 61.77; H, 6.91; P, 5.32%.

Yields and microanalytical results of analogues are collected in Table V.

Physical data of **5d**: ^{1}H NMR ($CDCl_3$) δ = 0.88–0.91(6H, m, CH_3), 1.20–1.48(38H,

m, alkyl, $P(CH_2C\underline{H}_3)_3$), 1.76–1.84(4H, m, $OCH_2C\underline{H}_2$), 2.14–2.23(12H, m, $P(C\underline{H}_2CH_3)_3$), 3.95(2H, t, J = 7 Hz, OCH_2), 4.04(2H, t, J = 7 Hz, OCH_2), 6.91(2H, d, J = 9 Hz, Ar), 6.96(2H, d, J = 9 Hz, Ar), 7.05(2H, d, J = 8 Hz, Ar), 7.10(2H, d, J = 9 Hz, Ar), 7.30(2H, d, J = 8 Hz, Ar), 7.35(2H, d, J = 8 Hz, Ar), 8.03(2H, d, J = 9 Hz, Ar), 8.13(2H, d, J = 9 Hz, Ar); ^{31}P NMR (CD_2Cl_2) δ = 17.6 ppm (J_{P-Pt} = 2350 Hz); IR(KBr) 2100(C≡C), 1730 (C=O), 1600, 1500(Ar), 1250(C—O) cm^{-1}; Anal. Calcd for $C_{58}H_{80}O_6P_2Pt$: C, 61.63; H, 7.13; P, 5.48%. Found: C, 61.51; H, 6.95; P, 5.22%.

Yields and microanalytical results of analogues are collected in Table V.

Physical data of **7** *(n = 8):* ^{1}H NMR ($CDCl_3$) δ = 0.89(3H, t, J = 7 Hz, CH_3), 1.30–1.48(10H, m, alkyl), 1.79(2H, tt, J = 7 Hz, $OCH_2C\underline{H}_2$), 3.26(1H, s, ≡C—H), 3.96(2H, t, J = 7 Hz, OCH_2), 6.92(2H, d, J = 9 Hz, Ar), 7.11(2H, d, J = 9 Hz, Ar), 7.61(2H, d, J = 8 Hz, Ar), 8.14(2H, d, J = 9 Hz, Ar); IR(nujol) 3200(≡C—H), 1755(C=O), 1610(Ar), 1260 cm^{-1}(C—O); Anal. Calcd for $C_{23}H_{26}O_3$: C, 78.83; H, 7.48%. Found: C, 79.02; H, 7.30%. m.p. 88.3–89.0°C.

Physical data of **9** *(n = 8):* ^{1}H NMR ($CDCl_3$) δ = 0.88(3H, t, J = 7 Hz, CH_3), 1.15–1.31(28H, m, alkyl, $P(CH_2C\underline{H}_3)_3$), 1.76(2H, tt, J = 7 Hz, $OCH_2C\underline{H}_2$), 2.02–2.10(12H, m, $P(C\underline{H}_2CH_3)_3$), 3.91(2H, t, J = 7 Hz, OCH_2), 6.76(2H, d, J = 9 Hz, Ar), 7.17(2H, d, J = 9 Hz, Ar); IR(neat) 2120(C≡C), 1600(Ar), 1240, 1040 cm^{-1}(C—O). n_D = 1.583(17°C); Anal. Calcd for $C_{28}H_{51}ClOP_2Pt$: C, 48.31; H, 7.38; Cl, 5.09; P, 8.90%. Found: C, 48.15; H, 7.44; Cl, 4.99; P, 8.93%.

Physical data of **10** *(n = 8):* m.p. 58.0–58.7°C; ^{1}H NMR ($CDCl_3$) δ = 0.88–0.91(3H, m, CH_3), 1.16–1.48(28H, m, alkyl, $P(CH_2C\underline{H}_3)_3$), 1.82(2H, tt, J = 7 Hz, $OCH_2C\underline{H}_2$), 2.03–2.11(12H, m, $P(C\underline{H}_2CH_3)_3$), 4.04(2H, t, J = 7 Hz, OCH_2), 6.96(2H, d, J = 9 Hz, Ar), 7.04(2H, d, J = 9 Hz, Ar), 7.27(2H, d, J = 9 Hz, Ar), 8.12(2H, d, J = 9 Hz, Ar); Anal. Calcd for $C_{35}H_{55}ClO_3P_2Pt$: C, 51.50; H, 6.76; Cl, 4.34; P, 7.59%. Found: C, 51.69; H, 6.55; Cl, 4.11; P, 7.38%.

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