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Synthesis, structure, and liquid crystal properties of a series of platinum(II) complexes containing chiral 4-(4-alkoxyphenylethynyl) phenylisocyanide ligands

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Dedicated to Prof. E.O. Fischer on the occasion of his 85th birthday

Abstract

Several platinum(II) isocyanide complexes of the type $\text{PtI}_2(\text{CNC}_6\text{H}_2-2,6-\text{R}_2-4\text{-CC}-(\text{C}_6\text{H}_2-3,5-\text{R}'_2-4-(\text{R} \text{ or } \text{S})\text{-OCHMeC}_{n-1}(\text{H}_2)_{(n-1)}\text{CH}_3)_2)$ have been prepared and their mesomorphic properties have been investigated. The complexes with $\text{R} = \text{Me}$, $\text{R}' = \text{H}$, and $n = 4-7$ exhibit a broader N^* phase than the corresponding complexes with $\text{R} = \text{R}' = \text{H}$, indicating that the methyl substituents on the phenylisocyanide group improve the liquid crystal properties by creating a smooth transition between the bulky PtI_2 center and the more slender organic units. The complexes with $\text{R} = \text{Me}$ and $\text{R}' = \text{Me}$ exhibit a SmA phase. The presence of methyl groups in the R' -positions in addition to the methyl groups in the R -positions increases the melting point, but does not significantly change the clearing temperature. For the complexes with $\text{R} = \text{Me}$ and $\text{R}' = \text{H}$ the temperature-dependent pitches of the N^* phase range from 350 to 400 nm.

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1. Introduction

Linear metal complexes of isocyanides with rigid central cores and flexible terminal chains have been demonstrated by Takahashi and coworkers [1–4] and by Espinet and coworkers [5–16] to exhibit liquid crystal properties. In typical examples, the rigid cores of the isocyanides contain one or several phenyl rings while alkoxy groups form the flexible chains. By introducing chiral alkoxy groups, Serrano, Veciana and coworkers have furthermore shown that metal complexes of this type can form ferroelectric liquid crystals [17], and Espinet and coworkers were able to obtain complexes exhibiting twist-grain boundaries and blue phases [15].

We have recently prepared palladium and platinum complexes of the same general type based on 4-isocyanobenzylidene-4-alkoxyphenylimines [18]. Complexes **I** are distinguished from other mesomorphic isocyanide metal complexes primarily by the presence of the imine bridge between the aromatic rings and the lateral methyl substituents on the isocyanophenyl groups. The imine linkage provides a convenient means of assembling the elongated rigid core, but its hydrolytic ability also limits the potential utility of the liquid crystals. In the present complexes **1**, we replaced the imino bridge by the hydrolytically stable, but sterically similar ethynylene connector. The lateral methyl substituents on the isocyanide ligands in complexes **I** were suggested to have a favorable influence on the liquid crystal properties, by smoothing out the protrusions created by the lateral iodide ligands. In order to evaluate this notion, we included in this study also isocyanides without methyl substituents and isocyanides with addi-

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tional methyl substituents on the second aromatic ring. The results confirm that the lateral methyl substituents on the isocyanophenyl groups indeed exert a beneficial influence on the liquid crystal properties.

As a further modification, we introduced chiral 1-methylalkoxy chains in complexes **1**. Complexes **I** were found to exhibit a nematic (N) and/or a smectic C (SmC) phase, the latter covering a broad temperature range. The observation of a broad SmC phase suggested to us that analogues with chiral alkoxy groups might exhibit a chiral smectic C (Sm**C*) phase. However, this expectation could not be confirmed in the present study, presumably because the alkoxy chains of complexes **1** are too short. For the chain lengths covered in this study ($n = 4-7$) both complexes **I** and **1** exhibit only nematic phases, N and N*, respectively.

2. Experimental

The ^1H - and ^{13}C -NMR spectra were recorded on a Bruker DPX 300 or a JEOL 270 NMR spectrometer, using tetramethylsilane as internal standard. IR spectra were measured in CH_2Cl_2 solution using a Shimadzu FTIR-8201PC infrared spectrophotometer. Mass spectra were obtained with a Finnigan MAT 95 MS spectrometer. The textures of the mesophases were studied with a Leica polarizing microscope equipped with a Mettler FP82 hot stage. The transition temperatures were obtained by differential scanning calorimetry using a Perkin–Elmer DSC7 instrument with heating rates of 10 K min^{-1} under a nitrogen atmosphere. Elemental microanalyses were performed by Butterworth Laboratories Ltd.

The reflectance spectra were measured in the following way: A few milligrams of a sample were dropped onto a cleaned glass substrate and heated to the temperature of the liquid crystal phase. Then, a cleaned microscopy cover glass was carefully placed on top of the sample and gently pressed to create a flow-induced alignment. After the alignment test cell was cooled to room temperature, it was transferred to a polarizing microscope, and the reflective spectrum was measured with an ORIEL MS257 imaging spectrometer connected to the crossed polarizer microscope via an optic fiber. The temperature of the sample was controlled with a Mettler FP82 hot stage. The data were analyzed using ORIEL Instaspec software.

Methylene chloride, *n*-hexane, and triethylamine were dried over calcium hydride and distilled prior to use. All other solvents and reagents were used as received. 4-Iodoaniline, 4-iodophenol, (*R*)- and (*S*)-2-hexanol, (*R*)-2-pentanol, (*S*)-2-heptanol, and (*R*)- and (*S*)-2-octanol were obtained from Aldrich or Acros. 4-Iodo-2,6-dimethylaniline and 4-iodo-2,6-dimethylphenol were prepared by iodination of 2,6-dimethylaniline and 2,6-

dimethylphenol [19,20]. 4-Ethynylaniline and 4-ethynyl-2,6-dimethylaniline [21] were prepared from the corresponding 4-iodoanilines via palladium(0)–copper(I)-catalyzed coupling with trimethylsilylacetylene, followed by hydrolytic desilylation [22]. The compounds (*R*)- or (*S*)-4-I-2,6-R₂-C₆H₂-OC*(Me)H-C_{*n*-1}H_{2(*n*-1)+2} ($n = 4-7$, R = H, Me) were prepared from the corresponding alcohols and phenols following an established literature procedure [23]. All of the ligands and their metal complexes were prepared in the same manner as outlined in Scheme 1. Typical preparative procedures and physical data for intermediates, ligands, and metal complexes are given below.

2.1. Synthesis of anilines **2**

2.1.1. (*R*)-4-(4-(1-methylheptyloxy)phenylethynyl)-2,6-dimethylaniline (**2e**)

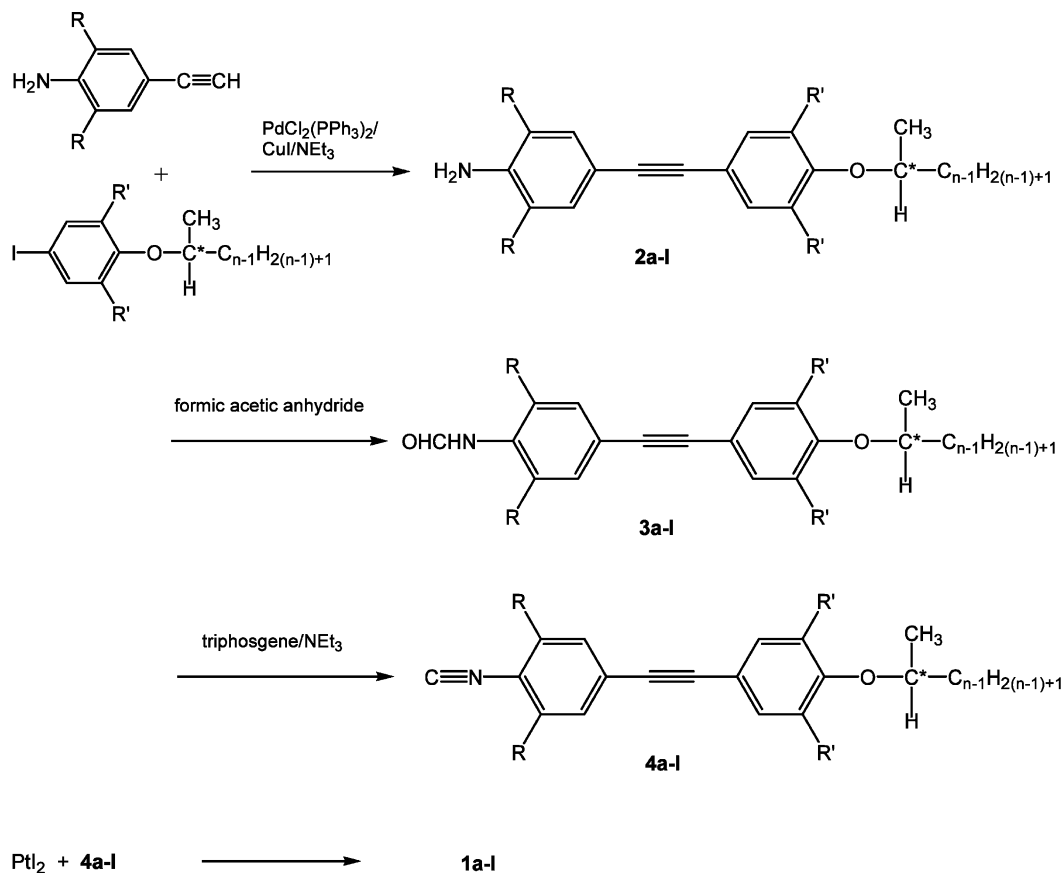
Under an atmosphere of nitrogen, a 100 ml flask is charged with (*R*)-4-iodo-(1-methylheptyloxy)benzene (664 mg, 2 mmol), 4-ethynyl-2,6-dimethylaniline (290 mg, 2 mmol), bis(triphenylphosphine)palladium dichloride (28.6 mg) and copper (I) iodide (57 mg) [24]. Then triethylamine (60 ml) is added, and the reaction mixture is stirred at 50–70 °C for 24 h. The solvent is removed under reduced pressure. The residue is extracted with dichloromethane (3 × 100 ml). After evaporation of the solvent, the product is purified by chromatography on silica gel, using hexane–ethyl acetate (3:1/v:v) as the eluent, to afford 430 mg (62%) of an orange oil. ^1H -NMR (CDCl_3): δ 7.39 (2H, d, $J = 8.9$ Hz, Ar–H), 7.13 (2H, s, Ar–H), 6.82 (2H, d, $J = 8.9$ Hz, Ar–H), 4.33 (1H, m, CHMe₂), 3.73 (2H, br, NH₂), 2.17 (6H, s, CH₃) 1.73–1.28 (13H, m, C₅H₁₀, CH₃), 0.88 (3H, m, CH₃). IR (CH_2Cl_2 , cm^{-1}): 3404 (N–H), 2206 (C≡C). MS (EI): 349 (M).

2.1.2. (*R*)-4-(4-(1-Methylbutyloxy)phenylethynyl)-2,6-dimethylaniline (**2a**)

Orange oil. Yield: 67%. ^1H -NMR (CDCl_3): δ 7.39 (2H, d, $J = 8.9$ Hz, Ar–H), 7.13 (2H, s, Ar–H), 6.82 (2H, d, $J = 8.9$ Hz, Ar–H), 4.34 (1H, m, CHMe₂), 3.77 (2H, br, NH₂), 2.17 (6H, s, CH₃) 1.75–1.28 (7H, m, C₂H₄, CH₃), 0.88 (3H, m, CH₃). IR (CH_2Cl_2 , cm^{-1}): 3408 (N–H), 2216 (C≡C). MS (EI): 307 (M).

2.1.3. (*R*)-4-(4-(1-Methylpentylloxy)phenylethynyl)-2,6-dimethylaniline (**2b**)

Orange oil. Yield: 60%. ^1H -NMR (CDCl_3): δ 7.39 (2H, d, $J = 8.9$ Hz, Ar–H), 7.13 (2H, s, Ar–H), 6.82 (2H, d, $J = 8.9$ Hz, Ar–H), 4.33 (1H, m, CHMe₂), 3.73 (2H, br, NH₂), 2.17 (6H, s, CH₃) 1.73–1.28 (9H, m, C₃H₆, CH₃), 0.88 (3H, m, CH₃). IR (CH_2Cl_2 , cm^{-1}): 3408 (N–H), 2205 (C≡C). MS (EI): 321 (M).



2.1.4. (*S*)-4-(4-(1-Methylpentoxy)phenylethynyl)-2,6-dimethylaniline (2c**)**

Orange oil. Yield: 60%. $^1\text{H-NMR}$ (CDCl_3): δ 7.39 (2H, d, $J = 8.9$ Hz, Ar-H), 7.13 (2H, s, Ar-H), 6.82 (2H, d, $J = 8.9$ Hz, Ar-H), 4.33 (1H, m, CHMe_2), 3.73 (2H, br, NH_2), 2.17 (6H, s, CH_3) 1.73–1.28 (9H, m, C_3H_6 , CH_3), 0.88 (3H, m, CH_3). IR (CH_2Cl_2 , cm^{-1}): 3408 (N-H), 2205 ($\text{C}\equiv\text{C}$). MS (EI): 321 (M).

2.1.5. (*S*)-4-(4-(1-Methylhexyloxy)phenylethynyl)-2,6-dimethylaniline (2d**)**

Orange oil. Yield: 58%. $^1\text{H-NMR}$ (CDCl_3): δ 7.39 (2H, d, $J = 8.9$ Hz, Ar-H), 7.13 (2H, s, Ar-H), 6.82 (2H, d, $J = 8.9$ Hz, Ar-H), 4.33 (1H, m, CHMe_2), 3.73 (2H, br, NH_2), 2.16 (6H, s, CH_3) 1.73–1.28 (11H, m, C_4H_8 , CH_3), 0.88 (3H, m, CH_3). IR (CH_2Cl_2 , cm^{-1}): 3409 (N-H), 2206 ($\text{C}\equiv\text{C}$). MS (EI): 335 (M).

2.1.6. (*S*)-4-(4-(1-Methylheptyloxy)phenylethynyl)-2,6-dimethylaniline (2f**)**

Orange oil. Yield: 58%. $^1\text{H-NMR}$ (CDCl_3): δ 7.39 (2H, d, $J = 8.9$ Hz, Ar-H), 7.13 (2H, s, Ar-H), 6.82 (2H, d, $J = 8.9$ Hz, Ar-H), 4.33 (1H, m, CHMe_2), 3.73 (2H, br, NH_2), 2.17 (6H, s, CH_3) 1.73–1.28 (13H, m, C_5H_{10} , CH_3), 0.88 (3H, m, CH_3). IR (CH_2Cl_2 , cm^{-1}): 3409 (N-H), 2205 ($\text{C}\equiv\text{C}$). MS (EI): 349 (M).

2.1.7. (*R*)-4-(4-(1-Methylpentoxy)phenylethynyl)aniline (2g**)**

Orange oil. Yield: 66%. $^1\text{H-NMR}$ (CDCl_3): δ 7.40 (2H, d, $J = 8.8$ Hz, Ar-H), 7.31 (2H, d, $J = 8.6$ Hz, Ar-H), 6.83 (2H, d, $J = 8.8$ Hz, Ar-H), 6.63 (2H, $J = 8.5$ Hz, Ar-H), 4.36 (1H, m, CHMe_2), 3.77 (2H, br, NH_2), 1.74–1.26 (9H, m, C_3H_6 , CH_3), 0.88 (3H, m, CH_3). IR (CH_2Cl_2 , cm^{-1}): 3404 (N-H), 2206 ($\text{C}\equiv\text{C}$). MS (EI): 296 (M).

2.1.8. (*S*)-4-(4-(1-Methylhexyloxy)phenylethynyl)aniline (2h**)**

Yellow oil. Yield: 62%. $^1\text{H-NMR}$ (CDCl_3): δ 7.40 (2H, d, $J = 8.8$ Hz, Ar-H), 7.31 (2H, d, $J = 8.6$ Hz, Ar-H), 6.83 (2H, d, $J = 8.8$ Hz, Ar-H), 6.63 (2H, $J = 8.5$ Hz, Ar-H), 4.36 (1H, m, CHMe_2), 3.75 (2H, br, NH_2), 1.74–1.28 (11H, m, C_4H_8 , CH_3), 0.88 (3H, m, CH_3). IR (CH_2Cl_2 , cm^{-1}): 3404 (N-H), 2206 ($\text{C}\equiv\text{C}$). MS (EI): 310 (M).

2.1.9. (*R*)-4-(4-(1-Methylheptyloxy)phenylethynyl)aniline (2i**)**

Orange oil. Yield: 71%. $^1\text{H-NMR}$ (CDCl_3): δ 7.40 (2H, d, $J = 8.7$ Hz, Ar-H), 7.31 (2H, d, $J = 8.6$ Hz, Ar-H), 6.82 (2H, d, $J = 8.8$ Hz, Ar-H), 6.61 (2H, $J = 8.5$ Hz, Ar-H), 4.35 (1H, m, CHMe_2), 3.77 (2H, br, NH_2),

1.74–1.28 (13H, m, C₅H₁₀, CH₃), 0.88 (3H, m, CH₃). IR (CH₂Cl₂, cm⁻¹): 3404 (N–H), 2208 (C≡C). MS (EI): 324 (M).

2.1.10. (*S*)-4-(4-(1-Methylheptyloxy)phenylethynyl)aniline (**2j**)

Orange oil. Yield: 66%. ¹H-NMR (CDCl₃): δ 7.40 (2H, d, *J* = 8.8 Hz, Ar–H), 7.31 (2H, d, *J* = 8.6 Hz, Ar–H), 6.83 (2H, d, *J* = 8.8 Hz, Ar–H), 6.63 (2H, *J* = 8.5 Hz, Ar–H), 4.36 (1H, m, CHMe₂), 3.77 (2H, br, NH₂), 1.74–1.26 (13H, m, C₅H₁₀, CH₃), 0.88 (3H, m, CH₃). IR (CH₂Cl₂, cm⁻¹): 3404 (N–H), 2206 (C≡C). MS (EI): 324 (M).

2.1.11. (*S*)-4-(4-(1-Methylhexyloxy)-2,6-dimethylphenylethynyl)-2,6-dimethylaniline (**2k**)

Orange oil. Yield: 64%. ¹H-NMR (CDCl₃): δ 7.15 (2H, s, Ar–H), 7.12 (2H, s, Ar–H), 6.82 (2H, d, *J* = 8.9 Hz, Ar–H), 4.07 (1H, m, CHMe₂), 3.71 (2H, br, NH₂), 2.23 (6H, s, CH₃), 2.15 (6H, s, CH₃), 1.78–1.28 (13H, m, C₄H₈, CH₃), 0.88 (3H, m, CH₃). IR (CH₂Cl₂, cm⁻¹): 3404 (N–H), 2208 (C≡C). MS (EI): 363 (M).

2.1.12. (*R*)-4-(4-(1-Methylheptyloxy)-2,6-dimethylphenylethynyl)-2,6-dimethylaniline (**2l**)

Orange oil. Yield: 75%. ¹H-NMR (CDCl₃): δ 7.15 (2H, s, Ar–H), 7.12 (2H, s, Ar–H), 6.82 (2H, d, *J* = 8.9 Hz, Ar–H), 4.07 (1H, m, CHMe₂), 3.71 (2H, br, NH₂), 2.23 (6H, s, CH₃), 2.15 (6H, s, CH₃), 1.78–1.28 (13H, m, C₅H₁₀, CH₃), 0.88 (3H, m, CH₃). IR (CH₂Cl₂, cm⁻¹): 3404 (N–H), 2202 (C≡C). MS (EI): 377 (M).

2.2. Synthesis of formamides **3**

2.2.1. (*R*)-4-(4-(1-Methylheptyloxy)phenylethynyl)-2,6-dimethyl-1-formamidobenzene (**3e**)

A mixture of acetic anhydride (1.46 g, 14.4 mmol) and formic acid (0.66 g, 14.4 mmol) is heated for 2 hours at 50–60 °C in a flask fitted with a drying tube [25]. Compound **2e** (2.35 g, 6.8 mmol) is added to the stirred mixture over a 10-min period, using a water bath to maintain the temperature below 39 °C. After stirring for about 24 h at r.t., CH₂Cl₂ and water (50 ml/50 ml) are added. The organic phase is treated with 10% Na₂CO₃ (aq) and dried with magnesium sulfate. After removal of the solvent on a rotary evaporator, the residue is purified by chromatography on silica gel, using hexane–ethyl acetate (1:1/v:v) as the eluent, to afford 2.48 g (yield: 97%) of a yellow solid. ¹H-NMR (CDCl₃): δ 8.39, 8.12, 8.08 (1H, s, NHCHO), 7.44, 7.41 (2H, s, Ar–H), 7.28, 7.24 (2H, s, Ar–H), 7.14, 7.10, 6.89, 6.87 (1H, br, NHCHO), 6.86, 6.85, 6.83, 6.82 (2H, s, Ar–H), 4.36 (1H, m, CHMe₂), 2.29, 2.23 (6H, s, CH₃) 1.73–1.29 (13H, m, C₅H₁₀, CH₃), 0.88 (3H, m, CH₃). IR (CH₂Cl₂, cm⁻¹): 3404 (N–H), 2208 (C≡C), 1697 (C=O). MS (EI): 377 (M).

2.2.2. (*R*)-4-(4-(1-Methylbutyloxy)phenylethynyl)-2,6-dimethyl-1-formamidobenzene (**3a**)

Yellow solid. Yield: 96%. ¹H-NMR (CDCl₃): δ 8.41, 8.13, 8.09 (1H, s, NHCHO), 7.44, 7.41 (2H, s, Ar–H), 7.28, 7.24 (2H, s, Ar–H), 7.14, 7.10, 6.89, 6.87 (1H, br, NHCHO), 6.86, 6.85, 6.83, 6.82 (2H, s, Ar–H), 4.36 (1H, m, CH(Me)), 2.29, 2.25 (6H, s, CH₃) 1.79–1.29 (7H, m, C₂H₄, CH₃), 0.88 (3H, m, CH₃). IR (CH₂Cl₂, cm⁻¹): 3404 (N–H), 2208 (C≡C), 1699 (C=O). MS (EI): 335 (M).

2.2.3. (*R*)-4-(4-(1-Methylpentyloxy)phenylethynyl)-2,6-dimethyl-1-formamidobenzene (**3b**)

Yellow solid. Yield: 98%. ¹H-NMR (CDCl₃): δ 8.39, 8.12, 8.08 (1H, s, NHCHO), 7.44, 7.41 (2H, s, Ar–H), 7.28, 7.24 (2H, s, Ar–H), 7.14, 7.10, 6.89, 6.87 (1H, br, NHCHO), 6.86, 6.85, 6.83, 6.82 (2H, s, Ar–H), 4.36 (1H, m, CHMe₂), 2.29, 2.23 (6H, s, CH₃) 1.73–1.29 (9H, m, C₃H₆, CH₃), 0.88 (3H, m, CH₃). IR (CH₂Cl₂, cm⁻¹): 3418 (N–H), 2216 (C≡C), 1699 (C=O). MS (EI): 349 (M).

2.2.4. (*S*)-4-(4-(1-Methylpentyloxy)phenylethynyl)-2,6-dimethyl-1-formamidobenzene (**3c**)

Yellow solid. Yield: 96%. ¹H-NMR (CDCl₃): δ 8.39, 8.12, 8.08 (1H, s, NHCHO), 7.44, 7.41 (2H, s, Ar–H), 7.28, 7.24 (2H, s, Ar–H), 7.14, 7.10, 6.89, 6.87 (1H, br, NHCHO), 6.86, 6.85, 6.83, 6.82 (2H, s, Ar–H), 4.36 (1H, m, CHMe₂), 2.29, 2.23 (6H, s, CH₃) 1.73–1.29 (9H, m, C₃H₆, CH₃), 0.88 (3H, m, CH₃). IR (CH₂Cl₂, cm⁻¹): 3418 (N–H), 2216 (C≡C), 1699 (C=O). MS (EI): 349 (M).

2.2.5. (*S*)-4-(4-(1-Methylhexyloxy)phenylethynyl)-2,6-dimethyl-1-formamidobenzene (**3d**)

Yellow solid. Yield: 98%. ¹H-NMR (CDCl₃): δ 8.39, 8.12, 8.08 (1H, s, NHCHO), 7.44, 7.41 (2H, s, Ar–H), 7.28, 7.24 (2H, s, Ar–H), 7.14, 7.10, 6.89, 6.87 (1H, br, NHCHO), 6.86, 6.85, 6.83, 6.82 (2H, s, Ar–H), 4.36 (1H, m, CHMe₂), 2.29, 2.23 (6H, s, CH₃) 1.73–1.29 (11H, m, C₄H₈, CH₃), 0.88 (3H, m, CH₃). IR (CH₂Cl₂, cm⁻¹): 3417 (N–H), 2212 (C≡C), 1697 (C=O). MS (EI): 363 (M).

2.2.6. (*S*)-4-(4-(1-Methylheptyloxy)phenylethynyl)-2,6-dimethyl-1-formamidobenzene (**3f**)

Yellow solid. Yield: 98%. ¹H-NMR (CDCl₃): δ 8.39, 8.12, 8.08 (1H, s, NHCHO), 7.44, 7.41 (2H, s, Ar–H), 7.28, 7.24 (2H, s, Ar–H), 7.14, 7.10, 6.89, 6.87 (1H, br, NHCHO), 6.86, 6.85, 6.83, 6.82 (2H, s, Ar–H), 4.36 (1H, m, CHMe₂), 2.29, 2.23 (6H, s, CH₃) 1.73–1.29 (13H, m, C₅H₁₀, CH₃), 0.88 (3H, m, CH₃). IR (CH₂Cl₂, cm⁻¹): 3417 (N–H), 2206 (C≡C), 1699 (C=O). MS (EI): 377 (M).

2.2.7. (*R*)-4-(4-(1-Methylpentylloxy)phenylethynyl)-1-formamidobenzene (**3g**)

Yellow solid. Yield: 92%. ¹H-NMR (CDCl₃): δ 8.74, 8.72, 8.39, 8.38, 7.84, 7.82 (1H, s, NHCHO), 7.05, 7.04 (1H, br, NHCHO), 7.54, 7.52, 7.50, 7.49, 7.48, 7.47, 7.44, 7.42, (6H, s, Ar-H), 6.85, 6.84, 6.83, (2H, s, Ar-H), 4.36 (1H, m, CHMe₂), 2.29, 2.23 (6H, s, CH₃) 1.73–1.25 (9H, m, C₃H₆, CH₃), 0.88 (3H, m, CH₃). IR (CH₂Cl₂, cm⁻¹): 3415 (N-H), 2216 (C≡C), 1703 (C=O). MS (EI): 321 (M).

2.2.8. (*S*)-4-(4-(1-Methylhexyloxy)phenylethynyl)-1-formamidobenzene (**3h**)

Yellow solid. Yield: 96%. ¹H-NMR (CDCl₃): δ 8.74, 8.73, 8.39, 8.38, 7.84, 7.83 (1H, s, NHCHO), 7.05, 7.04 (1H, br, NHCHO), 7.54, 7.52, 7.51, 7.49, 7.48, 7.47, 7.44, 7.43, (6H, s, Ar-H), 6.85, 6.84, 6.83, (2H, s, Ar-H), 4.36 (1H, m, CHMe₂), 2.29, 2.23 (6H, s, CH₃) 1.73–1.25 (11H, m, C₄H₈, CH₃), 0.88 (3H, m, CH₃). IR (CH₂Cl₂, cm⁻¹): 348 (N-H), 2206 (C≡C), 1705 (C=O). MS (EI): 335 (M).

2.2.9. (*R*)-4-(4-(1-Methylheptyloxy)phenylethynyl)-1-formamidobenzene (**3i**)

Yellow solid. Yield: 95%. ¹H-NMR (CDCl₃): δ 8.74, 8.72, 8.39, 8.38, 7.84, 7.82 (1H, s, NHCHO), 7.05, 7.04 (1H, br, NHCHO), 7.54, 7.52, 7.50, 7.49, 7.48, 7.47, 7.44, 7.42, (6H, s, Ar-H), 6.85, 6.84, 6.83, (2H, s, Ar-H), 4.36 (1H, m, CHMe₂), 2.29, 2.23 (6H, s, CH₃) 1.73–1.25 (13H, m, C₅H₁₀, CH₃), 0.88 (3H, m, CH₃). IR (CH₂Cl₂, cm⁻¹): 3415 (N-H), 2216 (C≡C), 1703 (C=O). MS (EI): 349 (M).

2.2.10. (*S*)-4-(4-(1-Methylheptyloxy)phenylethynyl)-1-formamidobenzene (**3j**)

Yellow solid. Yield: 96%. ¹H-NMR (CDCl₃): δ 8.74, 8.72, 8.40, 8.39, 7.84, 7.82 (1H, s, NHCHO), 7.05, 7.04 (1H, br, NHCHO), 7.54, 7.52, 7.51, 7.49, 7.48, 7.47, 7.44, 7.43, (6H, s, Ar-H), 6.85, 6.84, 6.83, (2H, s, Ar-H), 4.36 (1H, m, CHMe₂), 2.29, 2.23 (6H, s, CH₃) 1.73–1.26 (13H, m, C₅H₁₀, CH₃), 0.88 (3H, m, CH₃). IR (CH₂Cl₂, cm⁻¹): 3415 (N-H), 2216 (C≡C), 1699 (C=O). MS (EI): 349 (M).

2.2.11. (*S*)-4-(4-(1-Methylhexyloxy)-2,6-dimethylphenylethynyl)-2,6-dimethyl-1-formamidobenzene (**3k**)

Yellow solid. Yield: 96%. ¹H-NMR (CDCl₃): δ 8.39, 8.12, 8.08 (1H, s, NHCHO), 7.26, 7.24, 7.18 (4H, s, Ar-H), 7.08, 7.03, 6.87 (1H, br, NHCHO), 4.07 (1H, m, CHMe₂), 2.25, 2.24 (12H, s, -CH₃) 1.79–1.17 (11H, m, C₄H₈, CH₃), 0.89 (3H, m, CH₃). IR (CH₂Cl₂, cm⁻¹): 3406 (N-H), 2202 (C≡C), 1699 (C=O). MS (EI): 391 (M).

2.2.12. (*R*)-4-(4-(1-Methylheptyloxy)-2,6-dimethylphenylethynyl)-2,6-dimethyl-1-formamidobenzene (**3l**)

Yellow solid. Yield: 97%. ¹H-NMR (CDCl₃): δ 8.39, 8.12, 8.08 (1H, s, NHCHO), 7.26, 7.24, 7.18 (4H, s, Ar-H), 7.08, 7.03, 6.87 (1H, br, NHCHO), 4.07 (1H, m, CHMe₂), 2.25, 2.24 (12H, s, CH₃) 1.79–1.17 (13H, m, C₅H₁₀, CH₃), 0.89 (3H, m, CH₃). IR (CH₂Cl₂, cm⁻¹): 3406 (N-H), 2208 (C≡C), 1697 (C=O). MS (EI): 405 (M).

2.3. Synthesis of isocyanides **4**

2.3.1. (*R*)-4-(4-(1-Methylheptyloxy)phenylethynyl)-2,6-dimethylphenylisocyanide (**4e**)

A flask containing **3e** (900 mg, 2.4 mmol), triethylamine (0.12 ml, 0.8 mmol), and CH₂Cl₂ (50 ml) is cooled in a liquid nitrogen bath. Then a solution of triphosgene (37.2 mg, 0.8 mmol) in dry CH₂Cl₂ (5 ml) is added slowly [26]. The reaction mixture is allowed to warm to r.t. and stirred for 12 h. Then 10% Na₂CO₃ (aq) (30 ml) is added dropwise. The organic phase is separated and dried with MgSO₄. The solvent is evaporated, and the crude product is chromatographed on silica gel, using hexane–ethyl acetate (10:1 v/v) as the eluent, to afford 610 mg (71%) of **4e** as an orange oil. ¹H-NMR (CDCl₃): δ 7.42 (2H, d, *J* = 8.8 Hz, Ar-H), 7.24 (2H, s, Ar-H), 6.84 (2H, d, *J* = 8.8 Hz, Ar-H), 4.37 (1H, m, CHMe₂), 2.41 (6H, s, Ar-CH₃), 1.73–1.25 (13H, m, C₅H₁₀, CH₃), 0.88 (3H, m, CH₃). ¹³C-NMR (CDCl₃): δ 168.9, 158.9, 134.9, 133.2, 130.6, 126.5, 124.3, 115.7, 114.3, 91.6, 86.9, 74.1, 36.4, 31.8, 29.3, 25.5, 22.6, 19.7, 18.9, 14.2. IR (CH₂Cl₂, cm⁻¹): 2212 (C≡C), 2118 (C≡N). MS (EI): 359 (M).

2.3.2. (*R*)-4-(4-(1-Methylbutyloxy)phenylethynyl)-2,6-dimethylphenylisocyanide (**4a**)

Light yellow oil. Yield: 73%. ¹H-NMR (CDCl₃): δ 7.42 (2H, d, *J* = 8.8 Hz, Ar-H), 7.24 (2H, s, Ar-H), 6.85 (2H, d, *J* = 8.8 Hz, Ar-H), 4.39 (1H, m, CHMe₂), 2.41 (6H, s, Ar-CH₃), 1.75–1.25 (7H, m, C₂H₄, CH₃), 0.94 (3H, m, CH₃). ¹³C-NMR (CDCl₃): δ 168.9, 158.7, 134.9, 133.2, 130.6, 124.3, 115.8, 114.3, 91.6, 86.9, 73.7, 38.5, 29.7, 22.7, 19.7, 18.8, 18.7, 14.0. IR (CH₂Cl₂, cm⁻¹): 2210 (C≡C), 2117 (C≡N). MS (EI): 317 (M).

2.3.3. (*R*)-4-(4-(1-Methylpentylloxy)phenylethynyl)-2,6-dimethylphenylisocyanide (**4b**)

Light yellow oil. Yield: 74%. ¹H-NMR (CDCl₃): δ 7.42 (2H, d, *J* = 8.8 Hz, Ar-H), 7.24 (2H, s, Ar-H), 6.85 (2H, d, *J* = 8.8 Hz, Ar-H), 4.37 (1H, m, CHMe₂), 2.41 (6H, s, Ar-CH₃), 1.73–1.25 (9H, m, C₃H₆, CH₃), 0.88 (3H, m, CH₃). ¹³C-NMR (CDCl₃): δ 168.9, 158.7, 134.9, 133.2, 130.6, 126.4, 124.3, 115.8, 114.3, 91.6, 86.9, 74.0, 36.4, 27.7, 22.7, 19.7, 18.8, 14.0. IR (CH₂Cl₂, cm⁻¹): 2212 (C≡C), 2117 (C≡N). MS (EI): 331 (M).

2.3.4. (*S*)-4-(4-(1-Methylpentylloxy)phenylethynyl)-2,6-dimethylphenylisocyanide (**4c**)

Light yellow oil. Yield: 76%. ¹H-NMR (CDCl₃): δ 7.42 (2H, d, *J* = 8.8 Hz, Ar–H), 7.24 (2H, s, Ar–H), 6.85 (2H, d, *J* = 8.8 Hz, Ar–H), 4.37 (1H, m, CHMe₂), 2.41 (6H, s, Ar–CH₃), 1.73–1.25 (9H, m, C₃H₆, CH₃), 0.88 (3H, m, CH₃). ¹³C-NMR (CDCl₃): δ 168.9, 158.7, 134.9, 133.2, 130.6, 126.4, 124.3, 115.8, 114.3, 91.6, 86.9, 74.0, 36.4, 27.7, 22.7, 19.7, 18.8, 14.0. IR (CH₂Cl₂, cm⁻¹): 2212 (C≡C), 2117 (C≡N). MS (EI): 331 (M).

2.3.5. (*S*)-4-(4-(1-Methylhexylloxy)phenylethynyl)-2,6-dimethylphenylisocyanide (**4d**)

Light yellow oil. Yield: 78%. ¹H-NMR (CDCl₃): δ 7.42 (2H, d, *J* = 8.8 Hz, Ar–H), 7.24 (2H, s, Ar–H), 6.85 (2H, d, *J* = 8.8 Hz, Ar–H), 4.37 (1H, m, CHMe₂), 2.41 (6H, s, Ar–CH₃), 1.73–1.25 (11H, m, C₄H₈, CH₃), 0.88 (3H, m, CH₃). ¹³C-NMR (CDCl₃): δ 168.9, 158.9, 134.9, 133.2, 130.6, 128.4, 124.3, 115.7, 114.3, 91.6, 86.9, 74.0, 36.4, 31.8, 25.2, 22.6, 19.7, 18.8, 14.2. IR (CH₂Cl₂, cm⁻¹): 2206 (C≡C), 2117 (C≡N). MS (EI): 345 (M).

2.3.6. (*S*)-4-(4-(1-Methylheptyloxy)phenylethynyl)-2,6-dimethylphenylisocyanide (**4f**)

Light yellow oil. Yield: 77%. ¹H-NMR (CDCl₃): δ 7.42 (2H, d, *J* = 8.8 Hz, Ar–H), 7.24 (2H, s, Ar–H), 6.85 (2H, d, *J* = 8.8 Hz, Ar–H), 4.37 (1H, m, CHMe₂), 2.41 (6H, s, Ar–CH₃), 1.73–1.25 (13H, m, C₅H₁₀, CH₃), 0.88 (3H, m, CH₃). ¹³C-NMR (CDCl₃): δ 168.9, 158.9, 134.9, 133.2, 130.6, 126.5, 124.3, 115.7, 114.3, 91.6, 86.9, 74.1, 36.4, 31.8, 29.3, 25.5, 22.6, 19.7, 18.9, 14.2. IR (CH₂Cl₂, cm⁻¹): 2209 (C≡C), 2117 (C≡N). MS (EI): 359 (M).

2.3.7. (*R*)-4-(4-(1-Methylpentylloxy)phenylethynyl)phenylisocyanide (**4g**)

Light yellow oil. Yield: 70%. ¹H-NMR (CDCl₃): δ 7.51 (2H, d, *J* = 8.5 Hz, Ar–H), 7.44 (2H, d, *J* = 8.9 Hz, Ar–H), 7.34 (2H, d, *J* = 8.5 Hz, Ar–H), 6.86 (2H, d, *J* = 8.8 Hz, Ar–H), 4.39 (1H, m, CHMe₂), 1.77–1.26 (9H, m, C₃H₆, CH₃), 0.91 (3H, m, CH₃). ¹³C-NMR (CD₂Cl₂): δ 165.6, 158.9, 133.2, 132.3, 126.4, 125.3, 115.8, 114.1, 92.6, 86.5, 74.1, 36.1, 29.7, 22.7, 19.7, 14.0. IR (CH₂Cl₂, cm⁻¹): 2212 (C≡C), 2118 (C≡N). MS (EI): 303 (M).

2.3.8. (*S*)-4-(4-(1-Methylhexylloxy)phenylethynyl)phenylisocyanide (**4h**)

Light yellow oil. Yield: 72%. ¹H-NMR (CDCl₃): δ 7.51 (2H, d, *J* = 8.6 Hz, Ar–H), 7.44 (2H, d, *J* = 8.9 Hz, Ar–H), 7.34 (2H, d, *J* = 8.6 Hz, Ar–H), 6.86 (2H, d, *J* = 8.8 Hz, Ar–H), 4.39 (1H, m, CHMe₂), 1.76–1.25 (11H, m, C₄H₈, CH₃), 0.89 (3H, m, CH₃). ¹³C-NMR (CD₂Cl₂): δ 165.4, 158.9, 133.2, 132.3, 126.4, 125.3, 115.7, 114.0, 92.6, 86.5, 74.0, 36.3, 31.8, 25.1, 22.6, 19.7, 14.0. IR (CH₂Cl₂, cm⁻¹): 2216 (C≡C), 2125 (C≡N). MS (EI): 317 (M).

2.3.9. (*R*)-4-(4-(1-Methylheptyloxy)phenylethynyl)phenylisocyanide (**4i**)

Light yellow solid. Yield: 75%. ¹H-NMR (CDCl₃): δ 7.51 (2H, d, *J* = 8.5 Hz, Ar–H), 7.44 (2H, d, *J* = 8.8 Hz, Ar–H), 7.31 (2H, d, *J* = 8.5 Hz, Ar–H), 6.86 (2H, d, *J* = 8.8 Hz, Ar–H), 4.39 (1H, m, CHMe₂), 1.74–1.24 (13H, m, C₅H₁₀, CH₃), 0.88 (3H, m, CH₃). ¹³C-NMR (CD₂Cl₂): δ 165.4, 158.8, 133.2, 132.3, 126.4, 125.2, 115.7, 113.9, 92.6, 86.5, 73.9, 36.4, 31.8, 29.2, 25.5, 22.6, 19.7, 14.2. IR (CH₂Cl₂, cm⁻¹): 2212 (C≡C), 2117 (C≡N). MS (EI): 332 (M+1).

2.3.10. (*S*)-4-(4-(1-Methylheptyloxy)phenylethynyl)phenylisocyanide (**4j**)

Light yellow solid. Yield: 74%. ¹H-NMR (CDCl₃): δ 7.51 (2H, d, *J* = 8.5 Hz, Ar–H), 7.44 (2H, d, *J* = 8.8 Hz, Ar–H), 7.31 (2H, d, *J* = 8.5 Hz, Ar–H), 6.86 (2H, d, *J* = 8.8 Hz, Ar–H), 4.39 (1H, m, CHMe₂), 1.74–1.24 (13H, m, C₅H₁₀, CH₃), 0.88 (3H, m, CH₃). ¹³C-NMR (CD₂Cl₂): δ 165.4, 158.8, 133.2, 132.3, 126.4, 125.2, 115.7, 113.9, 92.6, 86.5, 73.9, 36.4, 31.8, 29.2, 25.5, 22.6, 19.7, 14.2. IR (CH₂Cl₂, cm⁻¹): 2212 (C≡C), 2117 (C≡N). MS (EI): 331 (M).

2.3.11. (*S*)-4-(4-(1-Methylhexylloxy)-2,6-dimethylphenylethynyl)-2,6-dimethylphenylisocyanide (**4k**)

Light yellow solid. Yield: 80%. ¹H-NMR (CDCl₃): δ 7.24 (2H, s, Ar–H), 7.18 (2H, s, Ar–H), 4.08 (1H, m, CHMe₂), 2.41 (6H, s, Ar–CH₃), 2.25 (6H, s, Ar–CH₃), 1.78–1.18 (11H, m, C₄H₈, CH₃), 0.89 (3H, m, CH₃). ¹³C-NMR (CDCl₃): δ 168.8, 155.5, 134.9, 132.3, 131.8, 130.7, 124.2, 117.0, 91.6, 87.1, 78.3, 36.9, 32.1, 25.1, 22.7, 19.7, 18.8, 17.2, 14.1. IR (CH₂Cl₂, cm⁻¹): 2206 (C≡C), 2117 (C≡N). MS (EI): 373 (M).

2.3.12. (*R*)-4-(4-(1-Methylheptyloxy)-2,6-dimethylphenylethynyl)-2,6-dimethylphenylisocyanide (**4l**)

Yellow solid. Yield: 83%. ¹H-NMR (CDCl₃): δ 7.24 (2H, s, Ar–H), 7.18 (2H, s, Ar–H), 4.10 (1H, m, CHMe₂), 2.40 (6H, s, Ar–CH₃), 2.25 (6H, s, Ar–CH₃), 1.78–1.18 (13H, m, C₅H₁₀, CH₃), 0.89 (3H, m, CH₃). ¹³C-NMR (CDCl₃): δ 168.9, 155.5, 134.9, 132.3, 131.8, 130.7, 124.2, 117.0, 91.6, 87.1, 78.3, 37.1, 31.9, 29.5, 25.7, 22.6, 19.7, 18.8, 17.2, 14.1. IR (CH₂Cl₂, cm⁻¹): 2208 (C≡C), 2119 (C≡N). MS (EI): 387 (M).

2.4. Synthesis of metal complexes I

2.4.1. Complex 1e

Under an atmosphere of nitrogen, PtI₂ (143.8 mg, 0.32 mmol) is added to a stirred solution of **4e** (230 mg, 0.64 mmol) in 15 ml CH₂Cl₂ [27]. After stirring for 6 h, the yellow solution is filtered, and the solvent is removed under vacuum. The residue is recrystallized from

dichloromethane–*n*-hexane to give a yellow solid. Yield: 262 mg (70%). $^1\text{H-NMR}$ (CDCl_3): δ 7.44 (2H, d, $J = 8.8$ Hz, Ar–H), 7.28 (2H, s, Ar–H), 6.86 (2H, d, $J = 8.8$ Hz, Ar–H), 4.38 (1H, m, CHMe_2), 2.56 (6H, s, Ar– CH_3), 1.74–1.28 (13 H, m, C_5H_{10} , CH_3), 0.88 (3H, m, CH_3). $^{13}\text{C-NMR}$ (CDCl_3): δ 158.9, 136.8, 133.3, 130.9, 126.1, 124.5, 115.8, 114.1, 93.0, 86.8, 74.1, 36.4, 31.8, 29.3, 25.5, 22.6, 19.7, 18.9, 14.2. IR (CH_2Cl_2 , cm^{-1}): 2216 ($\text{C}\equiv\text{C}$), 2189 ($\text{C}\equiv\text{N}$). MS (FAB) m/z : 1168 ($\text{M}+1$). Anal. Calc. for $\text{C}_{50}\text{H}_{58}\text{I}_2\text{N}_2\text{O}_2\text{Pt}$: C, 51.41; H, 4.97; N, 2.40. Found: C, 51.30; H, 5.05; N, 2.36%.

2.4.2. Complex **1a**

Yellow crystals. Yield: 81%. $^1\text{H-NMR}$ (CDCl_3): δ 7.44 (2H, d, $J = 8.8$ Hz, Ar–H), 7.29 (2H, s, Ar–H), 6.86 (2H, d, $J = 8.8$ Hz, Ar–H), 4.39 (1H, m, CHMe_2), 2.56 (6H, s, Ar– CH_3), 1.77–1.31 (9 H, m, C_3H_6 , CH_3), 0.88 (3H, m, CH_3). IR (CH_2Cl_2 , cm^{-1}): 2212 ($\text{C}\equiv\text{C}$), 2118 ($\text{C}\equiv\text{N}$). $^{13}\text{C-NMR}$ (CDCl_3): δ 158.9, 136.8, 133.3, 130.9, 126.1, 115.7, 114.0, 92.8, 86.8, 73.7, 38.5, 29.7, 19.7, 18.9, 18.7, 14.0. IR (CH_2Cl_2 , cm^{-1}): 2210 ($\text{C}\equiv\text{C}$), 2192 ($\text{C}\equiv\text{N}$). MS (FAB) m/z : 1083 (M). Anal. Calc. for $\text{C}_{44}\text{H}_{46}\text{I}_2\text{N}_2\text{O}_2\text{Pt}$: C 48.75; H, 4.25; N, 2.59. Found: C, 48.58; H, 4.14; N, 2.13.

2.4.3. Complex **1b**

Yellow crystals. Yield: 78%. $^1\text{H-NMR}$ (CDCl_3): δ 7.44 (2H, d, $J = 8.8$ Hz, Ar–H), 7.29 (2H, s, Ar–H), 6.86 (2H, d, $J = 8.8$ Hz, Ar–H), 4.39 (1H, m, CHMe_2), 2.56 (6H, s, Ar– CH_3), 1.77–1.31 (9 H, m, C_3H_6 , CH_3), 0.88 (3H, m, CH_3). IR (CH_2Cl_2 , cm^{-1}): 2212 ($\text{C}\equiv\text{C}$), 2118 ($\text{C}\equiv\text{N}$). $^{13}\text{C-NMR}$ (CDCl_3): δ 158.9, 136.8, 133.3, 130.9, 126.1, 124.4, 115.7, 114.0, 93.0, 86.8, 74.0, 36.4, 27.7, 22.7, 19.7, 18.9, 14.1. IR (CH_2Cl_2 , cm^{-1}): 2216 ($\text{C}\equiv\text{C}$), 2189 ($\text{C}\equiv\text{N}$). MS (FAB) m/z : 1111 (M). Anal. Calc. for $\text{C}_{46}\text{H}_{50}\text{I}_2\text{N}_2\text{O}_2\text{Pt}$: C, 49.69; H, 4.50; N, 2.52. Found: C, 49.26; H, 4.38; N, 2.19.

2.4.4. Complex **1c**

Yellow crystals. Yield: 82%. $^1\text{H-NMR}$ (CDCl_3): δ 7.44 (2H, d, $J = 8.8$ Hz, Ar–H), 7.29 (2H, s, Ar–H), 6.86 (2H, d, $J = 8.8$ Hz, Ar–H), 4.39 (1H, m, CHMe_2), 2.56 (6H, s, Ar– CH_3), 1.77–1.31 (9 H, m, C_3H_6 , CH_3), 0.88 (3H, m, CH_3). IR (CH_2Cl_2 , cm^{-1}): 2212 ($\text{C}\equiv\text{C}$), 2118 ($\text{C}\equiv\text{N}$). $^{13}\text{C-NMR}$ (CDCl_3): δ 158.9, 136.8, 133.3, 130.9, 126.1, 124.4, 115.7, 114.0, 93.0, 86.8, 74.0, 36.4, 27.7, 22.7, 19.7, 18.9, 14.1. IR (CH_2Cl_2 , cm^{-1}): 2216 ($\text{C}\equiv\text{C}$), 2189 ($\text{C}\equiv\text{N}$). MS (FAB) m/z : 1111 (M). Anal. Calc. for $\text{C}_{46}\text{H}_{50}\text{I}_2\text{N}_2\text{O}_2\text{Pt}$: C, 49.69; H, 4.50; N, 2.52. Found: C, 49.52; H, 4.49; N, 2.18%.

2.4.5. Complex **1d**

Yellow crystals. Yield: 82%. $^1\text{H-NMR}$ (CDCl_3): δ 7.44 (2H, d, $J = 8.8$ Hz, Ar–H), 7.29 (2H, s, Ar–H), 6.86 (2H, d, $J = 8.8$ Hz, Ar–H), 4.39 (1H, m, CHMe_2), 2.56 (6H, s, Ar– CH_3), 1.79–1.29 (11 H, m, C_4H_8 , CH_3), 0.89

(3H, m, CH_3). IR (CH_2Cl_2 , cm^{-1}): 2212 ($\text{C}\equiv\text{C}$), 2118 ($\text{C}\equiv\text{N}$). $^{13}\text{C-NMR}$ (CDCl_3): δ 158.9, 136.8, 133.3, 130.9, 126.1, 124.4, 115.8, 114.0, 93.0, 86.8, 74.0, 36.3, 31.8, 25.2, 22.6, 19.7, 18.9, 14.1. IR (CH_2Cl_2 , cm^{-1}): 2212 ($\text{C}\equiv\text{C}$), 2191 ($\text{C}\equiv\text{N}$). MS (FAB) m/z : 1140 ($\text{M}+1$). Anal. Calc. for $\text{C}_{48}\text{H}_{54}\text{I}_2\text{N}_2\text{O}_2\text{Pt}$: C, 50.57; H, 4.74; N, 2.46. Found: C, 50.65; H, 4.52; N, 2.51.

2.4.6. Complex **1f**

Yellow crystals. Yield: 80%. $^1\text{H-NMR}$ (CDCl_3): δ 7.44 (2H, d, $J = 8.8$ Hz, Ar–H), 7.29 (2H, s, Ar–H), 6.86 (2H, d, $J = 8.8$ Hz, Ar–H), 4.39 (1H, m, CHMe_2), 2.56 (6H, s, Ar– CH_3), 1.74–1.29 (13 H, m, C_5H_{10} , CH_3), 0.88 (3H, m, CH_3). IR (CH_2Cl_2 , cm^{-1}): 2212 ($\text{C}\equiv\text{C}$), 2189 ($\text{C}\equiv\text{N}$). $^{13}\text{C-NMR}$ (CDCl_3): δ 158.9, 136.8, 133.3, 130.9, 126.1, 124.4, 115.7, 114.0, 93.0, 86.8, 74.0, 36.4, 31.8, 29.3, 25.5, 22.6, 19.7, 18.9, 14.1. IR (CH_2Cl_2 , cm^{-1}): 2216 ($\text{C}\equiv\text{C}$), 2189 ($\text{C}\equiv\text{N}$). MS (FAB) m/z : 1168 ($\text{M}+1$). Anal. Calc. for $\text{C}_{50}\text{H}_{58}\text{I}_2\text{N}_2\text{O}_2\text{Pt}$: C, 51.41; H, 4.97; N, 2.40. Found: C, 51.67; H, 4.80; N, 2.46%.

2.4.7. Complex **1g**

Yellow crystals. Yield: 81%. $^1\text{H-NMR}$ (CDCl_3): δ 7.59 (2H, d, $J = 8.6$ Hz, Ar–H), 7.51 (2H, d, $J = 8.6$ Hz, Ar–H), 7.46 (2H, d, $J = 8.7$ Hz, Ar–H), 6.87 (2H, d, $J = 8.8$ Hz, Ar–H), 4.39 (1H, m, CHMe_2), 1.78–1.26 (9H, m, C_3H_6 , CH_3), 0.91 (3H, m, CH_3). $^{13}\text{C-NMR}$ (CD_2Cl_2): δ 159.1, 133.4, 132.5, 127.2, 126.8, 124.3, 115.8, 113.7, 94.1, 86.4, 74.0, 36.1, 27.7, 22.6, 19.7, 14.1. IR (CH_2Cl_2 , cm^{-1}): 2214 ($\text{C}\equiv\text{C}$), 2194 ($\text{C}\equiv\text{N}$). MS (FAB) m/z : 1056 ($\text{M}+1$). Anal. Calc. for $\text{C}_{42}\text{H}_{42}\text{I}_2\text{N}_2\text{O}_2\text{Pt}$: C, 47.77; H, 3.98; N, 2.65. Found: C, 47.85; H, 3.96; N, 2.43.

2.4.8. Complex **1h**

Yellow crystals. Yield: 74%. $^1\text{H-NMR}$ (CDCl_3): δ 7.59 (2H, d, $J = 8.8$ Hz, Ar–H), 7.51 (2H, d, $J = 8.7$ Hz, Ar–H), 7.48 (2H, d, $J = 8.7$ Hz, Ar–H), 6.88 (2H, d, $J = 8.8$ Hz, Ar–H), 4.39 (1H, m, CHMe_2), 1.79–1.25 (11H, m, C_4H_8 , CH_3), 0.89 (3H, m, CH_3). $^{13}\text{C-NMR}$ (CD_2Cl_2): δ 159.1, 133.4, 132.5, 127.2, 126.8, 124.3, 115.8, 113.7, 94.1, 86.4, 74.0, 36.3, 31.8, 25.2, 22.6, 19.7, 14.0. IR (CH_2Cl_2 , cm^{-1}): 2214 ($\text{C}\equiv\text{C}$), 2194 ($\text{C}\equiv\text{N}$). MS (FAB) m/z : 1083 (M). Anal. Calc. for $\text{C}_{44}\text{H}_{46}\text{I}_2\text{N}_2\text{O}_2\text{Pt}$: C 48.75; H, 4.25; N, 2.59. Found: C, 48.77; H, 4.29; N, 2.60%.

2.4.9. Complex **1i**

Yellow crystals. Yield: 78%. $^1\text{H-NMR}$ (CDCl_3): δ 7.59 (2H, d, $J = 8.7$ Hz, Ar–H), 7.51 (2H, d, $J = 8.9$ Hz, Ar–H), 7.46 (2H, d, $J = 8.7$ Hz, Ar–H), 6.88 (2H, d, $J = 8.9$ Hz, Ar–H), 4.39 (1H, m, CHMe_2), 1.76–1.29 (13H, m, C_5H_{10} , CH_3), 0.88 (3H, m, CH_3). $^{13}\text{C-NMR}$ (CD_2Cl_2): δ 159.1, 133.4, 132.5, 127.2, 126.8, 124.3, 115.8, 113.7, 94.1, 86.4, 73.9, 36.4, 31.8, 29.2, 25.5, 22.6, 19.7, 14.1. IR (CH_2Cl_2 , cm^{-1}): 2216 ($\text{C}\equiv\text{C}$), 2194 ($\text{C}\equiv\text{N}$). MS (FAB) m/z : 1111 (M). Anal. Calc. for

$C_{46}H_{50}I_2N_2O_2Pt$: C, 49.68; H, 4.50; N, 2.52. Found: C, 49.38; H, 4.45; N, 2.47%.

2.4.10. Complex **1j**

Yellow crystals. Yield: 72%. 1H -NMR ($CDCl_3$): δ 7.59 (2H, d, $J = 8.7$ Hz, Ar–H), 7.51 (2H, d, $J = 8.7$ Hz, Ar–H), 7.48 (2H, d, $J = 8.7$ Hz, Ar–H), 6.88 (2H, d, $J = 8.9$ Hz, Ar–H), 4.39 (1H, m, $CHMe_2$), 1.76–1.25 (13H, m, C_5H_{10} , CH_3), 0.88 (3H, m, CH_3). ^{13}C -NMR (CD_2Cl_2): δ 159.1, 133.4, 132.5, 127.2, 126.8, 124.3, 115.8, 113.7, 94.1, 86.4, 74.0, 36.4, 31.8, 29.2, 25.5, 22.6, 19.7, 14.1. IR (CH_2Cl_2 , cm^{-1}): 2216 ($C\equiv C$), 2194 ($C\equiv N$). MS (FAB) m/z : 1111 (M). Anal. Calc. for $C_{46}H_{50}I_2N_2O_2Pt$: C, 49.68; H, 4.50; N, 2.52. Found: C, 49.77; H, 4.99; N, 2.21%.

2.4.11. Complex **1k**

Yellow crystals. Yield: 81%. 1H -NMR ($CDCl_3$): δ 7.27 (2H, s, Ar–H), 7.19 (2H, s, Ar–H), 4.11 (1H, m, $CHMe_2$), 2.55 (6H, s, Ar– CH_3), 2.26 (6H, s, Ar– CH_3), 1.78–1.18 (11H, m, C_4H_8 , CH_3), 0.90 (3H, m, CH_3). ^{13}C -NMR ($CDCl_3$): 155.7, 136.8, 132.3, 131.8, 131.0, 126.0, 124.5, 116.8, 92.9, 87.0, 78.3, 37.0, 32.0, 25.4, 22.5, 19.8, 18.9, 17.2, 14.1. IR (CH_2Cl_2 , cm^{-1}): 2210 ($C\equiv C$), 2189 ($C\equiv N$). Anal. Calc. for $C_{52}H_{62}I_2N_2O_2Pt$: C, 52.21; H, 5.19; N, 2.34. Found: C, 51.84; H, 5.14; N, 2.33%.

2.4.12. Complex **1l**

Yellow solid. Yield: 93%. 1H -NMR ($CDCl_3$): δ 7.27 (2H, s, Ar–H), 7.19 (2H, s, Ar–H), 4.09 (1H, m, $CHMe_2$), 2.55 (6H, s, Ar– CH_3), 2.26 (6H, s, Ar– CH_3), 1.78–1.15 (13H, m, C_5H_{10} , CH_3), 0.89 (3H, m, CH_3). ^{13}C -NMR ($CDCl_3$): 155.7, 136.8, 132.3, 131.8, 131.0, 126.1, 124.5, 116.8, 92.9, 87.0, 78.3, 37.0, 31.8, 29.5, 25.6, 22.6, 19.8, 18.9, 17.2, 14.1. IR (CH_2Cl_2 , cm^{-1}): 2210 ($C\equiv C$), 2189 ($C\equiv N$). Anal. Calc. for $C_{54}H_{66}I_2N_2O_2Pt$: C, 52.98; H, 5.39; N, 2.29. Found: C, 52.82; H, 5.46; N, 2.01%.

2.5. X-ray crystal structure analyses of complexes **1a**, **1d** and **1k**

The crystal parameters of compounds **1a**, **1d**, and **1k** and information on data collection and refinement are summarized in Table 1. The diffraction data for compounds **1a** were collected on a Rigaku AFC7R four-circle diffractometer using X-ray radiation from a Rigaku RU-200 rotating anode generator at 50 kV and 160 mA and processed by the MSC/Rigaku diffractometer control software. The diffraction data for complex **1d** were collected on a Siemens SMART CCD diffractometer. The diffraction data for complex **1k** were collected on a MAR imaging plate detector system using X-ray radiation from an MAR generator (sealed tube 50 kV and 50 mA), and processed by

DENZO [28]. The X-ray radiation from all generators was graphite-monochromatized $Mo-K_{\alpha}$ X-ray radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections based on the ψ -scan of five strong reflections were applied to the data of **1a**. The structure determinations were done using the MSC crystal structure analysis package TEXSAN [29] and the full-matrix least squares refinements were on F using reflections with $I > 3$ or $2\sigma I$. Hydrogen atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were included in the calculations, but not refined.

3. Results and discussion

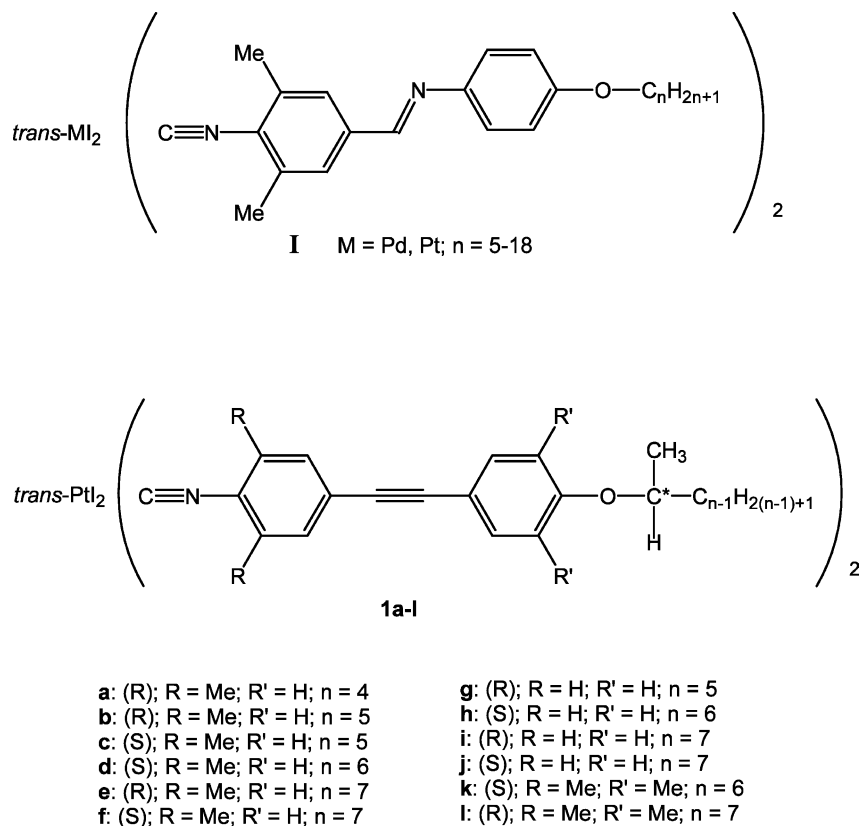
3.1. Synthesis and spectroscopic characterization of the isocyanide metal complexes

The *trans*-diiodo-bis(isocyanide)platinum(II) complexes **1a–l** were prepared as shown in Scheme 1 by reaction of two equivalents of the corresponding isocyanides **4a–l** with platinum(II) iodide in CH_2Cl_2 . The isocyanides **4a–l** were obtained from the anilines **2a–l** via the formamide derivatives **3a–l**, following established procedures [25,26].

The ethynyl and isocyanide groups of the free ligands give rise to characteristic IR absorptions in the ranges of 2200–2220 and 2115–2125 cm^{-1} , respectively. Upon coordination of the isocyanides to platinum(II), the $C\equiv C$ stretching frequencies remain largely unchanged while the $N\equiv C$ stretching frequencies increase by about 70 wavenumbers to 2189–2194 cm^{-1} [27]. For the free isocyanide groups, ^{13}C -NMR signals were observed at δ 165–170 [30]. The corresponding resonances of the coordinated isocyanide carbon atoms could not be detected due to their low intensity. The ^{13}C -NMR signals of the ethynyl groups occur between δ 85 and 95 and are little affected by coordination of the isocyanide groups to the metal center [31].

3.2. Crystal structures of complexes **1a**, **1d** and **1k**

The crystal structures of complexes **1a**, **1d** and **1k** have been determined by X-ray crystallography. The crystal parameters and information on data collection and refinement are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2, and the molecular structures are shown in Fig. 1. All three structures confirm the *trans* arrangement of the isocyanide ligands, giving rise to the overall linear shapes of the molecules. The individual bond distances and bond angles are unexceptional. The length of the unsaturated core, as measured by the distance between the two oxygen atoms in the 4-positions of the outer phenyl rings, is about 30.7 Å, slightly longer than in complexes **1**. A common feature of the three solid state structures is



the arrangement of the flat linear molecules in slanted stacks, whereby neighboring molecules are shifted relative to each other to such an extent that each bulky platinum center is flanked on either side by a slender ethynylene group from the neighboring molecules. This situation is illustrated for **1k** in Fig. 2. Since there are no unusually short intermolecular distances, this arrangement is apparently a consequence of the crystal packing forces. Complex **1k** differs from complexes **1a** and **1d** by the presence of two methyl substituents on the outer phenyl rings. The increased steric bulk at the ends of the rigid core creates extra room to fill for the adjacent flexible alkoxy chains, which do so by adopting a non-zigzag conformation. In all other solid-state structures of mesogenic isocyanide metal complexes determined so far only alkoxy chains with fully stretched-out conformations have been found. While linear zigzag conformations of alkoxy chains are the norm in crystalline mesogens [32–35], twists in the conformations nevertheless appear to be induced readily by particular structural features or general crystal packing forces [36–38].

3.3. Liquid crystal properties

The thermal properties of complexes **1a–l** were studied by a combination of differential scanning

calorimetry (DSC) and polarized optical microscopy. The phase transition temperatures and the associated enthalpies are listed in Table 3. Complexes **1a–j** exhibit an oil streak texture, indicating the presence of a chiral nematic (N*) phase [39]. Complexes **1k** and **1l** display a smectic A (SmA) phase characterized by a fan-shaped texture [40].

A plot of the phase transition temperatures of complexes **1a–l** versus the length of the alkyl chains is shown in Fig. 3. All complexes have terminal 1-methyl-alkoxy chains. They are divided into three groups. In complexes **1a–1f**, the isocyanophenyl groups bear two methyl groups, as in complexes **I**. In complexes **1g–j**, these methyl substituents have been removed, and in complexes **1k** and **1l**, two additional methyl groups have been introduced on the outer phenyl rings. Compared to complexes **1a–f**, complexes **1g–j** have lower phase transition temperatures and a significantly narrower range for the liquid crystal phase. The broadness of the liquid crystal phase of complexes **1a–f** supports our previous conclusion that the lateral methyl substituents adjacent to the metal center improve the liquid crystal properties. Complexes **1k** and **1l** have higher melting points and slightly lower clearing temperatures than complexes **1d** and **1e,f**, which have alkoxy chains of the same length. Apparently, the additional methyl substituents at the periphery of the rigid core stabilize the

Table 1
Crystal and data collection parameters for complexes **1a**, **1d** and **1k**

	1a	1d	1k
Formula	C ₄₄ H ₄₆ I ₂ N ₂ O ₂ Pt	C ₄₈ H ₅₄ I ₂ N ₂ O ₂ Pt	C ₅₂ H ₆₂ I ₂ N ₂ O ₂ Pt
Formula weight	1083.76	1139.8	1195.97
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$ (no. 2)	<i>C</i> 2	<i>P</i> 2 ₁ / <i>n</i> (no. 14)
Unit cell dimensions			
<i>a</i> (Å)	8.866(1)	20.851(4)	10.578(2)
<i>b</i> (Å)	10.651(2)	11.517(2)	20.381(3)
<i>c</i> (Å)	12.792(2)	10.798(2)	12.154(2)
α (°)	71.28(1)		
β (°)	69.81(1)	116.16(3)	97.12(2)
γ (°)	79.74(1)		
<i>V</i> (Å ³)	1070.6(3)	2327.3(25)	2600.1(7)
<i>Z</i>	1	2	2
<i>T</i> (K)	301	296	301
Crystal color	Yellow	Yellow	Yellow
Crystal dimensions (mm ³)	0.35 × 0.1 × 0.1	0.15 × 0.20 × 0.35	0.30 × 0.07 × 0.07
<i>D</i> _{calc} (g cm ⁻³)	1.681	1.626	1.527
μ cm ⁻¹ (<i>o</i>)	47.42	4.378	39.13
Scan mode	ω -2 θ	ω	–
2 θ _{max} (°)	48	50.0	50.9
Unique reflections	3355	3258	4029
Reflections used in LS refinement	2346 (<i>I</i> > 3 σ (<i>I</i>))	2565 (<i>F</i> > 4.0 σ (<i>F</i>))	2541 (<i>I</i> > 3 σ (<i>I</i>))
No. of variables	232	249	268
<i>R</i>	0.042 ^a	0.065	0.062 ^a
<i>R</i> _w	0.066 ^b	0.086	0.092 ^b
(Δ / σ) _{max}	0.05		0.05
Goodness-of-fit	1.84	1.58	2.85
$\Delta\rho$ (e Å ⁻³)	–0.65/1.03	–1.09/1.98	–1.07/0.97

^a $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$.

^b $R_w = [\Sigma w (|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}$, where $w = F_o^2 / [\sigma^2(I) + (pF_o^2)^2]$.

Table 2
Selected bond lengths (Å) and bond angles (°) for complex **1a**, **1d** and **1k**

1a		1d		1k	
<i>Bond lengths</i>					
Pt(1)–I(1)	2.6017(7)	Pt(1)–I(1)	2.596(3)	Pt(1)–I(1)	2.597(1)
N(1)–C(1)	1.16(1)	Pt(1)–C(1)	1.81(2)	N(1)–C(1)	1.19(1)
C(5)–C(8)	1.41(1)	N(1)–C(2)	1.43(2)	C(5)–C(8)	1.44(1)
C(9)–C(10)	1.40(1)	C(10)–C(11)	1.23(3)	C(9)–C(10)	1.42(1)
Pt(1)–C(1)	1.947(9)	Pt(1)–I(2)	2.606(4)	Pt(1)–C(1)	1.93(1)
N(1)–C(2)	1.39(1)	N(1)–C(1)	1.25(3)	N(1)–C(2)	1.38(1)
C(8)–C(9)	1.21(1)	C(5)–C(10)	1.47(3)	C(8)–C(9)	1.19(1)
		C(11)–C(12)	1.47(3)		
<i>Bond angles</i>					
I(1)–Pt(1)–C(1)	91.1(3)	I(1)–Pt(1)–I(2)	180.0(1)	I(1)–Pt(1)–C(1)	91.3(4)
C(1)–N(1)–C(2)	178.1(9)	I(2)–Pt(1)–C(1)	90(1)	C(1)–N(1)–C(2)	178(1)
C(8)–C(9)–C(10)	173(1)	C(1)–N(1)–C(2)	177(3)	C(8)–C(9)–C(10)	174(1)
Pt(1)–C(1)–N(1)	178.5(8)	C(10)–C(11)–C(12)	177(3)	Pt(1)–C(1)–N(1)	174(1)
C(5)–C(8)–C(9)	176(1)	I(1)–Pt(1)–C(1)	90(1)	C(5)–C(8)–C(9)	172(1)
C(13)–O(1)–C(16)	129(1)	Pt(1)–C(1)–N(1)	176(3)		
		C(5)–C(10)–C(11)	173(4)		

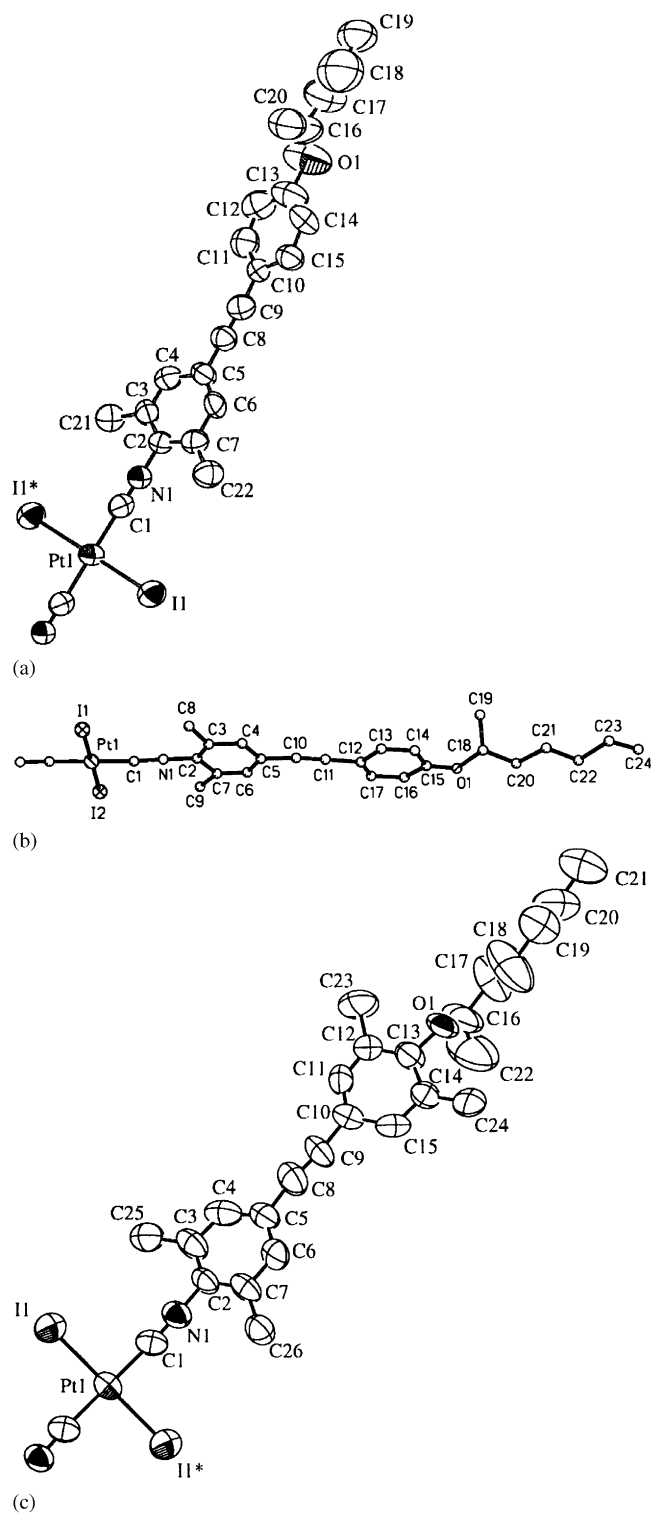


Fig. 1. (a) ORTEP drawing of compound **1a**. The thermal ellipsoids are shown at the 40% probability level. (b) Molecular structure of compound **1d**. (c) ORTEP drawing of compound **1k**. The thermal ellipsoids are shown at the 40% probability level.

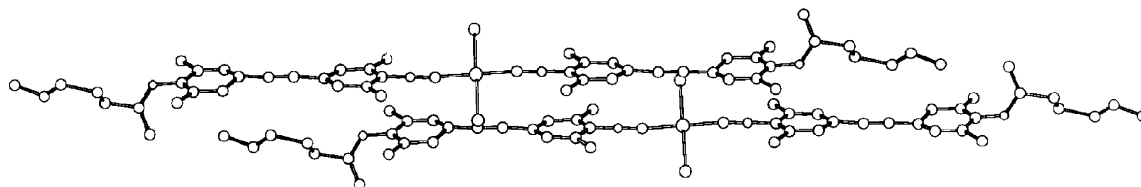
crystal phase due to increased intermolecular interactions between the enlarged rigid cores, but they do not stabilize the mesophase. As the results of the crystal structure determination of complex **1k** suggest, these methyl groups create an abrupt transition between a wide rigid core and a narrow flexible chain, thereby creating space for the alkoxy chains to adopt non-stretched-out conformations. Thus, the additional methyl groups on the peripheral phenyl rings of the isocyanide ligands do not enhance the liquid crystal properties. We also observed that complexes **1k** and **1l** display a higher viscosity than complexes **1a–j**.

Complexes **I** with $n = 5, 6$ and 8 exhibit an N phase with C–N transition temperatures varying from 244 to 206 °C and N–I transition temperatures ranging from 318 to 295 °C. The liquid crystal phase of complexes **1a–f** ($n = 4–7$) is narrower, but overlaps with the lower end of that range. Considering the difference in the alkyl chains, this result shows that the replacement of the imino unit in complexes **I** by an ethynylene bridge does not dramatically alter the liquid crystal properties and suggests that a comparison of the thermal behavior of complexes **I** and complexes **1a–f** is meaningful. Like complexes **I** with $n = 5–8$, complexes **1a–f** do exhibit a nematic phase. In the series of complexes **I**, an SmC phase emerges at an alkyl chain length of $n = 10$. We conclude that the alkyl chains in complexes **1a–f** are too short for a smectic phase to be observed, but would expect a SmC* phase to emerge in this series at longer chain lengths. In contrast, among the isocyanide complexes reported by Serrano to exhibit a SmC* phase was also the related compound PdI₂(CNC₆H₄-4-(CO₂C₆H₄-4-O-(R)-CHMeC₅H₁₁)) with an alkyl chain length of $n = 6$ [17].

For complexes **1a**, **1c**, **1d** and **1f**, the reflection spectra of films with the planar texture were measured [41]. The results are summarized in Table 4. The reflection spectrum of **1f** at 190 °C is shown in Fig. 4 as a representative example. For compound **1d**, the pitch [42] ranges from 394 to 352 nm in the temperature range of 175–220 °C, for compound **1f** from 462 to 365 nm in the temperature range of 170–210 °C.

3.4. Conclusions

This study confirms our earlier suggestion that lateral methyl substituents on the isocyanophenyl groups in *trans*-diiodo-bis(isocyanide)palladium(II) and platinum(II) complexes exert a beneficial influence on the liquid crystal properties. Additional methyl substituents on arene groups that are further removed from the bulky metal center appear to have a negative effect. Complexes **1a–1f** exhibit an N* phase with pitches ranging from 350 to 400 nm.

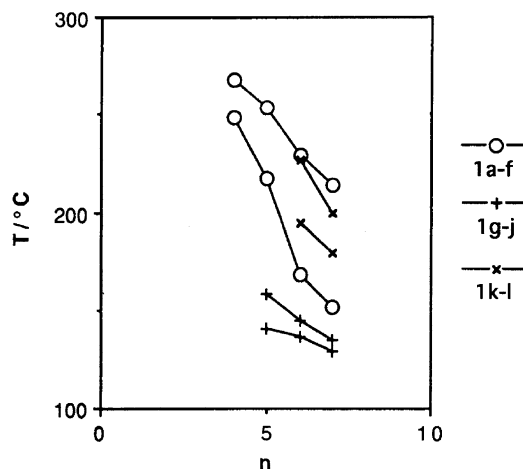
Fig. 2. Drawing of two neighboring molecules in the crystal structure of **1k**.Table 3
Mesomorphic properties of complexes **1a–l**

Compound	Transition	T ($^{\circ}\text{C}$)	ΔH (kJ mol^{-1})
1a	C–N*	249	29.6
	N*–I	268 (dec.)	
1b	C–N*	218	31.0
	N*–I	254 (dec.)	
1c	C–N*	217	28.2
	N*–I	255 (dec.)	
1d	C–N*	169	26.7
	N*–I	229	0.9
	I–N*	220	^a
	N*–C	161	^a
1e	C–N*	152	25.5
	N*–I	214	1.0
	I–N*	208	^a
	N*–C	144	^a
1f	C–N*	151	26.6
	N*–I	215	1.1
	I–N*	207	^a
	N*–C	141	^a
1g	C–N*	141	25.8
	N*–I	159	^a
	I–N*	145	^a
	N*–C	131	24.2
1h	C–N*	137	23.2
	N*–I	145	^a
	I–N*	130	^a
	N*–C	127	24.4
1i	C–N*	129	28.1
	N*–I	135	^a
	I–N*	121	^a
	N*–C	114	20.5
1j	C–N*	130	27.1
	N*–I	136	^a
	I–N*	121	^a
	N*–C	113	19.1
1k	C–S _A	195	39.2
	S _A –I	227	^a
	I–S _A	210	^a
	S _A –C	181	21.5
1l	C–S _A	180	36.2
	S _A –I	200	1.1
	I–S _A	198	^a
	S _A –C	168	12.6

^a Not detected by DSC.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 205900–205902 for com-

Fig. 3. Plot of phase transition temperatures of complexes **1a–l** versus number of carbon atoms in the longest alkoxy chains. Only the data obtained from heating the samples are included.Table 4
Reflection data and pitches for the planar texture of selected complexes

Complex	T ($^{\circ}\text{C}$)	λ (nm)	P_o (nm) ^a
1a	252	730	457
1c	228	752	470
1d	175	630	394
	180	622	389
	190	604	378
	200	589	368
	210	570	357
	220	563	352
1f	170	739	462
	180	693	433
	190	649	406
	200	615	385
	210	584	365

^a $\lambda = \bar{n} \times P_o$; λ is the wavelength of the center of the reflectance peak; \bar{n} is the average refractive index of the liquid crystal sample (1.6); P_o is the pitch.

pounds **1a**, **1d**, and **1k**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

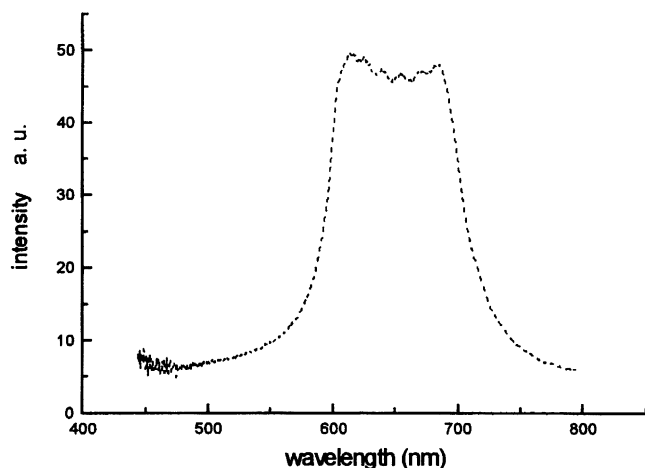


Fig. 4. Reflection spectrum of complex **1f** at 190 °C.

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