Columnar Organization in Mesogenic *cis*- and *trans*-[MX₂(C≡NR)₂] Complexes (M = Pd, Pt)

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Palladium and platinum(II) complexes [MX₂{C≡NC₆H₂(3,4,5-OC$_n$H$_{2n+1}$)₃}₂] (X = Cl, Br, I; n = 4, 6, 8, 10, 12) have been prepared. The free isocyanides are not liquid crystals, but most of their complexes [MX₂{C≡NC₆H₂(3,4,5-OC$_n$H$_{2n+1}$)₃}₂] (M = Pd, Pt; X = Cl, Br, I) show hexagonal columnar phases. For M = Pd and X = Cl and Br, an isomerization is observed going from the condensed phases to the solution. In the mesophase all the complexes seem to be cis for X = Cl and Br and trans for X = I. Their melting points depend mostly on the peripheral chains and are little sensitive to the configuration cis or trans or to the metal (Pd or Pt). The clearing points depend more on the core interactions and show noticeable variations (cis > trans; Pt > Pd). The reasons for this behavior are discussed.

Introduction

Liquid crystals containing transition metals (so-called "metallomesogens") represent a growing area in liquid crystals research due to the expected advantages of combining the properties of mesomorphic systems with those of transition metals. A large number of metallomesogens have been synthesized, and molecular design and synthesis of new metal complexes with novel mesophases or improved physical properties is an active research area in mesogenic materials.[1–5] Different types of ligands, particularly N-donor ligands, have been used. Surprisingly isocyanides, which give very stable complexes with many transition metals in different oxidation states, have been used only recently, and liquid crystals based in isocyanide metal complexes are restricted to some isocyanide complexes of Au(I),[6–11] Pd(II), and Pt(II).[12,13] In the case of the complexes of the latter two metals, only calamitic phases have been described. On the other hand, there is an increasing interest in discotic liquid crystals due to the fact that columnar mesophases can display interesting electronic properties.[14,15]

We have been studying systematically the effect of structural modifications on the liquid crystal behavior in the coordinatively simple mesogenic system [AuX(C≡NC₆H₄OC$_n$H$_{2n+1}$-*p*)] (X = halogen). These linearly coordinated gold complexes show smectic A phases, although their isonitrile ligands are not mesogenic and contain only one aryl ring. We have reported and discussed the effects of the following: (i) substitution of the halogen by other anionic ligands such as alkynyls and perhalophenyls;[8,11] (ii) modifications in the isocyanide ligand, such as incorporation of a second phenyl ring,[9] introduction of a lateral substituent on the phenyl ring by substituting H for F at the 2- and 3-positions,[10] or modification of its rodlike shape by addition of two alkoxylic chains in the *meta* positions.[10] The halogeno-(3,4,5-trialkoxyphenylisonitrile)gold(I) derivatives show room-temperature hexagonal columnar mesophases by stacking of disks formed by the assembly of two molecules of the complex in antiparallel disposition.[10]

Moving to a more complex system we report here the preparation and liquid crystalline behavior of square-planar dihalogenobis(3,4,5-trialkoxyphenylisonitrile)-palladium(II) and platinum(II) complexes, where the possibility of cis or trans isomers, with very different geometrical features, is a source of complication.

Results

Synthesis and Structural Characterization. The dihalogenobis(3,4,5-trialkoxyphenyl isocyanide)palladium-

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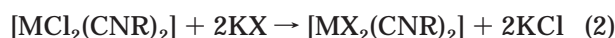(14) Eley, D. D. *Mol. Cryst. Liq. Cryst.* **1990**, *171*, 1.
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Table 1. Number of ν(C≡N) Absorptions Observed for the [MX$_2$(C≡NR)$_2$] Complexes with Isomeric Composition in CDCl$_3$ Solution from ^{1}H NMR in Parentheses (Cis/Trans)

M (phase)	Cl	Br	I
Pd (solution)	2	1	1
Pd (NMR)	(65/35),^{a} (100/0)^b	(5/95),^{a} (80/20)^b	(0/100)^c
Pd (solid)	2	2	1
Pd (mesophase)	2	2	1
Pt (solution)	2	2	1
Pt (NMR)	(100/0)^c	(100/0)^c	(0/100)^c
Pt (solid)	2	2	1
Pt (mesophase)	2	2	1

^{a} At 293 K, average value. Small variations occur for different chain lengths. ^{b} For R = C$_8$H$_{17}$ at 223 K. ^{c} No change at low or high temperature.

(II) and -platinum(II) complexes were prepared according to eqs 1 and 2.

$$[MCl_2(tht)_2] + CNR \rightarrow [MCl_2(CNR)_2] + 2tht \quad (1)$$

$$[MCl_2(CNR)_2] + 2KX \rightarrow [MX_2(CNR)_2] + 2KCl \quad (2)$$

The reactions of the corresponding isocyanides with [MCl$_2$(tht)$_2$] (M = Pd, Pt; tht = tetrahydrothiophene) in acetone afforded the pale yellow complexes [MCl$_2$-(CNR)$_2$] (R = C$_6$H$_2$-3,4,5-OC$_n$H$_{2n+1}$, n = 4, 6, 8, 10). Exchange reactions in acetone with the appropriate potassium salt gave the corresponding bromo or iodo derivatives. The C, H, N analyses for the complexes, yields, and relevant IR data are given in the Experimental Section. To try to ascertain the cis or trans configuration of the complexes, IR spectra were taken in the solid state, in chloroform solution, and in the mesophase. ^{1}H NMR spectra were taken in CDCl$_3$ solution at room temperature, and some (those of the chain with n = 8) were also recorded after dissolving the solid (or the frozen mesophase; the result was the same) at low temperature and monitoring the evolution of the solution as it reached room temperature. These results are summarized in Table 1.

The IR spectra show the ν(C≡N) absorptions for the isonitrile groups at higher wavenumbers (ca. 60 cm^{-1}) than for the free isonitrile, as reported for other palladium- and platinum(II) isocyanide compounds.[13,16] Two ν(C≡N) absorptions are expected for a cis arrangement of the isonitrile ligands (C_{2v} symmetry), and only one is expected for a trans arrangement (D_{2h} symmetry).[16] The number of absorptions actually observed depends on the metal, the halide, and the physical state of the sample, as shown in Table 1. It must be noted that the observation of only one absorption allows one to reject the presence of significant amounts of the cis isomer, but the observation of two bands does not guarantee the absence of the trans isomer, as its absorption can be overlapped with those of the cis.

The Pt complexes are isomerically pure in solution (cis for X = Cl, Br; trans for X = I) and seem to maintain the same configuration in the solid state or in the mesophase. The same applies to the complexes [PdI$_2$-(CNR)$_2$], which are isomerically pure trans in all phases. For X = Cl and Br the palladium complexes are a mixture of the two isomers in solution at room temperature, the trans being very predominant (95%) for the

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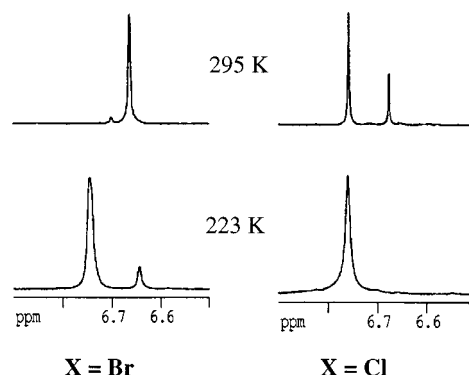
Figure 1. ^{1}H NMR spectra (aromatic region) at different temperatures of [PdX$_2${C≡NC$_6$H$_2$(3,4,5-OC$_8$H$_{17}$)$_3$}$_2$] in CDCl$_3$: (a) X = Cl; (b) X = Br. The samples were disolved at 223 K.

bromo complexes and the cis for the chloro derivatives (65%). In the solid and in the mesophase these compounds show two bands, indicating the abundant presence of the cis isomer, but not excluding that of the trans isomer, for which the corresponding absorption is expected in the same range and can be overlapped by those of the cis compound. In fact when a solid sample of [PdCl$_2$(CNC$_8$H$_{17}$)$_2$] was dissolved at 223 K, the NMR revealed only the presence of the cis isomer, and the spectrum changed to show a mixture containing 45% of the trans isomer when the solution was let to stand at room temperature for several hours. Similarly, when the complex [PdBr$_2$(CNC$_8$H$_{17}$)$_2$] was dissolved at 223 K, it showed by NMR a mixture cis/trans = 80/20, which remained almost invariant up to 243 K. At 293 K the isomerization started to be faster, to reach the equilibrium concentrations (cis/trans = 5/95) in about 6 h (Figure 1). Thus, probably the isomeric composition in the solid is close to that observed at low temperature, that is, totally or very much enriched in the cis form compared to the solution (recrystallization and redissolution reproduced the values; thus, the isomerization is reversible). These observations indicate the following: (i) The iodo complexes strongly favor the trans isomer. (ii) For Pt (a more inert metal toward isomerization) the compounds are isomerically pure and maintain their configuration in solution and in the condensed phases (trans for iodide, cis for the other halides). (iii) For Pd the iodide also maintains its trans configuration in all circumstances. (iv) The Cl and Br derivatives of palladium consist of only (or mainly) the cis isomer in the condensed phases, although in solution they establish an equilibrium with an important (Cl) or predominant (Br) presence of the trans isomer. This warns against cursory structural assignment for this type of complexes based on solution data only.

In summary it seems that the Cl and Br derivatives in the mesophase are cis or very predominantly cis whereas the I derivatives are trans.

Mesogenic Behavior. *Cis Compounds.* The mesogenic behavior of the complexes *cis*-[MX$_2$(C≡NC$_6$H$_2$-{OC$_n$H$_{2n+1}$}$_3$)$_2$] (M = Pd, Pt; X = Cl, Br) is summarized in Table 2.

Although the free isocyanides used are not mesomorphic, most of their complexes show mesogenic behavior. This is a new example of induction of mesogenic properties upon attachment to a metal center, as we have discussed somewhere else.[10] All the cis palladium

Table 2. Optical, Thermal, and Thermodynamic Data for the Complexes [MX$_2$\{CNC$_6$H$_2$(3,4,5-OC$_n$H$_{2n+1}$)$_3$\}$_2$]

M	X	n	phase transition (°C) and corresponding enthalpy changes (KJ mol^{-1})^a heating	cooling
Pd	Cl	4	$C^{70.1(21.9)}Col_h^{220}I^{b,c}$	
Pd	Cl	6	$Col_h^{190}I^{b,c}$	
Pd	Cl	8	$Col_h^{183.8(10.7)}I^{c}$	
Pd	Cl	10	$Col_h^{176.3(11.2)}I$ $Col_h^{166.4(9.8)}I$	$I^{165}Col_h^{b}$
Pd	Br	4	$C^{77.1(21.3)}Col_h^{146.9(10.6)}I$ $Col_h^{144.7(9.4)}I$	$I^{140.9(-9.4)}Col_h$
Pd	Br	6	$Col_h^{161.4(17.8)}I$ $Col_h^{154.6(13.2)}I$	$I^{155.5(-13.1)}Col_h$
Pd	Br	8	$C^{42.2(21.2)}Col_h^{142.7(13.7)}I$ $Col_h^{139.9(11.1)}I$	$I^{139.6(-11.0)}Col_h$
Pd	Br	10	$Col_h^{126.7(9.0)}I$ $Col_h^{121.1(12.0)}I$	$I^{123.4(-6.5)}Col_h$
Pd	I	4	$C^{78.3(29.5)}C'^{138.4(25.6)}I$ $C'^{38.4(26.0)}I$	$I^{133.6(-24.7)}C'$
Pd	I	6	$C^{52.1(61.9)}I$ $Col_h^{35.9(7.3)}I$	$I^{29.5(-6.1)}Col_h$
Pd	I	8	$C^{44.7(59.6)}I$ $Col_h^{27.3(4.2)}I$	$I^{22.5(-3.8)}Col_h$
Pd	I	10	$C^{53.0(61.2)}I$ $Col_h^{33.1(4.5)}I$	$I^{28.3(-4.3)}Col_h$
Pt	Cl	4	$C^{73.4(11.2)}Col_h^{248}I^{b,c}$	
Pt	Cl	6	$Col_h^{235.8(8.5)}I^{c}$	
Pt	Cl	8	$Col_h^{170}I^{b,c}$	
Pt	Cl	10	$Col_h^{113.5(13.7)}I^{c}$	
Pt	Br	4	$C^{67.3(5.7)d}Col_h^{219.8(9.8)}I^{c}$	
Pt	Br	6	$Col_h^{224.5(16.7)}I$ $Col_h^{213.2(10.8)}I$	$I^{217.2(-10.9)}Col_h$
Pt	Br	8	$Col_h^{200.3(13.7)}I$ $Col_h^{199.6(13.3)}I$	$I^{199.9(-12.4)}Col_h$
Pt	Br	10	$Col_h^{171(7.1)}I^{d}$ $Col_h^{168(5.8)}I^{d}$	$I^{164(-7.3)}Col_h^{d}$
Pt	I	4	$C^{76.6(30.2)}C'^{133.4(21.4)}I$ $C'^{132.6(21.6)}I$	$I^{126.0(-19.9)}C'$
Pt	I	6	$C^{48.0(67.3)}I$ $Col_h^{41.0}I^{b}$	$I^{32.0}Col_h^{b}$
Pt	I	8	$C^{31.7(32.8)}Col_h^{41.0(21.5)}I$ $Col_h^{40.0}I^{b}$	$I^{35.0}Col_h^{b}$
Pt	I	10	$C^{44.0b,e}Col_h^{56.0}I^{b,e}$ $Col_h^{52.0}I^{b}$	$I^{43}Col_h^{b}$

^{a} C, crystal; Col$_h$, hexagonal columnar; I, isotropic liquid. Data on first line are from the first heating and cooling scans, and data on the second line are from the second heating scan. ^{b} Microscopic data. ^{c} Transition with decomposition. ^{d} Peak temperature. ^{e} The DSC scan shows a large peak (54.3 °C; 55.2 KJ mol^{-1}) from the overlaping of two transitions observed by microscopy.

and platinum complexes display enantiotropic liquid crystal behavior at room temperature, except the chlorometal compounds with $n = 4$ which melt in the range 60−70 °C. The *cis*-chloropalladium, and the *cis*-chloro- and *cis*-bromoplatinum compounds with the shortest alkoxy chain ($n = 4$) undergo some decomposition above the clearing point, possibly due to the high temperature at which this clearing happens.

The textures observed in a polarizing microscope, on cooling from the isotropic liquid, are characteristic of hexagonal columnar phases and display linear birefringent defects, large areas of uniform extinction, and fan domains.[18,19] Low-angle X-ray diffraction patterns for *cis*-[PdCl$_2$\{C≡NC$_6$H$_2$(3,4,5-OC$_4$H$_9$)$_3$\}$_2$] and *cis*-[PdBr$_2$-

\{C≡NC$_6$H$_2$(3,4,5-OC$_8$H$_{17}$)$_3$\}$_2$] in the mesophase are very similar, consisting of four low-angle rings and two broad rings at wide angle. The *d* spacing of the four first diffraction rings scale as 1:($^1/_3$)$^{1/2}$:$^1/_2$:($^1/_7$)$^{1/2}$, consistent with a hexagonal lattice ($a = 2.02$ nm for the chloro compound and $a = 2.67$ nm for the bromo derivative). In both cases, the inner broad halo corresponds with a 0.44 nm spacing indicative of the weak liquid like interactions between the mesogens. The outer broad ring reveals a periodic stacking of the molecular cores inside a column with a low correlation length. From the diameter of this ring a distance of 0.34 nm between cores is calculated, consistent with a disk formed by only one molecule of the complex.

Cis chloro and bromo palladium and platinum complexes, when the isocyanide has a short tail ($n = 4$), exhibit a melting transition only in the first heating scan. No crystallization exotherm is observed in the cooling thermogram, nor does a melting endoterm appear in the subsequent reheating scan, possibly due to the supercooling of the mesophase.

Trans Compounds. The complexes *trans*-[MI$_2$\{C≡NC$_6$H$_2$(3,4,5-OC$_n$H$_{2n+1}$)$_3$\}$_2$] ($n = 4, 6, 8, 10$) are mesomorphic, except for $n = 4$. Their optical, thermal, and thermodynamic data are presented in Table 2. The textures observed are similar to those of the cis complexes above-discussed, except for the compound *trans*-[PdI$_2$\{C≡NC$_6$H$_2$(3,4,5-OC$_6$H$_{13}$)$_3$\}$_2$], which shows a mosaic texture on cooling from the isotropic phase. X-ray diffraction from this mesophase shows the low-angle rings with the same stacking as above, consistent with a hexagonal lattice ($a = 2.44$ nm). In the wide angle region, only one broad halo is seen with a 0.44 nm spacing corresponding to the distance between fused alkyl chains.

Similarly to the cis complexes discused above, the mesomorphic *trans*-iodopalladium and -platinum complexes exhibit a melting transition only in the first heating scan, and supercooling of the mesophases occurs in the cooling cycle.

Discussion

The stacking arrangement in the mesophase is the result from the minimization of electrostatic repulsion and the maximization of electrostatic attraction between the molecules.[20] Moreover, the molecular arrangement has to produce an efficient filling of the space. Thus the thermal behavior is dependent on both electronic and steric factors.

For the complexes discussed in this paper, the cis complexes exhibit a net dipolar moment, whereas the trans derivatives are apolar. It can be expected that in the cis complexes energetically favorable dipole−dipole interaction between molecules will induce a stacking of the molecules in antiparallel disposition. In fact this is the arrangement observed in the crystalline state of *cis*-[PtCl$_2$(CNC$_6$H$_5$)], where a short Pt−Pt distance (3.48 Å) is found.[21] Moreover, the stacking of the molecules in an alternating fashion generates a complementary distribution of the alkoxy chains along the columns and

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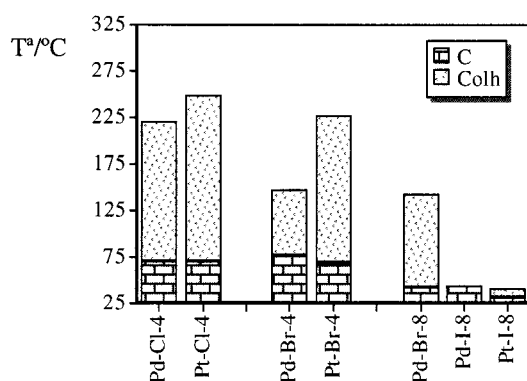
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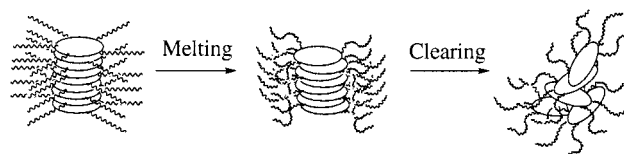(21) Jovanovic, B.; Muir, L. M.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1972**, 1178.
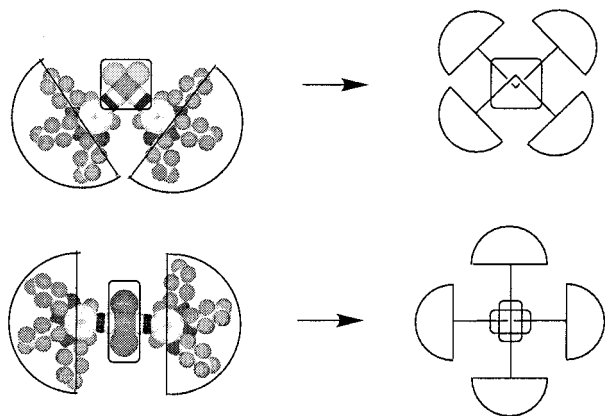
Figure 2. Shape analysis and proposed assembly of *cis*- (top) and *trans*- (bottom) [$MX_2\{C\equiv NC_6H_2(3,4,5\text{-}OC_nH_{2n+1})_3\}_2$] complexes into a discotic columnar superstructure (viewed along the columns).

Figure 4. Melting transition of a columnar crystal involving mainly melting of the chains, while core interactions maintain the columnar order. The latter is lost at the clearing transition.

stacking of the cores (Figure 4).[22] In fact both isomers can attain similarly efficient columnar distributions of the chains as sketched in Figure 2, and the melting of the chains should be little affected by the nature of the metal; hence, similar melting points for the complexes with the same chain length (regardless of the metal or the conformation) is found. On the other hand the core interactions should be stronger for the conformation possessing a permanent dipole (cis), and for the more electron-rich metal (Pt), leading to higher clearing points as observed.

Finally, it is interesting to compare the thermal behavior of metal complexes described here with that of previously reported halobis(biphenyl isocyanide)-palladium and -platinum complexes.[13] The mesomorphic behavior of those (biphenyl isocyanide)palladium and -platinum compounds depended on the kind of halogen and the metal used. All the iodo- and bromopalladium, and iodoplatinum derivatives, which have the trans configuration, behaved as liquid crystals, while the chloro- and bromoplatinum and the chloropalladium compounds, with cis configuration, did not show mesomorphic properties. This shows that for rodlike molecules the configuration of the complex has a decisive effect on the molecular shape, while this influence is very much attenuated in disklike derivatives.

Figure 3. Comparison of the transition temperatures of cis/trans and Pd/Pt [$MX_2\{C\equiv NC_6H_2(3,4,5\text{-}OC_nH_{2n+1})_3\}_2$] complexes. The bars are labeled M−X-n, where M denotes the metal, X the halogen, and n the number of carbons in the alkoxy chains.

a more efficient space filling (Figure 2). Each pair of molecules complete an almost perfect discotic arrangement of chains (it is not meant, however, that the molecules are forming discrete pairs). On the other hand the trans isomers can also achieve an overall disk shape if their molecules pile in an alternating perpendicular packing. Furthermore, this distribution is probably favored, since a parallel packing would lead to a repulsive parallel alignment of the local bond dipoles.

The complex multipolar structure of these molecules prevents a detailed understanding of the transition temperatures observed, but the most prominent features can be justified on the basis of very simple ideas. The general trends observed can be summarized as follows: (i) The melting temperatures are rather similar for the Pd and the Pt compounds, whereas the clearing points are noticeably higher for the latter. (ii) The clearing points for the trans derivatives are much lower than for the cis complexes, whereas the melting points are not so much different, and consequently the trans compound show a narrower range of mesophase. In other words, the melting points are quite insensitive to the type of isomer (cis or trans) and to the metal (Pd or Pt), whereas the clearing points are sensitive to both circumstances (Figure 3). This behavior fits well with the model that considers that the crystal-to-discotic phase transition is associated to disordering of the peripheral chains, whereas the clearing involves un-

Conclusions

The coordination of 3,4,5-trialkoxyphenyl isocyanides, which are not liquid crystals themselves, produces mesomorphic palladium and platinum complexes [$MX_2(CNR)_2$] (X = halogen). This induction of mesogenic behavior is associated with an increase in the molecular polarizability of the complex compared to the free ligand. Both cis and trans isomers produce a hexagonal columnar packing, probably with the molecules alternating in an antiparallel arrangement for the cis and in a perpendicular arrangement for the trans derivatives. The melting points, depending mostly on the peripheral chains, are little sensitive to the configuration or to the metal, but the clearing points, depending more on core interactions, show noticeable variations. This behavior is very different from that observed for rodlike (biphenyl isocyanide)palladium and platinum complexes, for which only the trans isomers are liquid crystals.

Experimental Section

Combustion analyses were made with a Perkin-Elmer 2400 microanalyzer. IR spectra (cm⁻¹) were recorded on a Perkin-Elmer FT 1720X instrument and ¹H NMR spectra on Bruker AC 300 or ARX 300 instruments in CDCl₃. IR spectra of

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samples in the mesophase were recorded between thin plates (about 0.5 mm) of NaCl, KBr, or KI, depending of the halogen present in the complex, using a Mettler FP82HT hot stage without the glass heat shields and a Mettler FP90 central processor. Microscopy studies were carried out on a Leica DMRB microscope at a heating rate of 10 °C min^{-1}. For differential scanning calorimetry (DSC) a Perkin-Elmer DSC7 instrument was used, which was calibrated with water and indium; the scanning rate was 10 °C min^{-1}, the samples were sealed in aluminum capsules in the air, and the holder atmosphere was dry nitrogen. The temperatures are referred to the onset or to the peak temperatures when the transition is very broad.

Literature methods were used to prepare [C≡NC$_6$H$_2$-(3,4,5-OC$_n$H$_{2n+1}$)$_3$],[10] [PdCl$_2$(tht)$_2$], and [PtCl$_2$(tht)$_2$][23] (tht = tetrahydrothiophene).

Only examples are described as the syntheses were similar for the rest of the complexes. Yields, IR, and analytical data are given for all the Pd and Pt isonitrile complexes.

Preparation of [MCl$_2$\{C≡NC$_6$H$_2$(3,4,5-OC$_n$H$_{2n+1}$)$_3$\}$_2$]. To a solution of [MCl$_2$(tht)$_2$] (M = Pd, Pt) (0.195 mmol) in 40 mL of acetone was added [C≡NC$_6$H$_2$-(3,4,5-OC$_n$H$_{2n+1}$)$_3$] (0.390 mmol). After being stirred for 1 h at room temperature and overnight at −15 °C, the compounds crystallize as a cream solid for $n = 4$, and a viscous fluid separates for the rest.

Yields, IR, ^{1}H NMR, and Analytical Data for M = Palladium. $n = 4$: Yield: 40%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2218, 2234; (KBr) 2222, 2246. ^{1}H NMR (CDCl$_3$): δ 6.79 (s, C$_6$H$_2$, 4H), 3.96 (m, OCH$_2$, 12H), 1.86−0.88 (m, alkyl chain, 42H). Anal. Calcd for C$_{38}$H$_{58}$PdCl$_2$N$_2$O$_6$: C, 55.92; H, 7.16; N, 3.43. Found: C, 55.97; H, 6.98; N, 3.36.

$n = 6$. Yield: 40%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2220, 2230; (KBr) 2228, 2238. ^{1}H NMR (CDCl$_3$): δ 6.79 (s, C$_6$H$_2$, 4H), 3.94 (m, OCH$_2$, 12H), 1.82−0.87 (m, alkyl chain, 66H). Anal. Calcd for C$_{50}$H$_{82}$PdCl$_2$N$_2$O$_6$: C, 61.00; H, 8.39; N, 2.84. Found: C, 60.88; H, 8.06; N, 3.00.

$n = 8$. Yield: 60%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2219, 2230; (KBr) 2227, 2238. ^{1}H NMR (CDCl$_3$): δ 6.77 (s, C$_6$H$_2$, 4H), 3.95 (m, OCH$_2$, 12H), 1.83−0.85 (m, alkyl chain, 90H). Anal. Calcd for C$_{62}$H$_{106}$PdCl$_2$N$_2$O$_6$: C, 64.60; H, 9.27; N, 2.43. Found: C, 65.01; H, 8.96; N, 2.59.

$n = 10$. Yield: 80%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2220, 2236; (KBr) 2227, 2238. ^{1}H NMR (CDCl$_3$): δ 6.76 (s, C$_6$H$_2$, 4H), 3.93 (m, OCH$_2$, 12H), 1.81−0.85 (m, alkyl chain, 114H). Anal. Calcd for C$_{74}$H$_{130}$PdCl$_2$N$_2$O$_6$: C, 67.28; H, 9.92; N, 2.12. Found: C, 67.39; H, 9.56; N, 2.12.

For all the chloropalladium complexes described here their ^{1}H NMR spectra reveal that, in solution, besides the cis isomer, there is a considerable amount (about 35%) of the trans isomer. Their signals are overlapped with those of the cis isomer, except the resonance from aromatic protons which appears ca. δ 6.6

Cis Chloro Complexes with M = Platinum. $n = 4$. Yield: 60%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2211, 2236; (KBr) 2214, 2245. ^{1}H NMR (CDCl$_3$): δ 6.76 (s, C$_6$H$_2$, 4H), 4.44 (t, OCH$_2$-*meta*, 8H), 3.02 (t, OCH$_2$-*para,* 4H), 1.81−0.90 (m, alkyl chain, 42H). Anal. Calcd for C$_{38}$H$_{58}$PtCl$_2$N$_2$O$_6$: C, 50.43; H, 6.46; N, 3.09. Found: C, 50.69; H, 6.56; N, 3.29.

$n = 6$. Yield: 40%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2211, 2237; (KBr) 2220, 2245. ^{1}H NMR (CDCl$_3$): δ 6.72 (s, C$_6$H$_2$, 4H), 3.94 (m, OCH$_2$, 12H), 1.84−0.87 (m, alkyl chain, 66H). Anal. Calcd for C$_{50}$H$_{82}$PtCl$_2$N$_2$O$_6$: C, 55.45; H, 7.70; N, 2.61. Found: C, 55.85; H, 7.45; N, 3.00.

$n = 8$. Yield: 40%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2210, 2236; (KBr) 2213, 2240. ^{1}H NMR (CDCl$_3$): δ 6.70 (s, C$_6$H$_2$, 4H), 3.95 (m, OCH$_2$, 12H), 1.83−0.85 (m, alkyl chain, 90H). Anal. Calcd for C$_{62}$H$_{106}$PtCl$_2$N$_2$O$_6$: C, 59.98; H, 8.60; N, 2.25. Found: C, 60.27; H, 8.62; N, 2.20.

$n = 10$. Yield: 40%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2210, 2237; (KBr) 2212, 2239. ^{1}H NMR (CDCl$_3$): δ 6.73 (s, C$_6$H$_2$, 4H), 3.94 (m, OCH$_2$, 12H), 1.81−0.85 (m, alkyl chain, 114H). Anal.

Calcd for C$_{74}$H$_{130}$PtCl$_2$N$_2$O$_6$: C, 63.05; H, 9.29; N, 1.98. Found: C, 63.32; H, 9.21; N, 1.47.

Preparation of [MBr$_2$\{C≡NC$_6$H$_2$(3,4,5-OC$_n$H$_{2n+1}$)$_3$\}$_2$]. KBr (0.390 mmol) was added to [MCl$_2$(C≡NC$_6$H$_2$\{-3,4,5-OC$_n$H$_{2n+1}$\}$_3$)$_2$] (M = Pd, Pt) (0.195 mmol) dissolved in 40 mL of acetone. The mixture was stirred for 10 h, and the KCl formed was filtered off. After cooling of the solution overnight at −15 °C, the compounds crystallize as a yellow solid for $n = 4$ and the palladium derivative with $n = 8$. A viscous fluid separates for the rest.

Yields, IR, ^{1}H NMR, and Analytical Data for M = Palladium. $n = 4$. Yield: 50%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2215; (KBr) 2221, 2239. ^{1}H NMR (CDCl$_3$): δ 6.67 (s, C$_6$H$_2$, 4H), 3.96 (m, OCH$_2$, 12H), 1.84−0.93 (m, alkyl chain, 42H). Anal. Calcd for C$_{38}$H$_{58}$PdBr$_2$N$_2$O$_6$: C, 50.43; H, 6.46; N, 3.09. Found: C, 50.48; H, 6.30; N, 3.07.

$n = 6$. Yield: 50%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2215; (KBr) 2222, 2240. ^{1}H NMR (CDCl$_3$): δ 6.67 (s, C$_6$H$_2$, 4H), 3.94 (m, OCH$_2$, 12H), 1.86−0.87 (m, alkyl chain, 66H). Anal. Calcd for C$_{50}$H$_{82}$PdBr$_2$N$_2$O$_6$: C, 55.95; H, 7.70; N, 2.61. Found: C, 56.08; H, 7.63; N, 2.63.

$n = 8$. Yield: 65%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2215; (KBr) 2222, 2239. ^{1}H NMR (CDCl$_3$): δ 6.67 (s, C$_6$H$_2$, 4H), 3.95 (m, OCH$_2$, 12H), 1.83−0.86 (m, alkyl chain, 90H). Anal. Calcd for C$_{62}$H$_{106}$PdBr$_2$N$_2$O$_6$: C, 59.97; H, 8.60; N, 2.26. Found: C, 60.02; H, 8.13; N, 2.20.

$n = 10$. Yield: 70%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2215; (KBr) 2219, 2232. ^{1}H NMR (CDCl$_3$): δ 6.67 (s, C$_6$H$_2$, 4H), 3.94 (m, OCH$_2$, 12H), 1.85−0.86 (m, alkyl chain, 114H) Anal. Calcd for C$_{74}$H$_{130}$PdBr$_2$N$_2$O$_6$: C, 63.03; H, 9.29; N, 1.99. Found: C, 63.42; H, 9.09; N, 2.03.

For all the bromopalladium complexes described here, their ^{1}H NMR spectra reveal that in solution they are mainly the trans isomer, but there is a small amount (about 5%) of the corresponding cis isomer. Their signals are overlapped with those of the trans isomer, except the resonance from aromatic protons which appears ca. δ 6.7.

Cis Complexes with M = Platinum. $n = 4$. Yield: 50%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2210, 2234; (KBr) 2217, 2241. ^{1}H NMR (CDCl$_3$): δ 6.74 (s, C$_6$H$_2$, 4H), 3.96 (m, OCH$_2$, 12H), 1.81−0.92 (m, alkyl chain, 42H). Anal. Calcd for C$_{38}$H$_{58}$PtBr$_2$N$_2$O$_6$: C, 45.93; H, 5.88; N, 2.82. Found: C, 45.69; H, 5.74; N, 2.70.

$n = 6$. Yield: 40%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2209, 2234; (KBr) 2218, 2242. ^{1}H NMR (CDCl$_3$): δ 6.78 (s, C$_6$H$_2$,4H), 3.93 (m, OCH$_2$, 12H), 1.81−0.87 (m, alkyl chain, 66H). Anal. Calcd for C$_{50}$H$_{82}$PtBr$_2$N$_2$O$_6$: C, 51.68; H, 7.11; N, 2.41. Found: C, 51.68; H, 6.92; N, 2.39.

$n = 8$. Yield: 40%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2208, 2232; (KBr) 2218, 2241. ^{1}H NMR (CDCl$_3$): δ 6.78 (s, C$_6$H$_2$, 4H), 3.93 (m, OCH$_2$, 12H), 1.81−0.85 (m, alkyl chain, 90H). Anal. Calcd for C$_{62}$H$_{106}$PtBr$_2$N$_2$O$_6$: C, 55.97; H, 8.03; N, 2.11. Found: C, 55.71; H, 7.78; N, 2.04.

$n = 10$. Yield: 40%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2206, 2232; (KBr) 2211, 2236. ^{1}H NMR (CDCl$_3$): δ 6.78 (s, C$_6$H$_2$, 4H), 3.94 (m, OCH$_2$, 12H), 1.82−0.85 (m, alkyl chain, 114H). Anal. Calcd for C$_{74}$H$_{130}$PtBr$_2$N$_2$O$_6$: C, 59.30; H, 8.74; N, 1.87. Found: C, 59.85; H, 8.44; N, 1.85.

Preparation of *trans*-[MI$_2$\{C≡NC$_6$H$_2$(3,4,5-OC$_n$H$_{2n+1}$)$_3$\}$_2$]. The method followed was the same as above but using KI instead of KBr. Orange solids or viscous fluids were obtained.

Yields, IR, ^{1}H NMR, and Analytical Data for M = Palladium. $n = 4$. Yield: 80%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2206; (KBr) 2211. ^{1}H NMR (CDCl$_3$): δ 6.69 (s, C$_6$H$_2$, 4H), 3.98 (m, OCH$_2$, 12H), 1.83−0.93 (m, alkyl chain, 42H). Anal. Calcd for C$_{38}$H$_{58}$PdI$_2$N$_2$O$_6$: C, 45.68; H, 5.85; N, 2.80. Found: C, 45.79; H, 5.82; N, 2.78.

$n = 6$. Yield: 70%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2206; (KBr) 2207. ^{1}H NMR (CDCl$_3$): δ 6.68 (s, C$_6$H$_2$, 4H), 3.97 (m, OCH$_2$, 12H), 1.84−0.89 (m, alkyl chain, 66H). Anal. Calcd for C$_{50}$H$_{82}$-PdI$_2$N$_2$O$_6$: C, 51.44; H, 7.08; N, 2.40. Found: C, 51.46; H, 6.80; N, 2.48.

$n = 8$. Yield: 60%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2206; (KBr) 2207. ^{1}H NMR (CDCl$_3$): δ 6.69 (s, C$_6$H$_2$, 4H), 3.97 (m, OCH$_2$, 12H), 1.84−0.86 (m, alkyl chain, 90H). Anal. Calcd for

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C$_{62}$H$_{106}$PdI$_2$N$_2$O$_6$: C, 55.75; H, 7.99; N, 2.09. Found: C, 55.84; H, 7.60; N, 2.43.

　　n = 10. Yield: 80%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2206; (KBr) 2201. ^{1}H NMR (CDCl$_3$): δ 6.69 (s, C$_6$H$_2$, 4H), 3.96 (m, OCH$_2$, 12H), 1.86−0.86 (m, alkyl chain, 114H). Anal. Calcd for C$_{74}$H$_{130}$PdI$_2$N$_2$O$_6$: C, 59.09; H, 8.71; N, 2.86. Found: C, 59.28; H, 8.15; N, 2.35.

　　M = Platinum. *n = 4.* Yield: 40%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2202; (KBr) 2207. ^{1}H NMR (CDCl$_3$): δ 6.68 (s, C$_6$H$_2$, 4H), 4.44 (t, OCH$_2$-*meta*, 8H), 3.02 (t, OCH$_2$-*para,* 4H), 1.81−0.90 (m, alkyl chain, 42H). Anal. Calcd for C$_{38}$H$_{58}$PtI$_2$N$_2$O$_6$: C, 41.96; H, 5.37; N, 2.58. Found: C, 42.28; H, 5.46; N, 2.56.

　　n = 60. Yield: 50%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2202; (KBr) 2202. ^{1}H NMR (CDCl$_3$): δ 6.69 (s, C$_6$H$_2$, 4H), 3.94 (m, OCH$_2$, 12H), 1.84−0.87 (m, alkyl chain, 66H). Anal. Calcd for C$_{50}$H$_{82}$PtI$_2$N$_2$O$_6$: C, 47.81; H, 6.58; N, 2.23. Found: C, 48.00; H, 6.39; N, 2.23.

　　n = 8. Yield: 40%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2202; (KBr) 2199. ^{1}H NMR (CDCl$_3$): δ 6.70 (s, C$_6$H$_2$, 4H), 3.95 (m, OCH$_2$, 12H), 1.83−0.85 (m, alkyl chain, 90H). Anal. Calcd for C$_{62}$H$_{106}$PtI$_2$N$_2$O$_6$: C, 52.28; H, 7.50; N, 1.97. Found: C, 52.39; H, 7.24; N, 1.98.

　　n = 10. Yield: 40%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2202; (KBr) 2197. ^{1}H NMR (CDCl$_3$): δ 6.73 (s, C$_6$H$_2$, 4H), 3.94 (m, OCH$_2$, 12H), 1.81−0.85 (m, alkyl chain, 114H). Anal. Calcd for C$_{74}$H$_{130}$PtI$_2$N$_2$O$_6$: C, 55.80; H, 8.23; N, 1.76. Found: C, 56.16; H, 7.85; N, 1.69.

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