Effects of isocyanide substituents on the mesogenic properties of halogeno(isocyanide)gold complexes: calamitic and discotic liquid crystals

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The liquid crystal behaviour of linear $[AuX(CNC_6H_4OC_nH_{2n+1})]$ (X = halogen) complexes is tuned by systematically changing the structure of the isocyanide ligand. The changes studied are lateral fluorination at the 2- and 3-positions of the phenyl ring and modification of the rod-like structure of the complexes by addition of two alkoxy chains at the *meta* positions. None of the free isocyanides used here are liquid crystals, but all the gold complexes prepared display mesomorphic properties, except iodo(2-fluoro-4-butoxyphenyl isocyanide)gold(I). The (2- and (3-fluorophenyl isocyanide)gold(I) complexes show smectic A mesophases, except the 2-fluoro derivative with $n = 6$, which shows a nematic phase, while the (3,4,5-trialkoxyphenyl isocyanide)gold compounds display columnar hexagonal phases at room temperature.

In recent years there has been increasing interest in liquid crystals based on molecules containing transition metals (so-called metallomesogens).[1] Thermotropic liquid crystalline phases of calamitic molecules have been extensively studied, and many systematic studies on the influence of molecular constitution on mesomorphism have been reported on conventional organic liquid crystals. However, this kind of study of metallomesogens is rare.[1]

The continued development of liquid crystal-based technologies requires new types of mesomorphic materials. Therefore it is important to understand the influence of molecular structure on thermal behaviour in order to design and prepare new liquid-crystalline materials.

Most metallomesogens consist of coordinated compounds derived from a metal of d^8–d^{10} electron configuration, usually with planar or linear geometries. However, it is surprising that only a few examples of gold mesogens have been reported, namely a family of gold(III) alkoxydithiobenzoate complexes,[2] and some gold(I) derivatives containing styrylpyridine (stilbazole),[3] isocyanide[4–6] and carbene ligands.[7]

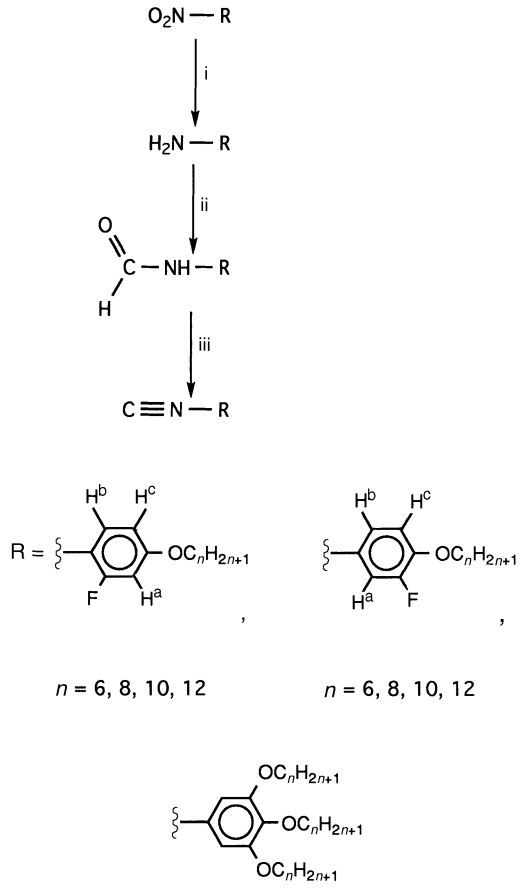
We have reported previously a family of gold complexes[6] $[AuX(CNC_6H_4OC_nH_{2n+1})]$ (X = halogen; $n = 2$, 4, 6, 8, 10, 12) which show smectic A phases in spite of the fact that the isocyanide ligands are not mesogenic, and contain only one aryl ring. These compounds show high thermal stability and have a very simple structure (linear coordination for gold), which makes them particularly suitable for studying the effect of modifications in the molecule on the liquid crystal behaviour of the material. Thus, we prepared similar mesogenic halogeno(biphenyl isocyanide)gold(I) complexes and studied the influence of the biphenyl moiety on transition temperatures.[5]

In a continuation of our previous studies of these coordinatively simple gold(I) isocyanide complexes, aimed at understanding the influence of molecular structure on liquid-crystalline behaviour, we now report the effect of two changes on the *p*-alkoxyphenyl isocyanide system, namely (i) the introduction of a lateral substituent on the phenyl ring by fluorination at the 2- and 3-positions, and (ii) the modification of its rod-like structure by addition of two alkoxy chains in the *meta* positions. The halogeno(3,4,5-trialkoxyphenyl isocyanide)gold(I) complexes prepared show room temperature hexagonal columnar mesophases.

Results and Discussion

Syntheses. The isocyanides used in this work have not been reported before and were prepared starting from the corresponding RNO_2 compounds in three steps, involving reduction to the amine RNH_2 by hydrazine–graphite or $SnCl_2$, formylation to the formamide RNHCHO, and finally dehydration with bis(trichloromethyl)carbonate ('triphosgene') and triethylamine to the isocyanide RNC as presented in Scheme 1.

None of the free ligands show liquid crystal behaviour. At room temperature, the fluorinated isocyanides are isotropic



Scheme 1 *Reagents*: i, N_2H_4–graphite or $SnCl_2$; ii, HCO_2H; iii, $(Cl_3CO)_2CO$, Et_3N

liquids, while the trialkoxyphenyl species are solids with melting points in the range 25 to 42 °C, except for the hexyloxy derivative which melts at 16 °C. They can be stored for long periods in the freezer.

The gold(I) compounds were easily prepared as shown in Scheme 2. The reactions of the isocyanides with [AuCl(tht)] (tht = tetrahydrothiophene) in CH_2Cl_2 afford white complexes [AuCl(CNR)] [R = 2-F-4-$OC_nH_{2n+1}C_6H_3$, 3-F-4-OC_nH_{2n+1}-C_6H_3, n = 6, 8, 10, 12; R = 3,4,5-$(OC_nH_{2n+1})_3C_6H_2$, n = 4, 6, 8, 10], and exchange reactions in acetone with the appropriate potassium salt give the corresponding white bromo and iodo derivatives [AuX(CNR)] [X = Br, I; R = 2-F-4-$OC_{12}H_{25}C_6H_3$; 3-F-4-$OC_{12}H_{25}C_6H_3$; R = 3,4,5-$(OC_{10}H_{21})_3C_6H_2$].

The elemental analyses for the complexes, the yields and relevant IR data are given in the Experimental section. The IR spectra show one $\nu_{(C\equiv N)}$ absorption in CH_2Cl_2 solution, in each case at higher wavenumbers (*ca.* 100 cm^{-1}) than for the free isocyanide. This shift is well documented and is due to two factors; the σ-donation of the antibonding carbon lone pair to Au, and the π-backbonding from the Au^I 5d orbital to the π^* ligand orbitals.[8] In Nujol mulls the IR spectra are similar but the 3-fluorinated gold derivatives show a splitting of the $\nu_{(C\equiv N)}$ isocyanide band, possibly due to solid state effects.

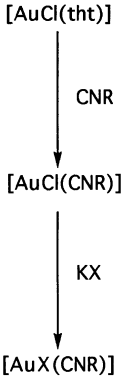
The ^1H NMR spectra of the complexes containing fluorinated isocyanides are all very similar (see Experimental section for details). At 300 MHz the hydrogen atoms of the aromatic ring give three resonances as expected for an AMNX spin system in the range δ 7.0–7.35. In addition, the first methylene group of the alkoxy chain is observed as a virtual triplet at *ca.* δ 4.0. The remaining chain hydrogens appear in the range δ 0.8–1.8. The ^{19}F NMR spectra of these compounds show one signal due to the fluorine atom present in the ring.

On the other hand, the ^1H NMR spectra of the trialkoxyphenyl isocyanide complexes are all very similar and show a singlet corresponding to two equivalent aromatic protons at *ca.* δ 7, plus signals for the aliphatic chains.

Mesogenic behaviour The behaviour of the fluorinated complexes is given in the Experimental section and summarized in Fig. 1 and Fig. 2.

All these gold complexes display a smectic A (S_A) mesophase except the 2-fluoro derivative with n = 6, which shows a nematic (N) mesophase, and the 2-fluoro iodo derivative, which is not mesomorphic. The S_A mesophase presents the typical mielinic and homeotropic textures reorganizing to the fan-shaped texture at temperatures close to the clearing point and the fan texture in the cooling from the isotropic melt. The nematic phase shows the *schlieren* texture.

The variation in properties observed is quite regular and can be summarized as follows. The transition temperatures of chlorogold derivatives decrease in the order 3-F > 2-F, while an increase of the length of the alkoxy chain produces little variation in the melting and clearing points. Moreover, the



Scheme 2

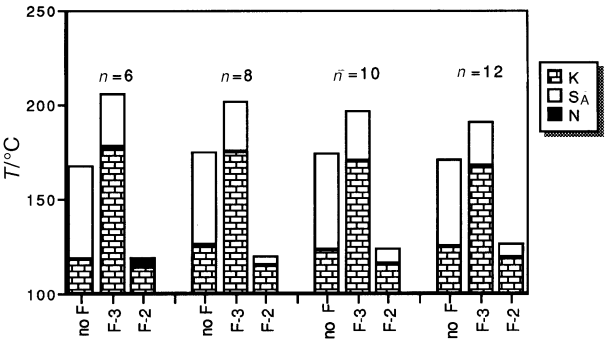


Fig. 1 Thermal behaviour of the complexes [AuCl($CNC_6H_4OC_nH_{2n+1}$-4)] (no F), [AuCl(CNC_6H_3F-2-OC_nH_{2n+1-4})] (F-2) and [AuCl(CNC_6H_3F-3-OC_nH_{2n+1}-4)] (F-3)

substitution of Cl by Br and I in the 3-F derivatives produces a decrease in the transition temperatures in the order Cl > Br > I (Fig. 2), according to the decrease in polarity of the Au–X bond, as reported for similar halogenogold isocyanide complexes.[6] However, the melting point of the monotropic bromo 2-F derivative is slightly lower than that of the non-mesomorphic iodo 2-F complex. The transition temperatures of the corresponding non-fluorinated derivatives are intermediate between the 3-F and 2-F fluorinated complexes.

Although some care has to be exercised when comparing conventional organic molecules with organometallic systems, in general lateral fluorination causes a broadening of the molecule, reducing intermolecular attractions and leading to lower transition temperatures. On the other hand, polarization effects can cause increased intermolecular interactions, leading to higher transition temperatures.[9] It is clear that the position of the fluorine atom (at either the 2- or 3-positions) does not affect significantly the breadth of the molecule. Thus the 2- and 3-fluorinated derivatives will differ mainly in their polarization effects, and it is not surprising that an electronegative substituent (F) *ortho* to the OR group (3-fluorination) produces a larger effect than when it is placed in the *meta* position (2-fluorination). Moreover the fluorine atom in the 3-position would possibly favour the more polar *anti* conformation of the fluorine and the alkoxy chain, as has been found on 2-fluoro-6-methoxy- and 2-fluoro-3-methoxy-pyridine derivatives.[10] Accordingly, the transition temperatures should decrease in the order 3-F > 2-F, in agreement with the trend observed for the melting and the clearing points.

The introduction of two new alkoxy chains in the phenyl moiety produces a dramatic change in the structure of the molecule, which cannot be considered rod-like any longer. All the (trialkoxyphenyl isocyanide)gold compounds [AuX{CNC_6H_2-3,4,5-$(OC_nH_{2n+1})_3$}] (X = Cl, n = 4, 6, 8, 10; X = Br, I, n = 10) display enantiotropic liquid crystal behaviour at room temperature, except the chloro derivative with n = 4, which is monotropic (Fig. 3 and Experimental section). The

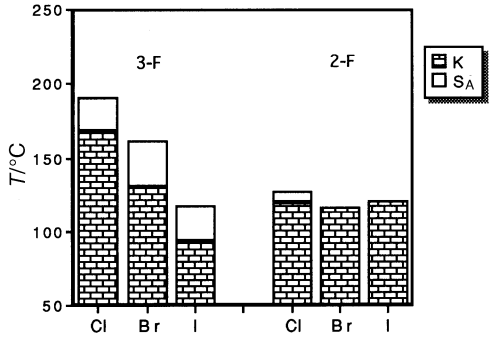


Fig. 2 Thermal behaviour of the complexes [AuX(CNC_6H_3F-2-$OC_{12}H_{25}$-4)] (F-2) and [AuX(CNC_6H_3F-3-$OC_{12}H_{25}$-4)] (F-3)

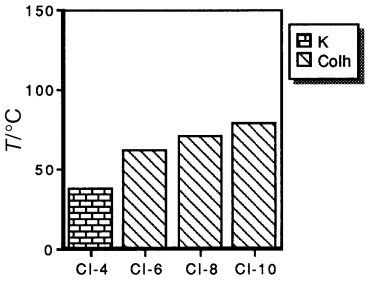


Fig. 3 Thermal behaviour of the complexes [AuCl{$CNC_6H_2(OC_nH_{2n+1})_3$-3,4,5}]

optical textures, when viewed with a polarizing microscope on cooling from the isotropic melt, are characteristic of hexagonal columnar phases[11] and display linear birefringent defects, large areas of uniform extinction and fan domains. X-Ray diffraction for the chlorogold complex with $n=10$ from the mesophase reveals four low-angle rings and a broad halo at wide angle. The *d*-spacing of the four first diffraction rings scales as $1:(1/3)^{1/2}:1/2:(1/7)^{1/2}$, consistent with a hexagonal lattice ($a=$ 2.97 nm). The presence of a single broad halo (0.45 nm) at wide angle indicates that there are only weak liquid-like interactions between the mesogens. Assuming an intracolumnar distance of 0.4 nm, the data are consistent with a disc formed by two molecules of the complex in antiparallel disposition, similar to the stacking in an alternating fashion reported for diketonate Schiff-base complexes of Ni, Cu and Pd.[12]

The chloro compound with $n=4$, as above discussed, shows only a mesophase on cooling from the isotropic melt (exothermic peak at 13.3 °C) and its crystallization is not observed, possibly due to supercooling of the mesophase (Fig. 4). The compound recrystallizes on heating (exothermic peak at 15 °C) and then undergoes a transition corresponding to the melting observed in the first heating cycle. The chloro compound with $n=6$ shows, in addition to the columnar to isotropic transition, a partial crystallization and the subsequent melting to the mesophase in the heating cycles. For the rest of the (trialkoxyphenyl isocyanide)gold(I) complexes, only the transitions between the hexagonal columnar mesophase and the isotropic liquid are observed in the heating and cooling cycles.

Experimental

Combustion analyses were performed with a Perkin Elmer 2400 microanalyser. IR spectra were recorded on a Perkin Elmer FT 1720X instrument. ^{1}H and ^{19}F NMR spectra were recorded at 300 and 282.38 MHz, respectively, on a Bruker AC 300 instrument in $CDCl_3$. Chemical shifts (δ) are reported in ppm relative to internal Me_4Si for ^{1}H and to external $CFCl_3$ for ^{19}F; *J* values are given in Hz. Microscopy studies were carried out using a Leitz microscope fitted with a hot stage and polarizers at a heating rate of *ca.* 10 °C min^{-1}. For differential scanning calorimetry (DSC), a Perkin Elmer DSC7 instrument was used, calibrated with water and indium; the scanning rate was 10 °C min^{-1}, the samples were sealed in aluminium capsules in the air and the holder atmosphere was dry nitrogen.

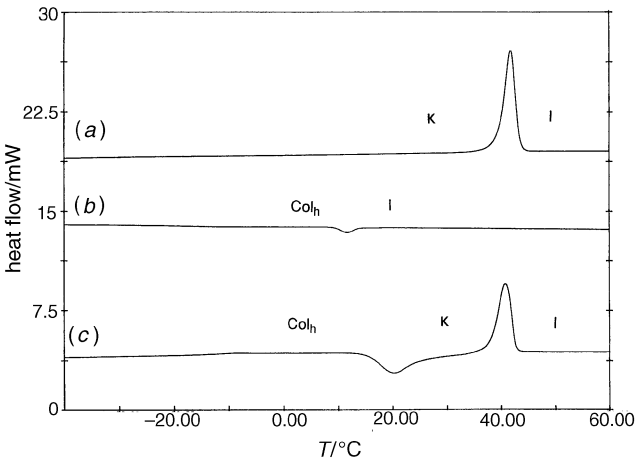


Fig. 4 DSC scans of [AuCl{$CNC_6H_2(OC_nH_{2n+1})_3$-3,4,5}] (*a*) first heating, (*b*) first cooling and (*c*) second heating

X-Ray diffraction experiments were performed with a point focussing beam with Cu-Kα and a flat film. The samples were held in Lindemann glass tubes situated in the gap of a magnet with a field strength of 0.3–1.7 T.

Literature methods were used to prepare [AuCl(tht)][13] (tht = tetrahydrothiophene) and 3,4,5-trialkoxyphenylamine.[14] Only example procedures are described as the syntheses were similar for the rest of the compounds. Yields, IR, analytical and thermal data (transition temperatures in °C and enthalpies in kJ mol^{-1} in parentheses) are given for all the gold complexes.

3-Fluoro-4-octyloxynitrobenzene

Anhydrous K_2CO_3 (0.879 g, 6.36 mmol) was added to a solution of 2-fluoro-4-nitrophenol (0.500 g, 3.18 mmol) and octyl bromide (0.738 g, 3.82 mmol) in 50 ml of dry acetone. The resulting suspension was refluxed under N_2 for 10 h and then allowed to cool to room temperature. The reaction mixture was poured into 200 ml of H_2O and the solution was acidified with dilute HCO_2H. To this was added CH_2Cl_2 and the organic layer was separated, dried over $MgSO_4$, filtered and the solvent evaporated on a rotary evaporator. The residue was chromatographed (silica gel, CH_2Cl_2 as eluent) and the CH_2Cl_2 was evaporated to obtain the product as an oil (0.742 g, 87%); ^{1}H NMR ($CDCl_3$) δ 7.98, 8.04 and 7.01 (H^a, H^b and H^c, AMNX spin system, $^4J_{ab}$ 2.7, $^3J_{bc}$ 8.5, Ar-H), 4.12 (t, *J* 6.5, CH_2O), 1.86–0.88 (m, 15 H, alkyl chain); ^{19}F NMR ($CDCl_3$) δ −131.0 (m, $^3J_{aF}$ 10.7, $^5J_{bF}$ 1.5, $^4J_{cF}$ 8.5).

2-Fluoro-4-octyloxynitrobenzene

^{1}H NMR ($CDCl_3$) δ 6.71, 8.08 and 6.74 (H^a, H^b and H^c, AMNX spin system, $^4J_{ac}$ 2.7, $^3J_{bc}$ 9.7, Ar-H), 4.02 (t, *J* 6.5, CH_2O), 1.86–0.88 (m, 15 H, alkyl chain); ^{19}F NMR ($CDCl_3$) δ −113.2 (m, $^3J_{aF}$ 13.1, $^4J_{bF}$ 9.0, $^5J_{cF}$ 1.3).

3-Fluoro-4-octyloxyaniline

$SnCl_2\cdot 2H_2O$ (3.1 g, 13.74 mmol) was added to a solution of 3-fluoro-4-octyloxynitrobenzene (0.740 g, 2.75 mmol) in 20 ml of EtOH. The flask was purged with N_2 and the suspension was refluxed for 30 min. The reaction mixture was allowed to cool to room temperature and poured into water. Solid K_2CO_3 was added until basic pH was achieved. The mixture was extracted with CH_2Cl_2 and the organic layer was separated, dried over $MgSO_4$ and filtered. The solvent was removed on a rotary evaporator to obtain the product as white crystals (0.461 g, 70%); ^{1}H NMR ($CDCl_3$) δ 6.46, 6.36 and 6.79 (H^a, H^b and H^c, AMNX spin system, $^4J_{ab}$ 2.7, $^3J_{bc}$ 8.9, Ar-H), 3.93 (t, *J* 6.5, CH_2O), 1.86–0.88 (m, 15 H, alkyl chain); ^{19}F NMR ($CDCl_3$) δ −133.2 (m, $^3J_{aF}$ 12.5, $^5J_{bF}$ 1.4, $^4J_{cF}$ 8.9).

2-Fluoro-4-octyloxyaniline

^{1}H NMR ($CDCl_3$) δ 6.61, 6.70 and 6.53 (H^a, H^b and H^c, AMNX spin system, $^4J_{ac}$ 2.7, $^3J_{bc}$ 8.6, Ar-H), 3.85 (t, *J* 6.5, CH_2O), 1.86–0.88 (m, 15 H, alkyl chain); ^{19}F NMR ($CDCl_3$) δ −132.4 (m, $^3J_{aF}$ 12.6, $^4J_{bF}$ 10.1, $^5J_{cF}$ 1.1).

N-(3-Fluoro-4-octyloxyphenyl)formamide

A flask fitted with a Dean–Stark apparatus was charged with a solution of 3-fluoro-4-octyloxyaniline (0.590 g, 2.47 mmol)

in 100 ml of toluene. Formic acid (10 ml, 98%) was added and the resulting solution was refluxed for 1 h and then cooled to room temperature. The solvent was removed on a rotary evaporator and the residue recrystallized in pentane to give white crystals of a mixture of *Z* and *E* isomers of the product (0.614 g, 93%); *Z*-isomer: ^{1}H NMR ($CDCl_3$) δ 7.43, 7.14 and 6.8–7.0 (overlapped with H^a and H^c of the *E*-isomer) (H^a, H^b and H^c, AMNX spin system, $^4J_{ab}$ 2.5, $^3J_{bc}$ 8.8, Ar-H), 8.32 (CH, *J* 1.6), 7.20 (NH, br), 4.03–3.99 (CH_2O, overlapped with the CH_2O of the *E*-isomer), 1.86–0.88 (m, alkyl chains of the two isomers); ^{19}F NMR ($CDCl_3$) δ −132.4 (m, $^3J_{aF}$ 12.5, $^5J_{bF}$ 1.3, $^4J_{cF}$ 9.1).

E-isomer: ^{1}H NMR ($CDCl_3$) δ 6.8–7.0 (H^a and H^c) (overlapped with H^c of the *Z*-isomer) and 6.79 (H^b) (AMNX spin system, $^4J_{ab}$ 2.6, $^3J_{bc}$ 8.8, Ar-H), 8.51 (CH, *J* 11.4), 7.70 (NH, br), 4.03–3.99 (CH_2O, overlapped with the CH_2O of the *Z*-isomer), 1.86–0.88 (m, alkyl chains of the two isomers); ^{19}F NMR ($CDCl_3$) δ −131.5 (m, $^3J_{aF}$ 11.5, $^5J_{bF}$ 1.4, $^4J_{cF}$ 8.8, J_{CH-F} 1.4).

N-(2-fluoro-4-octyloxyphenyl)formamide

Z-isomer: ^{1}H NMR ($CDCl_3$) δ 8.10 (H^b) and 6.73–6.64 (H^a and H^c) (overlapped with H^a and H^c of the *E*-isomer) (AMNX spin system, $^3J_{bc}$ 8.9, Ar-H), 8.40 (CH, *J* 1.6), 7.30 (NH, br), 3.94–3.89 (CH_2O, overlapped with the CH_2O of the *E*-isomer), 1.86–0.88 (m, alkyl chains of the two isomers); ^{19}F NMR ($CDCl_3$) δ −128.4 (m, $^4J_{bF}$ 8.9).

E-isomer: ^{1}H NMR ($CDCl_3$) δ 6.73–6.64 (H^a and H^c) (overlapped with H^a and H^c of the *Z*-isomer) and 7.11 (H^b) (AMNX spin system, $^3J_{bc}$ 8.8, Ar-H), 8.46 (CH, *J* 11.5), 7.35 (NH, br), 3.94–3.89 (CH_2O, overlapped with the CH_2O of the *Z*-isomer), 1.86–0.88 (m, alkyl chains of the two isomers); ^{19}F NMR ($CDCl_3$) δ −125.1 (m, $^4J_{bF}$ 8.8, J_{CH-F} 1.4).

3-Fluoro-4-octyloxyphenyl isocyanide

The procedure described by Ugi[15] was followed, using triphosgene as dehydrating agent. To a solution of 3-fluoro-4-octyloxyformanilide (0.156 g, 0.58 mmol) and triethylamine (0.2 ml, 1.17 mmol) in 50 ml of CH_2Cl_2 was added dropwise a solution of triphosgene (0.053 g, 0.19 mmol) in 25 ml of CH_2Cl_2. The mixture was stirred for 1 h and then the solvent was removed on a rotary evaporator. The resulting residue was chromatographed (silica gel, CH_2Cl_2–hexane, 3:1 as eluent) and the solvent was evaporated to obtain the product as a colourless oil (0.112 g, 77%); ^{1}H NMR ($CDCl_3$) δ 7.14–7.10 (H^a and H^b) and 6.91 (H^c) (AMNX spin system, $^3J_{bc}$ 8.5, Ar-H), 4.03 (t, *J* 6.5, CH_2O), 1.86–0.88 (m, 15 H, alkyl chain); ^{19}F NMR ($CDCl_3$) δ −131.4 (m, $^3J_{aF}$ 11.2, $^5J_{bF}$ 2.4, $^4J_{cF}$ 8.5).

2-Fluoro-4-octyloxyphenyl isocyanide

^{1}H NMR ($CDCl_3$) δ 6.69, 7.30 and 6.66 (H^a, H^b and H^c, AMNX spin system, $^4J_{ac}$ 2.6, $^3J_{bc}$ 8.8), 3.95 (t, *J* 6.5, CH_2O), 1.86–0.88 (m, 15 H, alkyl chain); ^{19}F NMR ($CDCl_3$) δ −116.2 (m, $^3J_{aF}$ 11.4, $^4J_{bF}$ 8.1, $^5J_{cF}$ 1.2).

3,4,5-Trioctyloxyphenyl isocyanide

^{1}H NMR ($CDCl_3$) δ 6.5 (s, 2 H, C_6H_2), 3.9 (m, 6 H, CH_2O), 1.9–0.8 (m, 45 H, alkyl chains).

Chloro(3-fluoro-4-octyloxyphenyl isocyanide)gold(I)

To a solution of [AuCl(tht)] (0.131 g, 0.41 mmol) in 30 ml of CH_2Cl_2 was added 3-fluoro-4-octyloxyphenyl isocyanide (0.112 g, 0.45 mmol). After stirring for 10 min the solvent was removed on a rotary evaporator and the residue was washed with diethyl ether. Recrystallization from CH_2Cl_2–EtOH afforded the product as white crystals (0.145 g, 74%); ^{1}H NMR ($CDCl_3$) δ 7.34–7.26 (H^a and H^b) and 7.00 (H^c) (AMNX spin system, $^3J_{bc}$ 8.3, Ar-H), 4.07 (t, *J* 6.5, CH_2O), 1.86–0.88 (m, 15 H, alkyl chain); ^{19}F NMR ($CDCl_3$) δ −129.2 (m, $^4J_{cF}$ 8.3); $\nu_{(C\equiv N)}$/cm^{-1} (CH_2Cl_2) 2217; (Nujol) 2233, 2218 (Calc. for $C_{15}H_{20}NAuClFO$: C, 37.40; H, 4.18; N, 2.91. Found: C, 37.65; H, 3.97; N, 3.08%); DSC/°C K–K′ 146.9 (2.1), K′–S_A 174.7 (17.3), S_A–I 201.5 (8.9).

Chloro(3-fluoro-4-hexyloxyphenyl isocyanide)gold(I)

Yield 66%; $\nu_{(C\equiv N)}$/cm^{-1} (CH_2Cl_2) 2218; (Nujol) 2238, 2220 (Calc. for $C_{13}H_{16}NAuClFO$: C, 34.42; H, 3.55; N, 3.09. Found: C, 34.54; H, 3.38; N, 3.57%). DSC: K–K′ 156.0 (2.6), K′–S_A 177.7 (16.1), S_A–I, 205.5 (8.9).

Chloro(3-fluoro-4-decyloxyphenyl isocyanide)gold(I)

Yield 69%; $\nu_{(C\equiv N)}$/cm^{-1} (CH_2Cl_2) 2217; (Nujol) 2235, 2218 (Calc. for $C_{17}H_{24}NAuClFO$: C, 40.05; H, 4.75; N, 2.75. Found: C, 40.27; H, 4.54; N, 2.65%); DSC/°C K–K′ 152.5 (2.2), K′–S_A 169.9 (17.5), S_A–I 196.5 (9.0).

Chloro(3-fluoro-4-dodecyloxyphenyl isocyanide)gold(I)

Yield 58%; $\nu_{(C\equiv N)}$/cm^{-1} (CH_2Cl_2) 2218; (Nujol) 2240, 2221 (Calc. for $C_{19}H_{28}NAuClFO$: C, 42.43; H, 5.25; N, 2.60. Found: C, 42.70; H, 5.07; N, 2.72%); DSC/°C K–K′ 148.0 (2.2), K′–S_A 167.7 (18.3), S_A–I 190.6 (8.7).

Chloro(2-fluoro-4-octyloxyphenyl isocyanide)gold(I)

Yield 64%; ^{1}H NMR ($CDCl_3$) δ 6.76, 7.46 and 6.75 (H^a, H^b and H^c, AMNX spin system, $^4J_{ac}$ 2.6, $^3J_{bc}$ 8.5, Ar-H), 3.99 (t, *J* 6.5, CH_2O), 1.86–0.88 (m, 15 H, alkyl chain); ^{19}F NMR ($CDCl_3$) δ −113.9 (m, $^3J_{aF}$ 8.0, $^4J_{bF}$ 8.5, $^5J_{cF}$ 1.7); $\nu_{(C\equiv N)}$/cm^{-1} (CH_2Cl_2) 2223; (Nujol) 2237 (Calc. for $C_{15}H_{20}NAuClFO$: C, 37.40; H, 4.18; N, 2.91. Found: C, 37.58; H, 4.04; N, 2.91%); DSC/°C K–S_A 114.7 (32.4), S_A–I 117.8 (4.8).

Chloro(2-fluoro-4-hexyloxyphenyl isocyanide)gold(I)

Yield 58%; $\nu_{(C\equiv N)}$/cm^{-1} (CH_2Cl_2) 2222; (Nujol) 2232 (Calc. for $C_{13}H_{16}NAuClFO$: C, 34.42; H, 3.55; N, 3.09. Found: C, 34.53; H, 3.38; N, 2.99%); DSC/°C K–K′ 62.4 (4.6), K′–N, N–I 114.1 (24.0).

Chloro(2-fluoro-4-decyloxyphenyl isocyanide)gold(I)

Yield 52%; $\nu_{(C\equiv N)}$/cm^{-1} (CH_2Cl_2) 2223; (Nujol) 2238 (Calc. for $C_{17}H_{24}NAuClFO$: C, 40.05; H, 4.75; N, 2.75. Found: C, 40.18; H, 4.47; N, 2.99%); DSC/°C K–K′, K′–S_A 115.7 (32.9), S_A–I 124.2 (6.0).

Chloro(2-fluoro-4-dodecyloxyphenyl isocyanide)gold(I)

Yield 68%; $\nu_{(C\equiv N)}$/cm^{-1} (CH_2Cl_2) 2223; (Nujol) 2237 (Calc. for $C_{19}H_{28}NAuClFO$: C, 42.43; H, 5.25; N, 2.60. Found: C, 42.52; H, 5.00; N, 2.65%); DSC/°C K–K′ 95.6 (0.9), K′–S_A 119.3 (38.9), S_A–I 126.7 (6.6).

Chloro(3,4,5-trioctyloxyphenyl isocyanide)gold(I)

Yield 83%; ^{1}H NMR ($CDCl_3$) δ 6.7 (s, 2 H, C_6H_2), 3.9 (m, 6 H, CH_2O), 1.9–0.8 (m, 45 H, alkyl chains); $\nu_{(C\equiv N)}$/cm^{-1} (CH_2Cl_2) 2223; (Nujol) 2225 (Calc. for $C_{31}H_{53}NAuClO_3$: C, 51.70; H, 7.42; N, 1.95. Found: C, 51.01; H, 7.05; N, 1.96%); DSC/°C Col_h–I 71.1 (3.2).

Chloro(3,4,5-tributoxyphenyl isocyanide)gold(I)

Yield 83%; $\nu_{(C\equiv N)}$/cm^{-1} (CH_2Cl_2) 2223; (Nujol) 2228 (Calc. for $C_{19}H_{29}NAuClO_3$: C, 41.35; H, 5.30; N, 2.54. Found: C, 41.42; H, 5.10; N, 2.57%); DSC/°C K–I 38.0 (8.8), I–Col_h 13.3 (−0.6).

Chloro(3,4,5-trihexyloxyphenyl isocyanide)gold(I)

Yield 79%; $\nu_{(C\equiv N)}/cm^{-1}$ (CH_2Cl_2) 2223; (Nujol) 2226 (Calc. for $C_{25}H_{41}NAuClO_3$: C, 47.21; H, 6.50; N, 2.20. Found: C, 46.84; H, 6.18; N, 2.54%); DSC/°C CoI_h–K 5.9 (−0.9), K–CoI_h 22.0 (0.9), Col_h–I 62.2 (2.3).

Chloro(3,4,5-tridecyloxyphenyl isocyanide)gold(I)

Yield 65%; $\nu_{(C\equiv N)}/cm^{-1}$ (CH_2Cl_2) 2223; (Nujol) 2226 (Calc. for $C_{37}H_{65}NAuClO_3$: C, 55.25; H, 8.15; N, 1.74. Found: C, 55.27; H, 7.85; N, 1.79%); DSC/°C Col_h–I 80.0 (3.0).

Iodo(3-fluoro-4-dodecyloxyphenyl isocyanide)gold(I)

Potassium iodide (0.077 g, 0.46 mmol) was added to chloro(3-fluoro-4-dodecyloxyphenyl isocyanide)gold(I) (0.050 g, 0.09 mmol) dissolved in acetone (30 ml). A white precipitate immediately appeared, and the resulting suspension was stirred for 10 min. The solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2 (2×15 ml). The volume was reduced to 10 ml and EtOH (10 ml) was added to obtain white crystals of the product (0.037 g, 63%); ^{1}H NMR ($CDCl_3$) δ 7.35–7.26 (H^a and H^b) and 7.00 (H^c) (AMNX spin system, $^3J_{bc}$ 8.3), 4.07 (t, J 6.5, CH_2O), 1.86–0.88 (m, 23 H, alkyl chain); ^{19}F NMR ($CDCl_3$) δ −129.2 (m, $^4J_{cF}$ 8.3); $\nu_{(C\equiv N)}/cm^{-1}$ (CH_2Cl_2) 2212; (Nujol) 2233, 2211 (Calc. for $C_{19}H_{28}NAuFIO$: C, 36.26; H, 4.49; N, 2.23. Found: C, 36.46; H, 4.25; N, 2.21%); DSC/°C K–K′ 56.0 (2.9), K′–S_A 93.0 (26.2), S_A–I 117.5 (4.5).

Iodo(2-fluoro-4-dodecyloxyphenyl isocyanide)gold(I)

Yield 87%; ^{1}H NMR ($CDCl_3$) δ 6.78–6.73 (H^a and H^c) and 7.45 (H^b) (AMNX spin system, $^3J_{bc}$ 8.5), 3.99 (t, J 6.5, CH_2O), 1.86–0.88 (m, 23 H, alkyl chain); ^{19}F NMR ($CDCl_3$) δ −113.8 (m, $^4J_{bF}$ 8.5); $\nu_{(C\equiv N)}/cm^{-1}$ (CH_2Cl_2) 2214; (Nujol) 2223 (Calc. for $C_{19}H_{28}NAuFIO$: C, 36.26; H, 4.49; N, 2.23. Found: C, 36.21; H, 4.24; N, 2.49%); DSC/°C K–I 120.6 (54.3).

Iodo(3,4,5-tridecyloxyphenyl isocyanide)gold(I)

Yield 90%; ^{1}H NMR ($CDCl_3$) δ 6.7 (s, 2 H, C_6H_2), 3.9 (m, 6 H, CH_2O), 1.9–0.8 (m, 57 H, alkyl chains); $\nu_{(C\equiv N)}/cm^{-1}$ (CH_2Cl_2) 2215; (Nujol) 2209 (Calc. for $C_{37}H_{65}NAuIO_3$: C, 49.61; H, 7.31; N, 1.56. Found: C, 49.55; H, 7.22; N, 1.44%); DSC/°C Col_h–I 45.1 (4.6).

Bromo(3-fluoro-4-dodecyloxyphenyl isocyanide)gold(I)

The method followed was the same as above, using KBr instead of KI and stirring overnight. Yield 71%; ^{1}H NMR ($CDCl_3$) δ 7.33–7.27 (H^a and H^b) and 7.00 (H^c) (AMNX spin system, $^3J_{bc}$ 8.6), 4.08 (t, J 6.5, CH_2O), 1.86–0.88 (m, 23 H, alkyl chain); ^{19}F NMR ($CDCl_3$) δ −129.2 (m, $^4J_{cF}$ 8.6); $\nu_{(C\equiv N)}/cm^{-1}$ (CH_2Cl_2) 2215; (Nujol) 2236, 2217 (Calc. for $C_{19}H_{28}NAuBrFO$: C, 39.19; H, 4.85; N, 2.41. Found: C, 39.17; H, 4.71; N, 2.33%); DSC/°C K–K′ 110.2 (2.4), K′–K″, K″–S_A 129.8 (22.7), S_A–I 161.5 (7.1).

Bromo(2-fluoro-4-dodecyloxyphenyl isocyanide)gold(I)

Yield 76%; ^{1}H NMR ($CDCl_3$) δ 6.78–6.73 (H^a and H^c) and 7.45 (H^b) (AMNX spin system, $^3J_{bc}$ 8.5), 3.99 (t, J 6.5, CH_2O), 1.86–0.88 (m, 23 H, alkyl chain); ^{19}F NMR ($CDCl_3$) δ −113.9 (m, $^4J_{bF}$ 8.5); $\nu_{(C\equiv N)}/cm^{-1}$ (CH_2Cl_2) 2219; (Nujol) 2231 (Calc. for $C_{19}H_{28}NAuBrFO$: C, 39.19; H, 4.85; N, 2.41. Found: C, 39.27; H, 4.73; N, 2.36%); DSC/°C K–K′ 109.4 (11.5), K′–I 116.4 (35.4), I–S_A 106.0 (−5.4), S_A–K′ 103.1 (−43.9).

Bromo(3,4,5-tridecyloxyphenyl isocyanide)gold(I)

Yield 88%; ^{1}H NMR ($CDCl_3$) δ 6.7 (s, 2 H, C_6H_2), 3.9 (m, 6 H, CH_2O), 1.9–0.8 (m, 57 H, alkyl chains); $\nu_{(C\equiv N)}/cm^{-1}$ (CH_2Cl_2) 2220; (Nujol) 2220 (Calc. for $C_{37}H_{65}NAuBrO_3$: C, 52.36; H, 7.72; N, 1.65. Found: C, 53.04; H, 7.62; N, 1.61%); DSC/°C Col_h–I 56.6 (2.1).

We gratefully acknowledge the Comisión Interministerial de Ciencia y Tecnología for financial support (Project MAT93-0329 and MAT96-0708).

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Paper 6/04258I; *Received* 18*th June*, 1996