

Mesomorphic trigonal bipyramidal iron(0) isocyanide complexes

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Received 24th December 1999, Accepted 3rd April 2000

Published on the Web 11th May 2000

The synthesis, characterization and mesomorphic properties of three series of isocyanides and their trigonal bipyramidal iron(0) complexes $[\text{Fe}(\text{CO})_4(\text{CNR})]$ ($\text{R} = \text{C}_6\text{H}_4\text{O}(\text{O})\text{CC}_6\text{H}_4\text{C}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$, $\text{C}_6\text{H}_4\text{C}(\text{O})\text{OC}_6\text{H}_4\text{C}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$, $\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{O}(\text{O})\text{CC}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$, $n = 6, 8, 10, 12$) are described. The free isocyanides exhibit nematic and/or smectic A phases for shorter chains ($n = 6, 8$) and only smectic A phases for longer chains, except the isocyanides $\text{CNC}_6\text{H}_4\text{O}(\text{O})\text{CC}_6\text{H}_4\text{C}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$ which melt with extensive decomposition and do not produce mesophases. Their coordination to give the iron complexes $[\text{Fe}(\text{CO})_4(\text{CNR})]$ produces a slight decrease of their transition temperatures. The iron isocyanide complexes prepared show only a smectic C phase. The relationship between the molecular structure of the complexes and their thermal behaviour is discussed.

Introduction

In the last years metal-containing liquid crystals with transition or post-transition metals (so called “metallomesogens”) have seen systematic research and development. The presence of the metal atom can introduce special electronic and magnetic properties in these materials. Moreover metallomesogens also provide a variety of coordination geometries allowing to test liquid crystal behaviour on complexes with new structural shapes not easily attainable in purely organic materials.^{1–9}

Most metallomesogens are based on d^8 – d^{10} coordination compounds with planar or linear geometries. However, in recent years the structural diversity of materials displaying liquid crystal properties has grown to include other structural types such as tetrahedral nickel(II)^{10–12} and Cu(I) complexes,¹³ some octahedral derivatives of several transition metals,^{14–19} distorted square-pyramidal complexes of iron^{20–22} and vanadyl,²³ a few Co, Cu and Zn trigonal bipyramidal complexes²⁴ and zirconium square-antiprismatic compounds.²⁵ Moreover the number of mesomorphic iron(0) derivatives known are restricted to butadiene iron(0)tricarbonyl complexes.^{26–28}

On the other hand, different types of ligands particularly N-donor ligands have been used to produce metallomesogens, but isocyanides, which give very stable complexes with many transition metals, have been exploited only recently, and liquid crystals based on isocyanide metal complexes are restricted to some isocyanide complexes of Au(I),^{9,29–36} Pd(II), and Pt(II).^{37–41}

The structural shapes of liquid crystals based on isocyanide metal complexes are extended in this paper, where the preparation of iron(0)isocyanide mesogens $[\text{Fe}(\text{CO})_4(\text{CNR})]$ ($\text{R} = \text{C}_6\text{H}_4\text{O}(\text{O})\text{CC}_6\text{H}_4\text{C}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$, $\text{C}_6\text{H}_4\text{C}(\text{O})\text{OC}_6\text{H}_4\text{C}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$, $\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{O}(\text{O})\text{CC}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$) containing a trigonal bipyramidal structure is reported.

Results and discussion

Synthesis and structural characterization

The nitro compounds, starting materials for the preparation of L^{A} , L^{B} and L^{C} , were obtained from the condensation of the corresponding acyl chloride with 4'-nitro-4-hydroxybiphenyl, 4-nitrophenol and 4'-alkoxy-4-hydroxybiphenyl respectively, as presented in Scheme 1.

The isocyanides used in this work have not been reported

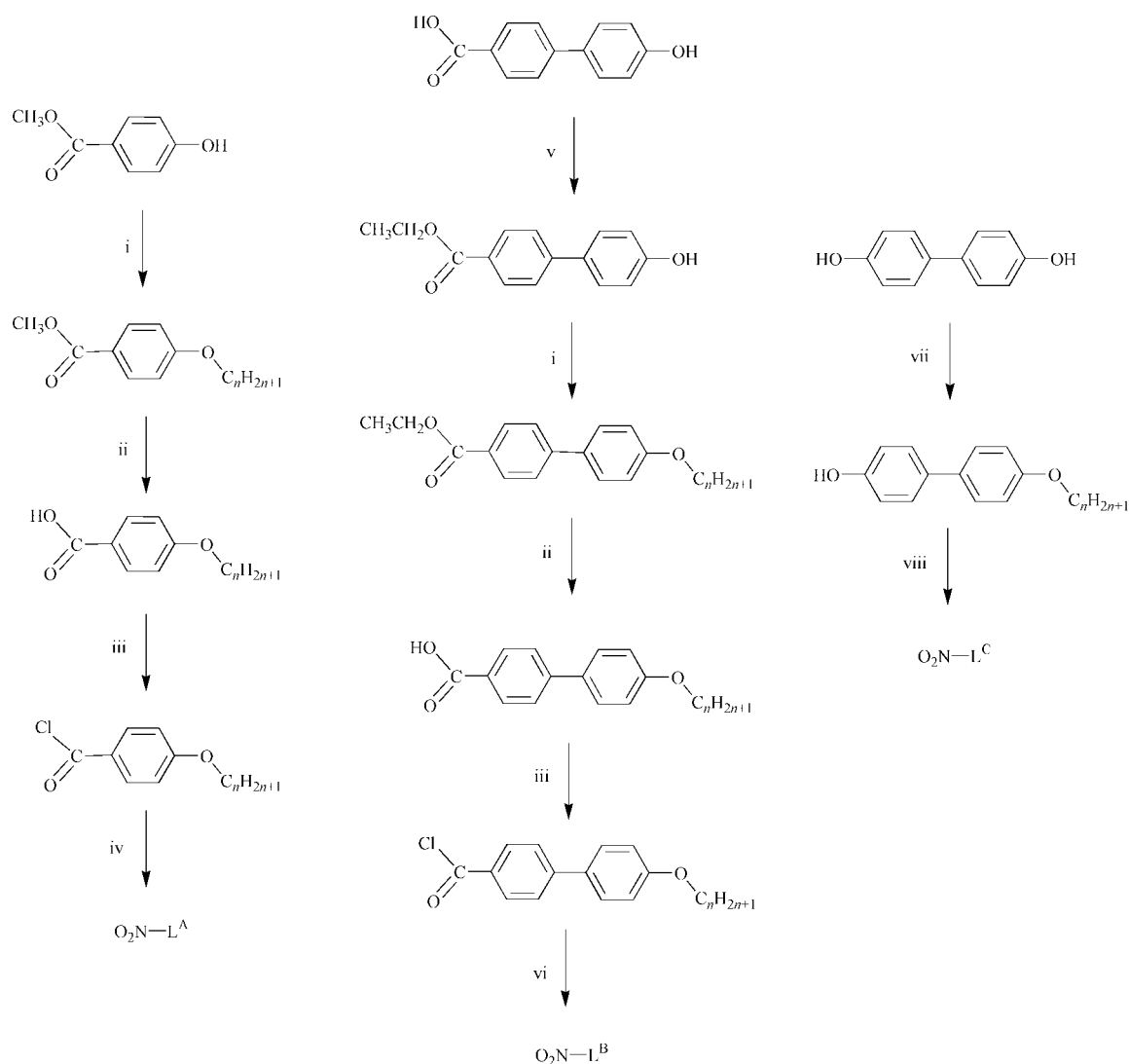
before, except $\text{CNC}_6\text{H}_4\text{C}(\text{O})\text{OC}_6\text{H}_4\text{C}_6\text{H}_4\text{OC}_8\text{H}_{17}$.⁴² They were prepared as white solids, starting from the corresponding nitro compounds, in three steps involving reduction to the amine by $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, formylation to the formamide, and finally dehydration to the isocyanide with bis(trichloromethyl) carbonate (“triphosgene”) and triethylamine, as presented in Scheme 2.

The new isocyanides exhibit a characteristic strong IR absorption in the range 2127 – 2130 cm^{-1} , in dichloromethane solution.

The iron(0) compounds, isolated as air stable pale yellow solids, were prepared by substitution of one CO in $[\text{Fe}(\text{CO})_5]$ for the corresponding isocyanide, in toluene at 60°C in the presence of a catalytic amount of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$, as reported for other isocyanide iron(0) complexes.⁴³

The C, H, N analyses for the complexes, yields, and relevant IR data are given in the experimental section. The IR spectra in CH_2Cl_2 solution show one $\nu(\text{CN})$ and three $\nu(\text{CO})$ absorptions for the isocyanide and for the carbonyl groups respectively, as expected for a trigonal bipyramidal structure with the isocyanide ligand coordinated in an axial position (C_{3v} point-group symmetry for which one CN stretching mode, A_1 , and three CO stretching modes, $2A_1 + E$, are predicted).⁴⁴ The $\nu(\text{CN})$ band appears at higher wavenumbers (*ca.* 35 cm^{-1}) than for the free isocyanides. The coordination of the isocyanide ligand to the iron involves σ donation of the antibonding carbon lone pair to Fe, and the back-donation of electrons from metal atom $d\pi$ orbitals to the π^* orbitals of the ligand. The σ donation should increase the CN bond order, while the π back-bonding should lower the CN bond order. In general the σ donation is more important, and as a consequence $\nu(\text{CN})$ increases upon coordination,^{43,44} as observed here. On the other hand, there are no significant differences in $\nu(\text{CN})$ for the free isocyanides prepared, but in their iron(0) isocyanide complexes $\nu(\text{CN})$ vary in the order $\text{Fe}-\text{L}^{\text{A}} \approx \text{Fe}-\text{L}^{\text{B}} > \text{Fe}-\text{L}^{\text{C}}$, suggesting that upon coordination the σ -donor component is quite similar for all the three isocyanides while the L^{C} isocyanides are noticeably better π -acceptors.

The ^1H NMR spectra of the metal complexes and the free isocyanides are all very similar, showing, as expected, four somewhat distorted “pseudodoublets” (a deceptively simple pattern for the strictly speaking AA'XX' spin systems) for the biphenyl group, plus two for the third aryl ring, at 300 MHz. Table 1 lists the assignments made for selected free isocyanides and iron isocyanide complexes.



Scheme 1 Reagents and conditions: i, $\text{BrC}_n\text{H}_{2n+1}$, K_2CO_3 , in acetone, reflux; ii, NaOH , in methanol/water, reflux; iii, thionyl chloride, reflux; iv, $\text{O}_2\text{NC}_6\text{H}_4\text{C}_6\text{H}_4\text{OH}$, in triethylamine, room temperature; v, ethanol, H_2SO_4 , reflux; vi, $\text{O}_2\text{NC}_6\text{H}_4\text{OH}$, in triethylamine, room temperature; vii, $\text{BrC}_n\text{H}_{2n+1}$, KOH , in ethanol, reflux; viii, $\text{O}_2\text{NC}_6\text{H}_4\text{C}(\text{O})\text{Cl}$, in triethylamine, room temperature.

Mesogenic behaviour

The mesogenic behaviour of the free isocyanides prepared is summarized in Table 2.

They melt in the range $90\text{--}110^\circ\text{C}$ displaying nematic and/or smectic A phases, except the series of ligands $\text{CNC}_6\text{H}_4\text{C}(\text{O})\text{OC}_6\text{H}_4\text{C}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$ (L^{C}), which undergo extensive decomposition in the solid state upon reaching 105°C . The isocyanides L^{A} and L^{B} become pale green after heating to the clearing temperatures. For this reason, calorimetric data are referred to the first DSC cycle. The green color observed on heating the isocyanide ligand is usually associated with the formation of polyisocyanide.⁴⁵ However we cannot assess the extent of polymerization, since the IR spectra in dichloromethane solution of heated isocyanides L^{A} and L^{B} still show a $\nu(\text{CN})$ band corresponding to the isocyanide group, and the ^1H NMR spectra show the sharp signal corresponding to the isocyanide ligand. Moreover, broad NMR signals expected for a polyisocyanide are not observed.

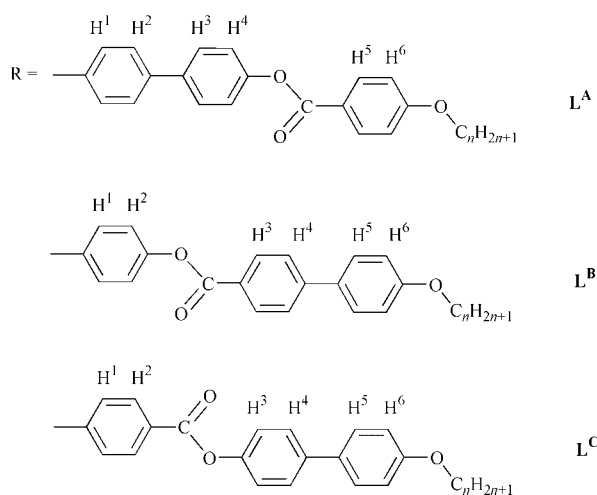
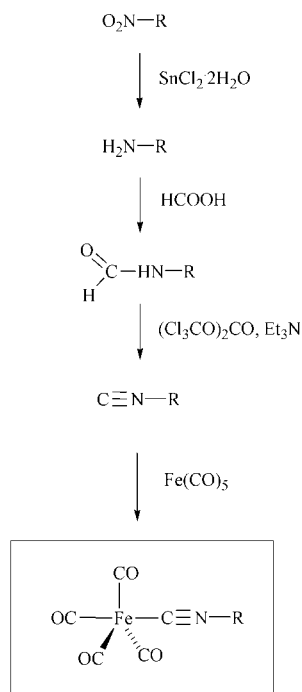
The smectic A (S_A) mesophase has been identified in optical microscopy by the typical melinlic and homeotropic textures (Fig. 1a) on heating, and the focal-conic fan texture on cooling from the nematic phase or the isotropic liquid (Fig. 1b). The nematic phases show a marbled texture (Fig. 1c) on heating, and on cooling they separate from the isotropic liquid in typical droplets with curved surfaces. The range of the S_A phase

increases, and that of the N phase decreases, as the length of the chain increases.

All the iron isocyanide complexes prepared, $[\text{Fe}(\text{CO})_4(\text{CNR})]$ [$\text{R} = \text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{O}(\text{O})\text{CC}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$ (Fe-L^{A}), $\text{C}_6\text{H}_4\text{O}(\text{O})\text{CC}_6\text{H}_4\text{C}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$ (Fe-L^{B}) and $\text{C}_6\text{H}_4\text{C}(\text{O})\text{OC}_6\text{H}_4\text{C}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$ (Fe-L^{C})], are mesomorphic and their optical, thermal and thermodynamic data are collected in Table 3. They show only a smectic C (S_C) mesophase, which has been optically identified by the typical schlieren texture (Fig. 2),^{46,47} and by the fact that under mechanical stress it is not possible to obtain either homeotropic regions or brownian flashes. However, schlieren textures are observed by mechanical displacement.

All the iron complexes described undergo extensive decomposition close to 120°C . For this reason, the significance and even the assignment of this as their clearing temperatures is probably low. Most likely their decomposition involves dissociation of the isocyanide ligand, but not as a clean reaction since TLC (thin-layer chromatography) reveals the formation of a complex mixture of products including free isocyanide.

The coordination of an isocyanide to a metal to give a metal isocyanide complex produces generally an increase of the molecular polarizability, and as a consequence an increase of transition temperatures, compared to the free isocyanide.^{31–38} However, the iron(0) isocyanide complexes described here show



Scheme 2

melting points slightly lower than the corresponding free isocyanides. Obviously the steric hindrance produced by the equatorial carbonyls in the [Fe(CO)₄(CNR)] complexes does

Table 1 ¹H NMR data (CDCl₃) for the free isocyanides L^A, L^B, L^C and their corresponding iron complexes (Fe-L) for *n*=10 (shifts in ppm downfield relative to internal TMS; coupling constants in Hz)

	Aromatic rings						<i>N</i> _{1,2} ^a	<i>N</i> _{3,4} ^b	<i>N</i> _{5,6} ^c	-O-CH ₂ -	-(CH ₂) _{<i>n</i>-2} -CH ₃
	H ¹	H ²	H ³	H ⁴	H ⁵	H ⁶					
L ^A	7.61 (d, 2H)	7.45 (d, 2H)	7.31 (d, 2H)	7.60 (d, 2H)	8.16 (d, 2H)	6.98 (d, 2H)	8.6	8.7	8.9	4.05 (<i>t</i> , <i>J</i> =6.6)	1.87–0.86 (m)
Fe-L ^A	7.65 (d, 2H)	7.44 (d, 2H)	7.31 (d, 2H)	7.62 (d, 2H)	8.16 (d, 2H)	6.99 (d, 2H)	8.6	8.7	8.9	4.05 (<i>t</i> , <i>J</i> =6.6)	1.85–0.86 (m)
L ^B	7.47 (d, 2H)	7.29 (d, 2H)	8.21 (d, 2H)	7.70 (d, 2H)	7.60 (d, 2H)	7.01 (d, 2H)	8.8	8.4	8.8	4.09 (<i>t</i> , <i>J</i> =6.5)	1.91–0.93 (m)
Fe-L ^B	7.45 (d, 2H)	7.33 (d, 2H)	8.22 (d, 2H)	7.70 (d, 2H)	7.60 (d, 2H)	7.01 (d, 2H)	8.9	8.3	8.7	4.02 (<i>t</i> , <i>J</i> =6.6)	1.84–0.86 (m)
L ^C	7.60 (d, 2H)	7.25 (d, 2H)	8.27 (d, 2H)	7.53 (d, 2H)	7.51 (d, 2H)	6.97 (d, 2H)	8.8	8.3	8.8	4.09 (<i>t</i> , <i>J</i> =6.5)	1.83–0.86 (m)
Fe-L ^C	7.61 (d, 2H)	7.26 (d, 2H)	8.30 (d, 2H)	7.51 (d, 2H)	7.50 (d, 2H)	6.98 (d, 2H)	8.5	8.6	8.7	4.00 (<i>t</i> , <i>J</i> =6.5)	1.81–0.86 (m)

^a*N*_{1,2}=³*J*_{1,2}+⁵*J*_{1,2}. ^b*N*_{3,4}=³*J*_{3,4}+⁵*J*_{3,4}. ^c*N*_{5,6}=³*J*_{5,6}+⁵*J*_{5,6}.

Table 2 Optical, thermal and thermodynamic data of free ligands

L	<i>n</i>	Transition ^a	Temperature ^{b/c} /°C	Δ <i>H</i> ^b /kJ mol ⁻¹
L ^A	6	C-S _A S _A -N N-I	97.9 140 ^c 220 ^c (decomp.)	26.6
L ^A	8	C-S _A S _A -N N-I	90.0 190 ^c 220 ^c (decomp.)	31.3
L ^A	10	C-S _A S _A -I	91.2 220 ^c (decomp.)	40.9
L ^A	12	C-S _A S _A -I	91.3 220 ^c (decomp.)	47.6
L ^B	6	C-C' C'-N N-I	70.8 105.7 170 ^c (decomp.)	4.2 28.8
L ^B	8	C-N N-I	105.9 170 ^c (decomp.)	42.6
L ^B	10	C-S _A S _A -I	108.0 170 ^c (decomp.)	50.9
L ^B	12	C-S _A S _A -I	109.2 170 ^c (decomp.)	57.6

^aC, crystal; S, smectic; N, nematic; I, isotropic liquid. ^bData referred to the first DSC cycle starting from the crystal. Temperature data as peak onset. ^cMicroscopic data.

not allow a close packing of the molecules thus reducing the intermolecular interactions and the melting points.

The variation in the melting points of the iron complexes is small, but quite regular. In each series, the melting points decrease with increasing length of the alkoxy chain and they also decrease in the order Fe-L^C > Fe-L^A > Fe-L^B, except for *n*=12 when the Fe-L^B derivatives show higher melting temperatures than the rest (Fig. 3). This inversion is due to the lowest rate at which the melting point decreases for the Fe-L^B complexes.

The influence of the length of the terminal alkoxy chain on the thermal behaviour of the material is not a simple subject, but in general an increase of length of the alkoxy chain can cause mainly two opposite effects: an increase of the molecular polarizability, leading to higher transition temperatures; and an increase in the degree of disorder of the chain, producing lower transition temperatures. Consequently the variation of the transition temperatures against the length of the alkoxy chain depends on the predominant factor. In our iron complexes, where a decrease in the melting point for larger chains is observed, the increase in the degree of disorder of the chain seems to be the dominant factor.

In summary, by using isocyanide ligands which give stable complexes with many metals, it is possible to prepare liquid crystal complexes with different structural shapes. The coordination of the phenyl and biphenyl benzoate isocya-

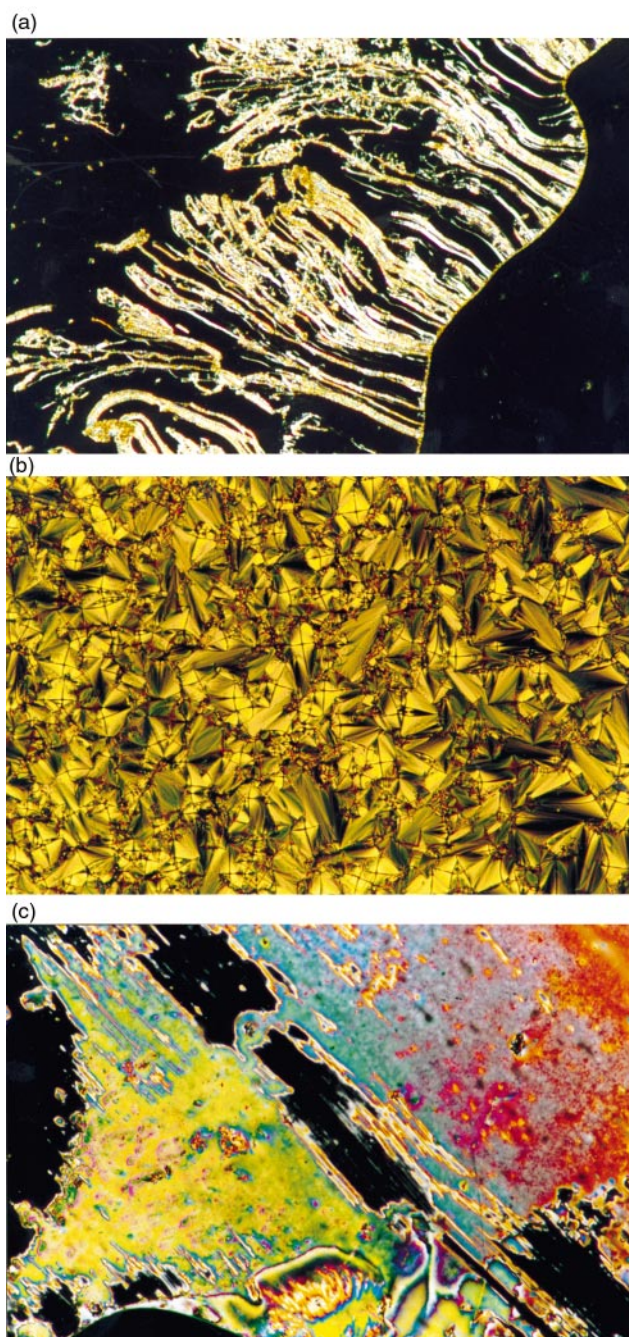


Fig. 1 Polarized optical microscopic textures ($\times 100$) observed for $\text{CNC}_6\text{H}_4\text{C}_6\text{H}_4\text{O}(\text{O})\text{CC}_6\text{H}_4\text{OC}_8\text{H}_{17}$: a) mielinic and homeotropic textures obtained on heating from the solid at 100°C ; b) fan-shaped focal-conic texture obtained on cooling from the nematic phase at 136°C ; c) marbled texture observed on heating from the smectic A phase at 198°C .

nides to $[\text{Fe}(\text{CO})_4]$ groups produces trigonal bipyramidal mesomorphic iron(0) complexes $[\text{Fe}(\text{CO})_4\text{CNR}]$, which display transition temperatures slightly lower than those of the free isocyanides but mesophases which are more ordered.

Experimental

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 CDCl_3 . Microscopy studies were carried out using a Leica DMRB microscope equipped with a Mettler FP82HT hot stage and a Mettler FP90 central processor, at a heating rate of $10^\circ\text{C min}^{-1}$. For differential

Table 3 Optical, thermal and thermodynamic data of iron complexes

Fe-L	<i>n</i>	Transition ^a	Temperature ^b / $^\circ\text{C}$	$\Delta H^b/\text{kJ mol}^{-1}$
Fe-L ^A	6	C-C'	70.2	-3.9
		C'-S _C	93.8	17.8
		S _C -I	120 ^c (decomp.)	
Fe-L ^A	8	C-S _C	79.8	18.5
		S _C -I	120 ^c (decomp.)	
Fe-L ^A	10	C-S _C	78.8	25.5
		S _C -I	120 ^c (decomp.)	
Fe-L ^A	12	C-C'	53.3	-3.6
		C-S _C	70.4	24.5
		S _C -I	120 ^c (decomp.)	
Fe-L ^B	6	C-S _C	87.7	26.9
		N-I	120 ^c (decomp.)	
Fe-L ^B	8	C-S _C	86.7	26.6
		S _C -I	120 ^c (decomp.)	
Fe-L ^B	10	C-C'	67.3	0.7
		C'-S _C	78.4	11.2
		S _C -I	120 ^c (decomp.)	
Fe-L ^B	12	C-S _C	76.9	14.8
		S _C -I	120 ^c	
		S _C -I	120 ^c (decomp.)	
Fe-L ^C	6	C-S _C	97.8	23.6
		S _C -I	120 ^c (decomp.)	
Fe-L ^C	8	C-S _C	94.2	24.1
		S _C -I	120 ^c (decomp.)	
Fe-L ^C	10	C-S _C	91.8	25.3
		S _C -I	120 ^c (decomp.)	
Fe-L ^C	12	C-S _C	72.9	20.6
		S _C -I	120 ^c (decomp.)	

^aC, crystal; S, smectic; N, nematic; I, isotropic liquid. ^bData referred to the first DSC cycle starting from the crystal. Temperature data as peak onset. ^cMicroscopic data.

scanning calorimetry (DSC) a Perkin-Elmer DSC7 instrument was used, which was calibrated with water and indium; the scanning rate was $10^\circ\text{C min}^{-1}$, the samples were sealed in aluminium capsules in the air, and the holder atmosphere was dry nitrogen. The temperatures are referred to the onset.

Only typical examples are described as the syntheses were similar for the rest of the ligands and complexes. Yields, IR and analytical data are given for all the iron isocyanide complexes.

CAUTION! Aminobiphenyls are very carcinogenic materials and must be handled with extreme care.

Preparation of 4-aminobiphenyl-4'-yl 4-alkoxybenzoate

Solid $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (54.3 mmol) was added to a suspension of $\text{O}_2\text{NC}_6\text{H}_4\text{C}_6\text{H}_4\text{O}(\text{O})\text{CC}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$ (10.9 mmol) in 100 ml of ethanol. 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,

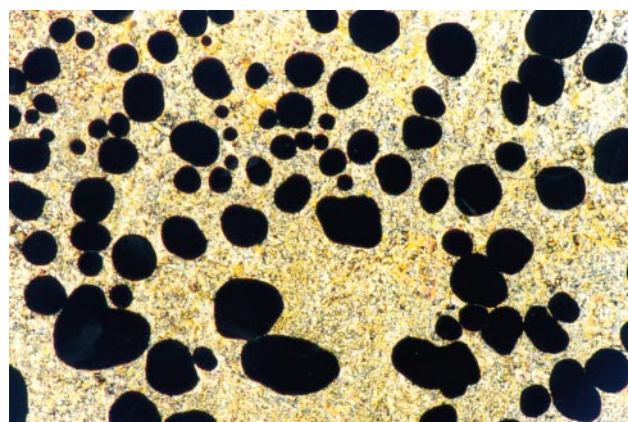


Fig. 2 Polarized optical microscopic textures ($\times 100$) observed for $[\text{Fe}(\text{CO})_4(\text{CNC}_6\text{H}_4\text{O}(\text{O})\text{CC}_6\text{H}_4\text{C}_6\text{H}_4\text{OC}_8\text{H}_{17})]$. The picture shows a schlieren texture on heating from the solid at 93°C .

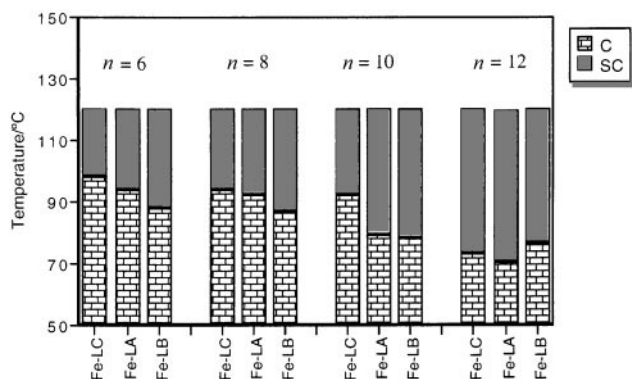


Fig. 3 Comparison of the transition temperatures of $[\text{Fe}(\text{CO})_4(\text{CNR})]$ $[\text{R} = \text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{O}(\text{O})\text{CC}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$ (L^{A}), $\text{C}_6\text{H}_4\text{O}(\text{O})\text{CC}_6\text{H}_4\text{C}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$ (L^{B}), $\text{C}_6\text{H}_4\text{C}(\text{O})\text{OC}_6\text{H}_4\text{C}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$ (L^{C})] complexes. The bars are labelled Fe-Lⁿ; Lⁿ denotes the isocyanide.

dried over MgSO_4 and filtered. The solvent was removed on a rotary evaporator to obtain the product as yellow solid (90% yield).

Preparation of 4-isocyanobiphenyl-4'-yl 4-alkoxybenzoate

The procedure described by Ugi and Meyr⁴⁸ was followed, using triphosgene as the dehydrating agent. To a solution of 4-formamidobiphenyl-4'-yl 4-alkoxybenzoate (6.71 mmol), prepared by reaction of the amine with formic acid, and triethylamine (3.40 mmol) in 50 ml of CH_2Cl_2 was added dropwise a solution of triphosgene (2.25 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, $\text{CH}_2\text{Cl}_2/\text{hexane}$, 4:1 as eluent) and the solvent was evaporated to obtain the product as a white solid (60% yield).

IR and analytical data

$\text{CNC}_6\text{H}_4\text{C}_6\text{H}_4\text{O}(\text{O})\text{CC}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$ (L^{A}). $n=6$: IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{N})$: 2128 s. Anal. Calcd. for $\text{C}_{26}\text{H}_{25}\text{NO}_3$: C, 78.17; H, 6.31; N, 3.51. Found: C, 77.92; H, 6.50; N, 3.44. $n=8$: IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{N})$: 2128 s. Anal. Calcd. for $\text{C}_{28}\text{H}_{29}\text{NO}_3$: C, 78.66; H, 6.84; N, 3.28. Found: C, 78.44; H, 6.89; N, 3.41. $n=10$: IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{N})$: 2128 s. Anal. Calcd. for $\text{C}_{30}\text{H}_{33}\text{NO}_3$: C, 79.09; H, 7.30; N, 3.07. Found: C, 78.89; H, 7.31; N, 3.12. $n=12$: IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{N})$: 2128 s. Anal. Calcd. for $\text{C}_{32}\text{H}_{37}\text{NO}_3$: C, 79.47; H, 7.71; N, 2.90. Found: C, 79.08; H, 7.76; N, 2.85.

$\text{CNC}_6\text{H}_4\text{O}(\text{O})\text{CC}_6\text{H}_4\text{C}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$ (L^{B}). $n=6$: IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{N})$: 2130 s. Anal. Calcd. for $\text{C}_{26}\text{H}_{25}\text{NO}_3$: C, 78.17; H, 6.31; N, 3.51. Found: C, 77.82; H, 6.36; N, 3.44. $n=8$: IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{N})$: 2130 s. Anal. Calcd. for $\text{C}_{28}\text{H}_{29}\text{NO}_3$: C, 78.66; H, 6.84; N, 3.28. Found: C, 78.22; H, 6.74; N, 3.23. $n=10$: IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{N})$: 2130 s. Anal. Calcd. for $\text{C}_{30}\text{H}_{33}\text{NO}_3$: C, 79.09; H, 7.30; N, 3.07. Found: C, 78.87; H, 7.24; N, 3.09. $n=12$: IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{N})$: 2130 s. Anal. Calcd. for $\text{C}_{32}\text{H}_{37}\text{NO}_3$: C, 79.47; H, 7.71; N, 2.90. Found: C, 79.21; H, 7.67; N, 2.89.

$\text{CNC}_6\text{H}_4\text{C}(\text{O})\text{OC}_6\text{H}_4\text{C}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$ (L^{C}). $n=6$: IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{N})$: 2127 s. Anal. Calcd. for $\text{C}_{26}\text{H}_{25}\text{NO}_3$: C, 78.17; H, 6.31; N, 3.51. Found: C, 77.97; H, 6.35; N, 3.38. $n=8$: IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{N})$: 2128 s. Anal. Calcd. for $\text{C}_{28}\text{H}_{29}\text{NO}_3$: C, 78.66; H, 6.84; N, 3.28. Found: C, 78.40; H, 6.87; N, 3.24. $n=10$: IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{N})$: 2128 s. Anal. Calcd. for $\text{C}_{30}\text{H}_{33}\text{NO}_3$: C, 79.09; H, 7.30; N, 3.07. Found: C, 78.68; H, 7.19; N, 3.18. $n=12$: IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{N})$: 2128 s. Anal. Calcd. for $\text{C}_{32}\text{H}_{37}\text{NO}_3$: C, 79.47; H, 7.71; N, 2.90. Found: C, 79.28; H, 7.57; N, 2.85.

Preparation of $[\text{Fe}(\text{CO})_4(\text{CNR})]$

$[\text{R} = \text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{O}(\text{O})\text{CC}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$, $\text{C}_6\text{H}_4\text{O}(\text{O})\text{CC}_6\text{H}_4\text{C}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$, $\text{C}_6\text{H}_4\text{C}(\text{O})\text{OC}_6\text{H}_4\text{C}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}]$

To a mixture of $[\text{Fe}(\text{CO})_5]$ (0.3 mmol), $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ (0.03 mmol) and 15 mL of toluene at 60°C , was added dropwise the corresponding isocyanide (0.39 mmol) in 20 mL of toluene, under nitrogen. After stirring for 20 minutes, the reaction mixture was cooled to room temperature and the solvent was removed under vacuum. Recrystallisation from $\text{CH}_2\text{Cl}_2/\text{hexane}$ at -15°C afforded air stable yellow crystals of the product.

Yields, IR and analytical data

$\text{R} = \text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{O}(\text{O})\text{CC}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$ (Fe-L^{A}). $n=6$: Yield 59%. IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{N})$: 2163 m, $\nu(\text{CO})$: 2055 s, 1998 m, 1970 s. Anal. Calcd. for $\text{C}_{30}\text{H}_{25}\text{FeNO}_7$: C, 63.51; H, 4.44; N, 2.47. Found: C, 62.99; H, 4.72; N, 2.35. $n=8$: Yield 42%. IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{N})$: 2162 m, $\nu(\text{CO})$: 2055 s, 1998 m, 1970 s. Anal. Calcd. for $\text{C}_{32}\text{H}_{29}\text{FeNO}_7$: C, 64.55; H, 4.91; N, 2.35. Found: C, 64.86; H, 5.15; N, 2.34. $n=10$: Yield 54%. IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{N})$: 2165 m, $\nu(\text{CO})$: 2055 s, 1995 m, 1967 s. Anal. Calcd. for $\text{C}_{34}\text{H}_{33}\text{FeNO}_7$: C, 65.51; H, 5.33; N, 2.25. Found: C, 64.95; H, 5.42; N, 2.10. $n=12$: Yield 46%. IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{N})$: 2163, $\nu(\text{CO})$: 2055 s, 1998 m, 1971 s. Anal. Calcd. for $\text{C}_{36}\text{H}_{37}\text{FeNO}_7$: C, 66.36; H, 5.72; N, 2.15. Found: C, 66.65; H, 5.93; N, 2.12.

$\text{R} = \text{C}_6\text{H}_4\text{O}(\text{O})\text{CC}_6\text{H}_4\text{C}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$ (Fe-L^{B}). $n=6$: Yield 56%. IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{N})$: 2165 m, $\nu(\text{CO})$: 2055 s, 1996 m, 1967 s. Anal. Calcd. for $\text{C}_{30}\text{H}_{25}\text{FeNO}_7$: C, 63.51; H, 4.44; N, 2.47. Found: C, 63.03; H, 4.55; N, 2.38. $n=8$: Yield 45%. IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{N})$: 2161 m, $\nu(\text{CO})$: 2055 s, 2000 m, 1973 s. Anal. Calcd. for $\text{C}_{32}\text{H}_{29}\text{FeNO}_7$: C, 64.55; H, 4.91; N, 2.35. Found: C, 64.21; H, 4.98; N, 2.35. $n=10$: Yield 49%. IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{N})$: 2164 m, $\nu(\text{CO})$: 2055 s, 1996 m, 1967 s. Anal. Calcd. for $\text{C}_{34}\text{H}_{33}\text{FeNO}_7$: C, 65.51; H, 5.33; N, 2.25. Found: C, 65.23; H, 5.18; N, 2.15. $n=12$: Yield 45%. IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{N})$: 2166, $\nu(\text{CO})$: 2055 s, 1996 m, 1967 s. Anal. Calcd. for $\text{C}_{36}\text{H}_{37}\text{FeNO}_7$: C, 66.36; H, 5.72; N, 2.15. Found: C, 66.01; H, 5.82; N, 2.14.

$\text{R} = \text{C}_6\text{H}_4\text{C}(\text{O})\text{OC}_6\text{H}_4\text{C}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$ (Fe-L^{C}). $n=6$: Yield 59%. IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{N})$: 2153 m, $\nu(\text{CO})$: 2052 s, 2004 m, 1977 s. Anal. Calcd. for $\text{C}_{30}\text{H}_{25}\text{FeNO}_7$: C, 63.51; H, 4.44; N, 2.47. Found: C, 63.65; H, 4.53; N, 2.47. $n=8$: Yield 56%. IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{N})$: 2159 m, $\nu(\text{CO})$: 2054 s, 1999 m, 1968 s. Anal. Calcd. for $\text{C}_{32}\text{H}_{29}\text{FeNO}_7$: C, 64.55; H, 4.91; N, 2.35. Found: C, 64.43; H, 5.03; N, 2.30. $n=10$: Yield 61%. IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{N})$: 2159 m, $\nu(\text{CO})$: 2054 s, 1999 m, 1968 s. Anal. Calcd. for $\text{C}_{34}\text{H}_{33}\text{FeNO}_7$: C, 65.51; H, 5.33; N, 2.25. Found: C, 66.07; H, 5.60; N, 2.13. $n=12$: Yield 46%. IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{N})$: 2158, $\nu(\text{CO})$: 2054 s, 2000 m, 1971 s. Anal. Calcd. for $\text{C}_{36}\text{H}_{37}\text{FeNO}_7$: C, 66.36; H, 5.72; N, 2.15. Found: C, 66.28; H, 5.92; N, 2.03.

Acknowledgements

We are indebted to the Comisión Interministerial de Ciencia y Tecnología (Project MAT99-0971) and to the Junta de Castilla y León (Projects VA16/99 and VA15/00B) for financial support.

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