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## Liquid Crystals

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## Preliminary communication

# Mesomorphic imines and their complexes with rhenium(I): a cubic mesophase in a rod-like mesogen with perfluorinated terminal chains

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A cubic mesophase is found in an extended rod-like mesogen in which the terminal chains are perfluorinated.

The first mesogens showing a cubic phase were the nitrophenyl carboxylic acids synthesized by Gray in the 1950s [1], and for many years after this the cubic phase remained a rare curiosity, at least in the field of thermotropic mesogens. More recently, the phase has received more attention and has been recognized in a wider range of materials, such as polyol and carbohydrate liquid crystals [2], silver stilbazole complexes [3], polycatenar and bi-swallow-tailed mesogens [4], dialkylphosphate salts [5], oligoalkylene amides [6], rod-coil calamitic mesogens [7] and, probably, in some silver thiolate complexes [8].

The driving force for the formation of these phases is not entirely clear, but it would seem that at least two types of material forming the phase are readily identified. In the first, such as Gray's original biphenyl carboxylic acids, the molecules are largely rod-like, but have some function somewhere towards the middle of the molecule which offers the possibility of a sideways-on intermolecular interaction. Secondly, there are the cubic phases formed by polycatenar mesogens, and here it is possible to understand the formation of the phase in terms of the interfacial curvature established at the aromatic/paraffinic interface in a treatment analogous to that used in lyotropic systems [9]. Possible driving forces for the formation of cubic phases have been recently discussed [10, 11].

As part of our studies on metallomesogens, we have been interested in the formation of mesomorphic complexes based around octahedral metal centres [12], and in one example [13] we have bound extended imine-based liquid crystal moieties to manganese(I) and rhenium(I) centres via orthometallation (figure 1). These

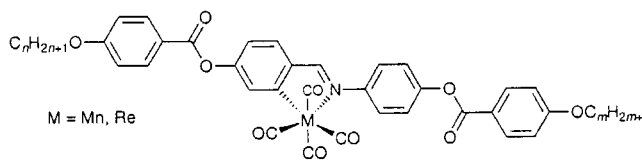


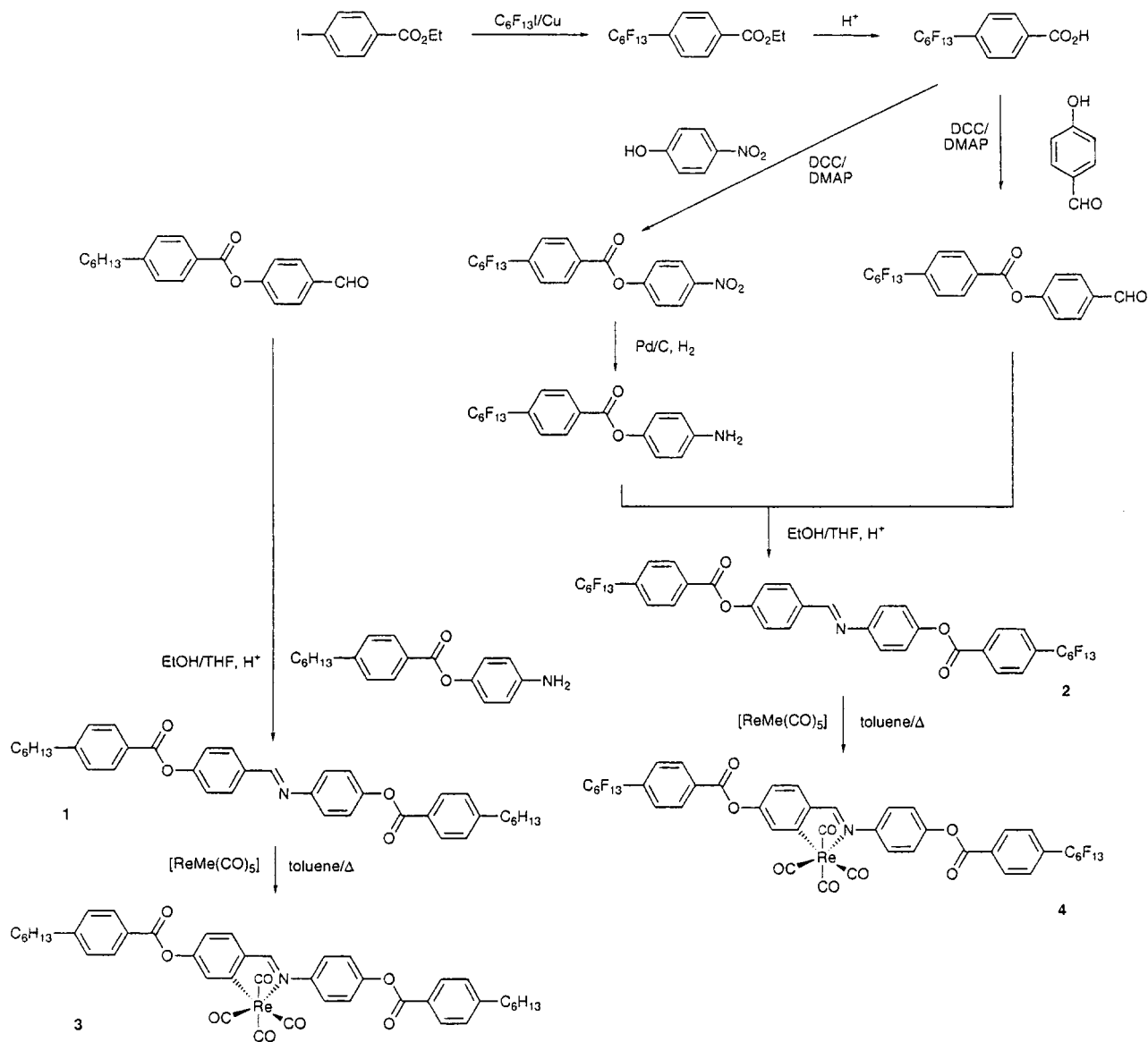
Figure 1. Structure of the orthometallated imine complexes of Mn(I) and Re(I).

complexes show, to date, only a liquid crystal nematic phase (or its chiral derivative [14]) whatever the nature of the imine ligand, something we have ascribed to the perturbation to the structural anisotropy of the ligand offered by the metal tetracarbonyl group. In order to try to see how far this tendency for nematic phase formation could be pushed, we undertook the synthesis of some imines in which the terminal chains were perfluorinated in nature. Such an approach is also rather topical as perfluorinated alkyl chains in mesogens are now beginning to be studied systematically [15].

The synthesis of the ligands is shown in the scheme, the only feature of note being the introduction of the perfluorinated chains which was accomplished via a copper-catalysed coupling reaction involving the perfluoroalkyl iodide and ethyl 4-iodobenzoate [16]. Note that these mesogens do not contain a dimethylene spacer between the fluorinated alkyl chain and the ring.

For the purposes of comparison, the mesomorphic properties of two imine ligands and their complexes are collected in the table. Thus, the imine with two hydrocarbon chains (1) showed a SmC and a N phase similar to related imines which we have studied previously. However, when the imine containing two perfluoroalkyl chains (2) was studied, it was found to show a smectic C and a cubic phase at 239 and 268°C, respectively, the latter being readily identified by the

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Scheme. Synthesis of the imines and their complexes.

slow growth of square-edged, optically isotropic domains into the highly coloured schlieren texture of the smectic C phase. Figure 2 shows the reverse transition from cubic to smectic C on cooling; the black, optically isotropic background of cubic phase contains islands of birefringent smectic C phase forming with pronounced straight edges. The cubic phase thus formed was highly viscous, much like that of the nitro- and cyano-biphenyl carboxylic acids. The space group of the phase is not yet known, but will be subject to investigation by X-ray diffraction in due course.

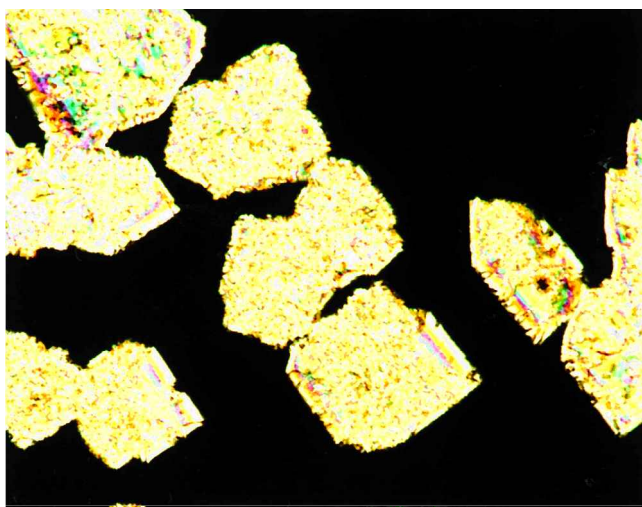
The mesomorphism of the rhenium complexes was rather different. Thus, **3** (using ligand with two hydrocarbon chains) showed only a nematic phase with a

clearing point much reduced compared to that of the parent ligand **1**; the SmC phase of **1** was not seen. We have commented on this before [13] and it is simply due to the reduction in molecular anisotropy which accompanies the formation of the rhenium complex and the concomitant reduction in ability to form a layered phase. However, **4** melted to form a smectic A phase at  $212^\circ C$  and then quickly proceeded to begin to decompose. Thus, by using the rather strong fluorophilic associations, we have been able to force these complexes to form a layered phase.

We believe that the formation of a cubic phase in ligand **2** is of some interest. Thus, as we outlined above, it is the case that simple rod-like mesogens forming

Table. Mesomorphism of the imines and their complexes.

Compound	Transition	$T/^\circ\text{C}$	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{J K}^{-1} \text{mol}^{-1}$
<i>Ligands</i>				
<b>1</b>	Cr–SmC	138	37.3	90
	SmC–N	181	1.9	4
	N–I	320	2.7	5
<b>2</b>	Cr–SmC	239	48.6	36
	SmC–Cub	268	2.4	5
	Cub–I	310	5.2	9
<i>Complexes</i>				
<b>3</b>	Cr–N	129	25.3	61
	N–I	167	1.5	3
<b>4</b>	Cr–SmA (decomp)	212	51.4	105

Figure 2. Photomicrograph at the cubic–SmC transition of **2** on cooling at 268°C.

cubic phases possess some feature in their molecules which would lead to the possibility of a lateral interaction, for example through hydrogen bonding or lateral ionic interaction. However, there is no such group present here. The other factor at play in these new mesogens is the introduction of the perfluoroalkyl chains. Thus, while it is known that aliphatic chains and aromatic groups will tend to phase separate when the alkyl chain is long enough (i.e. leading to the formation of smectic phases), the phase separation apparent between perfluoroalkyl groups and either aromatic rings or hydrocarbon chains is very much stronger. Thus, the mesomorphism of compounds substituted with perfluoroalkyl chains is heavily dominated by the formation of the smectic A phase due to strong microphase separation.

Perfluoroalkyl chains are clearly larger in volume than their hydrocarbon analogues and are also much more rigid. This latter fact is interesting, as it should lead to rather small changes in layer spacing with increasing temperature and, more importantly, a much smaller change in the volume occupied by the chain as the temperature is increased. However, it is not clear that any of these facts helps to rationalize the observation of the cubic phase in these compounds and they do not fall into the two broad categories of mesogen forming cubic phases described above. Further, although the fluorocarbon chain occupies a greater volume than the hydrocarbon equivalent, the size of the aromatic core of these compounds is such that we feel that it is unlikely that there is significant curvature at the aromatic/perfluorocarbon interface to allow the phase formation to be explained in the manner used for polycatenar mesogens. This simply emphasizes that while it has been possible to start to construct models to rationalize cubic phase formation, the factors governing the formation of the phase are rather subtle and a good deal of work needs to be done before they can be understood in any detail. We would also note that the formation of a smectic C phase in the all-perfluorinated compound is also rather surprising, as mesogens containing two such chains are normally prone to the formation of smectic A phases, with smectic C phases being very rare [17]. Indeed, mesogens containing *only* perfluorocarbon chains are not at all common, with most possessing a dimethylene spacer. Interestingly, the cubic phase of **2** disappears on complexation to rhenium. We are now looking at other derivatives of these perfluorinated mesogens to see what changes can be tolerated while maintaining the cubic phase.

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