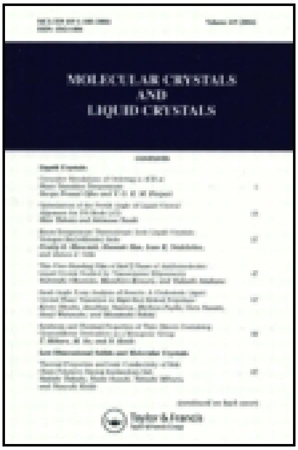

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The Synthesis and Mesomorphism of Mesogenic Imines with Fluorocarbon Chains and their Complexes with Rhenium(I): New Materials with Cubic Phases

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The Synthesis and Mesomorphism of Mesogenic Imines with Fluorocarbon Chains and their Complexes with Rhenium(I): New Materials with Cubic Phases

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In this paper, we describe the synthesis of some imine ligands bearing fluorinated chains and their metal complexes with Re(I). Whereas related ligands with hydrocarbon chains show nematic and S_C phases, the new ligands show S_A and S_C phases. However, when both terminal chains are fully fluorinated, then the ligand additionally show a cubic phase. Metal complexes of the fluorinated ligands show a S_A phase before decomposing.

The mesomorphism of both the complexes and the ligands is discussed and the formation of cubic phases in these imines is explored in relation to other materials showing a cubic phase.

INTRODUCTION

In considering the formation of liquid crystal mesophases, it is necessary to take into account a wide variety of factors which can act to stabilise (or otherwise) particular states of organisation. Thus, in very general terms, we consider that lamellar phases are promoted over the nematic phase as terminal alkyl chains are lengthened on account of the increased microphase separation between the (generally) polarisable core and the rather non-polarisable chains. However, in the case of polycatenar mesogens,[1] the mesomorphism is determined largely by the

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curvature which is introduced at the interface between the rigid core of the molecule and the flexible aliphatic chains. Hence, at zero or low curvature, nematic and smectic C phases result while at longer chain lengths, columnar phases are observed. In surfactant liquid crystal systems, the first-formed mesophase is that derived from the shape of the micelles in solution whose shape is, in turn, largely dependent on structural factors such as the length of the aliphatic chain and dimensions of the polar head group.

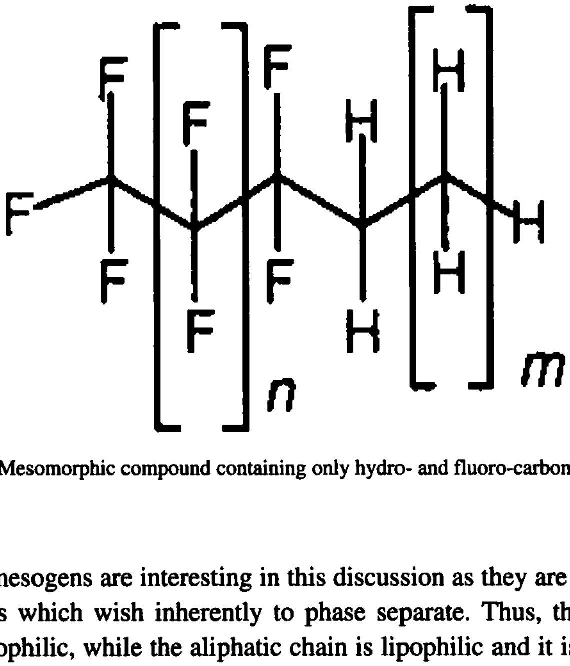


FIGURE 1 Mesomorphic compound containing only hydro- and fluoro-carbon fragments

Surfactant mesogens are interesting in this discussion as they are composed of two fragments which wish inherently to phase separate. Thus, the polar head group is hydrophilic, while the aliphatic chain is lipophilic and it is these mutually opposing driving forces which lead initially to the formation of micelles and ultimately mesophases.[2] Similar ideas of phase separation have been advanced in discussions of the mesomorphism of mesogens containing dimethylsiloxane terminal chains,[3] but in thermotropic systems, the most dramatic phase separations are observed when hydrocarbon and fluorocarbon fragments are introduced into the same system.[4] When mixed physically, hydrocarbons and fluorocarbons phase separate, but the chemist has a trick up the sleeve in the ability to bind a hydrocarbon and a fluorocarbon fragment *into the same molecule*, preventing them from phase separating. The simplest example of this effect is in the study of molecules which are simply part hydrocarbon, part fluorocarbon (Fig. 1) which are found to form hexagonal mesophases.[5] However, when the chains are present as part of a more conventional mesogen containing a rigid core, the effect is to promote strongly the formation of lamellar phases on account of the desire of the fluorocarbon parts to self-associate away from the hydrocarbon parts (or the argument can advanced the other way round!). Such an approach was used by Tournilhac in an effort to generate a non-chiral smectic A phase with a longitudinal spontaneous polarisation (Fig. 2), the idea being to control the microphase separation to such a degree that the orientation with successive layers was guaranteed.[6]

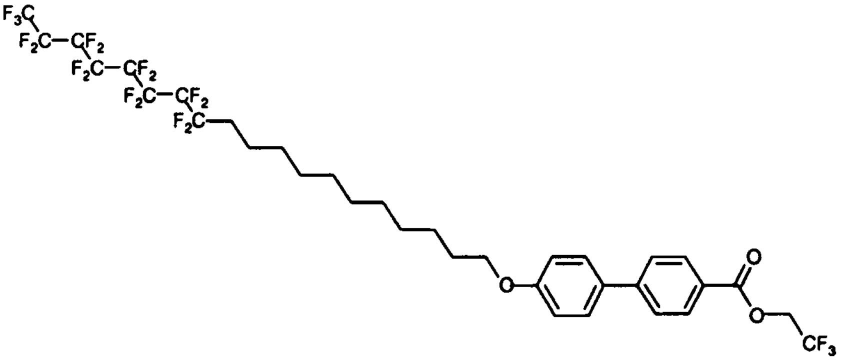


FIGURE 2 Tournhilac's fluorinated materials

As part of our studies of metallomesogens, we synthesised a series of Mn(I) and Re(I) complexes based on the binding of a [M(CO)$_4$] fragment to a mesomorphic imine *via* orthometallation (Fig. 3), giving mesogens containing an octahedral metal centre. We have studied these complexes rather extensively because they represent an example of a metallomesogenic system where the transition temperatures of the ligand are *reduced* on complexation.[7] However, another interesting feature of the materials is that while the ligands we have used are strongly smectogenic, all of the complexes so far synthesised have shown only a nematic phase. This we have attributed to the destablising effect which the lateral M(CO)$_4$ group would have on smectic phases, in effect preventing the formation of layers. However, this explanation is clearly not so simple as it seems. For example, in other, related complexes which we have synthesised, lateral ReX(CO)$_3$ groups (X = Cl, Br, I) do not suppress the formation of smectic phases when complexed to diazabutadienes[8] or to bipyridines (Figure 4)[9] and we have speculated that this difference may be dipolar in origin.[8]

Another instructive example is provided by Ghedini who looked at the related Pt(II) and Pt(IV) complexes shown in Figure 5.[10] For the planar Pt(II) species (Figure 5; **a**), he found nematic phases that were stable to 200 and 250 °C (for R = i and ii, respectively), while upon oxidative addition of I$_2$ (Figure 5, **b**, Z = I)

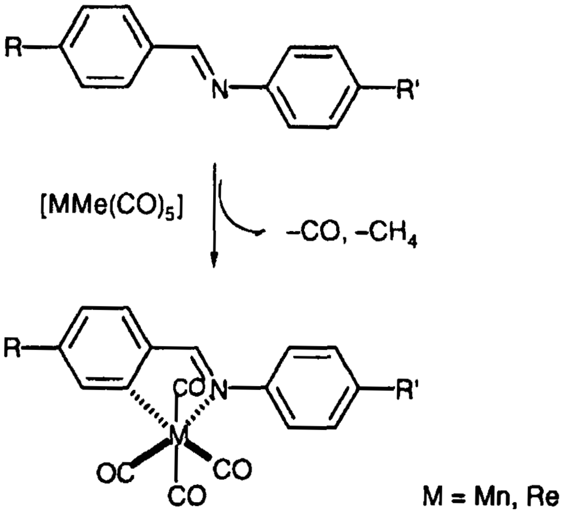


FIGURE 3 General approach to the synthesis of orthometallated imine complexes of Mn(I) and Re(I)

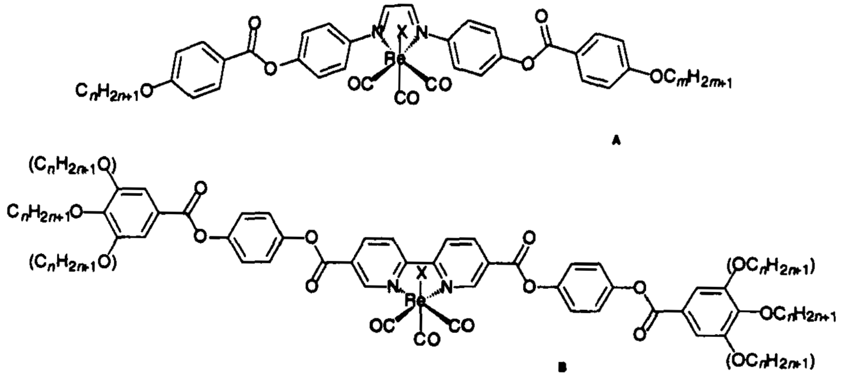


FIGURE 4 Octahedral Re(I) mesogens

the N phase was lost in one case (R = $C_{10}H_{21}O$) and destablised by 70 °C with respect to the Pt(II) species in the other (R = ii). For addition of MeI (Figure 5, **b**, Z = Me), the behaviour was different and the N phase was stabilised by some 30 °C by comparison with the Pt(II) species for R = $C_{10}H_{21}O$ and by some 20 °C (with respect to the Pt(II) species) for R = ii. Further, in this latter case, a S_C

phase was also introduced. These observations are interesting as in the case of the addition of I_2 to form the Pt(IV) species, no additional dipolar component is added into the system and the phases are destabilised (as in the case of our Re carbonyls), while in the case where MeI is added, a new dipolar component is added and the phases are stabilised (as is the case for the Re bipyridines and diazabutadienes). Thus, there would seem to be some corroborative evidence for the rôle of lateral dipoles in determining the transition temperatures in these systems. Finally, it is interesting to note that while we have not previously observed smectic phases in our Re carbonyls, we have seen them in both the Re-diazabutadiene and Re-bipyridine systems (where there is an off-axis dipole) and they are also observed in the polar Pt(IV) systems formed on addition of MeI. Studies are now underway to try to provide some quantitative measure of these effects.

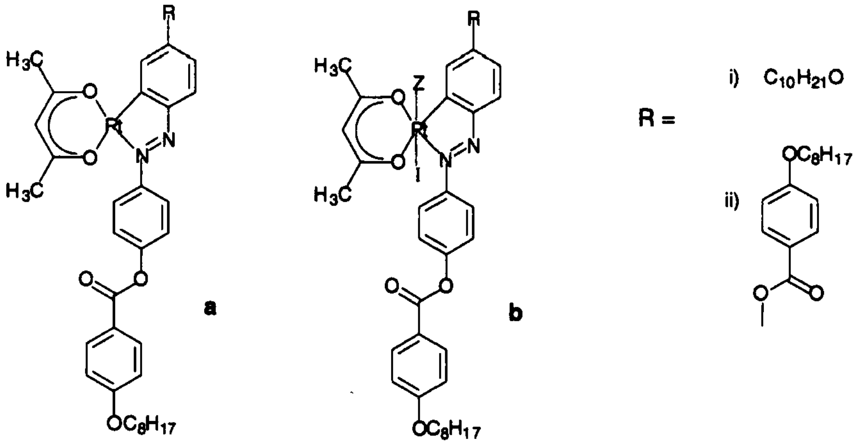


FIGURE 5 Octahedral Pt(IV) mesogens

RESULTS AND DISCUSSION

In order to try to understand the factors which come into play in determining the mesomorphism in these imine systems, we decided to stack the odds strongly in favour of the formation of lamellar phases by modification of the ligands so that they contained one or two fluorocarbon chains. This would then establish whether the system would support the formation of lamellar phases, or whether the lateral $M(CO)_4$ group would suppress their formation entirely.

The use of fluorocarbons as components in chemical systems is currently very topical. In the field of homogeneous catalysis, so-called fluorocarbon "pony-tails" are being attached to ligands bound to catalytic centres so as to confer fluorocarbon solubility on the catalysts, allowing them to be separated from the products in biphasic systems.[11] Similarly, in the field of liquid crystals, mesogens with fluorocarbon chains are being investigated in relation to issues of microphase separation and the formation of three-dimensional structures, particularly by Tschierscke.[12]

The systems we have chosen to investigate, shown in Figure 6, are based on the four-ring imine ligands which we have synthesised previously in studies of mesomorphic complexes of Mn(I) and Re(I), although in this study we have used only Re(I) whose complexes are more thermally stable. Previously, we have looked at four-ring imines with a variety of terminal alkoxy chain lengths (Fig. 6; R = $C_8H_{17}O$ or $C_{12}H_{25}O$, R′ = $C_5H_{11}O$-$C_{14}H_{29}O$) and have found that while the ligands showed N, S_C, S_I and J phases, only nematic phases were seen when the ligands were complexed to Re(I).

In this study, we therefore examined one ligand with two hydrocarbon chains (**9**; Scheme) and its complex (**13**), two mixed ligands (**10, 11**; Scheme) and their complexes (**14, 15**) and four ligands with two fluorocarbon chains (**12a-d**) and their complexes (**16a-d**). Four of these compounds (**9, 12a, 13, 16a**) have been reported in a preliminary communication.[13]

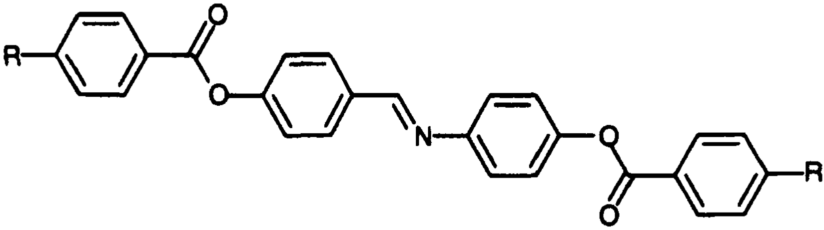
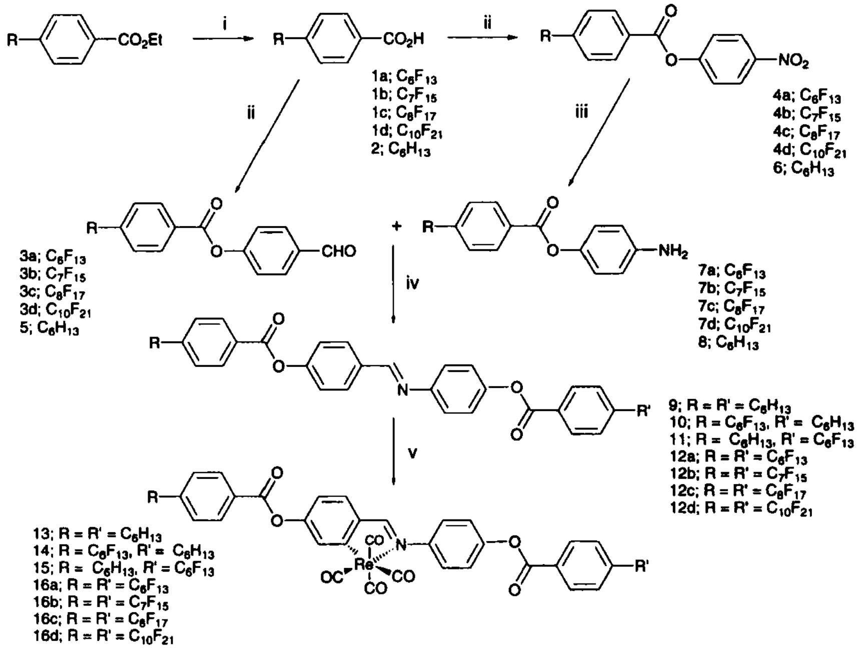


FIGURE 6 Ligands synthesised previously

The synthesis of the ligands and complexes is outlined in the Scheme and we would note that in these examples, the fluorocarbon chain is attached directly to the terminal ring and not *via* a -CH_2CH_2- spacer as is commonly the case.[14] Thus, ethyl perfluoroalkylbenzoates were synthesis *via* a copper-catalysed cross-coupling reaction[15] between a perfluoroalkyl iodide and ethyl 4-bromobenzoate. The esters were then hydrolysed to give the related benzoic acids

(**1a-d**) and these were then esterified with either 4-hydroxybenzaldehyde to give 4-perfluoroalkylbenzoyloxy-4-benzaldehyde (**3a-d**), or with 4-nitrophenol to give 4-perfluoroalkylbenzoyloxy-4-nitrobenzene (**4a-d**). 4-Hexylbenzoyloxy-4-benzaldehyde (**5**) and 4-hexylbenzoyloxy-4-nitrobenzene (**6**) were obtained in similar esterification reactions starting from 4-hexylbenzoic acid which was purchased commercially. The nitrophenyl esters (**4a-d, 6**) were then reduced to the corresponding anilines (**7a-d, 8**) and then condensed with the benzaldehydes (**3a-d, 5**) to give the target imines (**9–11, 12a-d**). The related rhenium complexes (**13–15, 16a-d**) were then obtained by reacting the imine with [ReMe(CO)$_5$] at reflux.

All of the new compounds were characterised by NMR spectroscopy and elemental analysis and, for the complexes, by infrared spectroscopy. Thus, on formation of the target ligands, the characteristic imine resonance appeared at around δ 8.5 in the ^{1}H NMR spectrum. On formation of the complexes, the three ν_{CO} bands of the starting [ReMe(CO)$_5$] at 2129, 2012 and 1975 cm^{-1} were replaced by those of the product at 2092, 1991, 1987 and 1934 cm^{-1} and one of the four AA'XX' spin systems in the ^{1}H NMR spectrum of the imine was replaced with an AMX spin system arising from the metallated ring.



SCHEME Synthesis of the ligands and complexes

Crystal and Molecular Structure of Complex 15

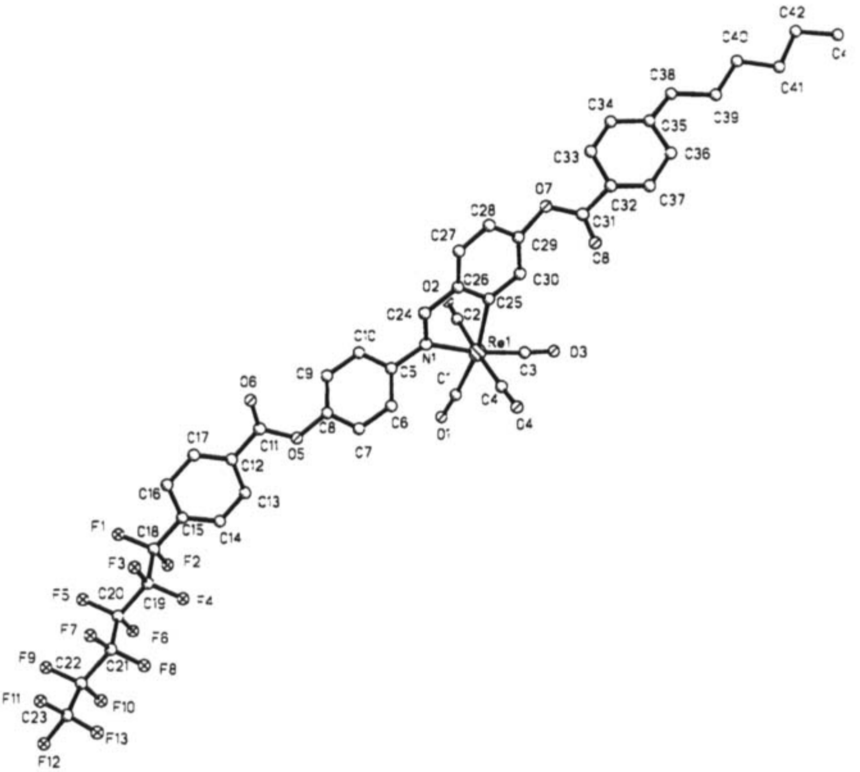
In the case of complex **15** which contains one fluorocarbon and one hydrocarbon chain, it was possible to grow single crystals suitable for X-ray diffraction. Crystallographic data are collected in Table I.

TABLE I Crystallographic data and structure refinement details for **15**

Formula	$C_{43}H_{29}F_{13}NO_8Re$
M	1120.87
Crystal system	Monoclinic
Space group	$P2_1/c$
Z	4
a [Å]	36.8678(3)
b [Å]	8.3405(3)
c [Å]	13.886(1)
β [°]	98.749(2)
V [$Å^3$]	4220.1(4)
Density calc. [Mg / m^3]	1.764
μ [mm^{-1}]	2.992
Crystal	Colourless block
Crystal size [mm^3]	0.10 × 0.10 × 0.07
θ range [°]	2.2 – 25.0
Reflections collected	16582
Independent reflections / R_{int}	7410 / 0.056
Completeness [%]	99.2
Data / restraints / parameters	7410 / 77 / 597
GOF on F^2	0.996
$R1$ / $wR2$ [$F^2 > 2\sigma(F^2)$]	0.056 / 0.134
$R1$ / $wR2$ (all data)	0.096 / 0.147
Largest diff. peak and hole [e $Å^{-3}$]	2.23 and –1.17

Compound **15** crystallises in the space group $P2_1/c$ with one molecule per asymmetric unit. The bonding parameters within the octahedral coordination sphere of the rhenium atom are in the expected range (Figure 7, Table II) and compare well with previous studies [7e]. The greatest departure from ideal geometry is observed in the intra-ring angle N1-Re1-C25 (75.1°).

The shape of the molecule is slightly bent with the C23...Re1...C43 angle being 173°. The carbon atoms of the fluorocarbon part are nearly planar and the



four respective C-C-C-C torsion angles are between −176° and 179°. Furthermore, the (C15, C18>C23) least-squares plane is orthogonal (89.9°) with respect to the accompanying (C12>C15) phenyl ring.

Torsion angles between the phenyl rings (C12>C15) and (C5>C10) and (C25>C30) and (C32>C37) are 48°, 66°, 18° and 53°, respectively. The chelating ring (Re1, N1, C24>C26) and the accompanying phenyl fragment (C25 > C30) are slightly out of plane forming an angle of 5°.

The hydrocarbon chain and the accompanying phenyl moiety are found to be disordered (Figure 8). In the first conformation C32>C43 all C-C-C-C torsion angles of the hydrocarbon chain are approximately *trans* (-163° to 175°). The least squares-plane of C32>C43 is distorted from the expected angle with the C32>C37 phenyl ring by 8°. In contrast, the alternative conformation C32′>C43′, shows a *trans-gauche-trans-trans* conformation. The positions of the two disordered rings are related by a rotation about 16°.

TABLE II Selected bond angles (°) and bond lengths (Å) for **15**

Bond Angles (°)		*Bond Lengths (Å)*	
C3-Re1-C1	94.7(3)	Re1-C3	1.927(10)
C3-Re1-C2	88.0(4)	Re1-C4	2.014(10)
C1-Re1-C2	88.2(4)	Re1-C1	1.961(9)
C3-Re1-C4	88.8(4)	Re1-N1	2.184(6)
C1-Re1-C4	92.6(4)	Re1-C2	1.993(10)
C2-Re1-C4	176.7(3)	Re1-C25	2.185(8)
C2-Re1-N1	92.3(3)		
C4-Re1-N1	90.8(3)		
C3-Re1-C25	95.8(3)		
C2-Re1-C25	85.5(3)		
C4-Re1-C25	94.3(3)		
N1-Re1-C25	75.1(3)		
C3-Re1-N1	170.8(3)		
C1-Re1-N1	94.6(3)		
C1-Re1-C25	167.6(3)		

In the crystal structure the molecules are arranged in such a way that the fluorocarbon parts of the two nearest neighbours lie almost parallel with the C15...C23 vector being approximately parallel to the crystallographic *b*-axis. The closest intermolecular F...F contacts are in the range of 2.8 Å. As a result, the structure is built up by fluorocarbon and hydrocarbon bands, both separated by the coordination sphere of the transition metal (Figure 9).

Mesomorphism of the Ligands and Intermediates

The mesomorphism of a number of the intermediate compounds was investigated in addition to that of the target imines; thermal data are collected in Tables III and IV. Thus, the nitrophenyl esters containing perfluoroalkyl chains (**4a-d**) all showed a S_A phase, the crystal phase melting in the range 82–107 °C and the S_A phase clearing in the range 98–155 °C. In addition, the perfluorodecyl derivative (**4d**) showed a monotropic S_B phase, while the hydrocarbon example (**6**) showed a monotropic nematic phase. The related anilines with perfluoroalkyl chains (**7a-d**) were also mesomorphic and each showed only a S_A phase although at a higher temperature than for the related nitro compounds. The comparison is summarised in Figure 10 and we suspect that the higher temperatures observed in the anilines are attributable to the stabilising influence of intermolecular hydro-

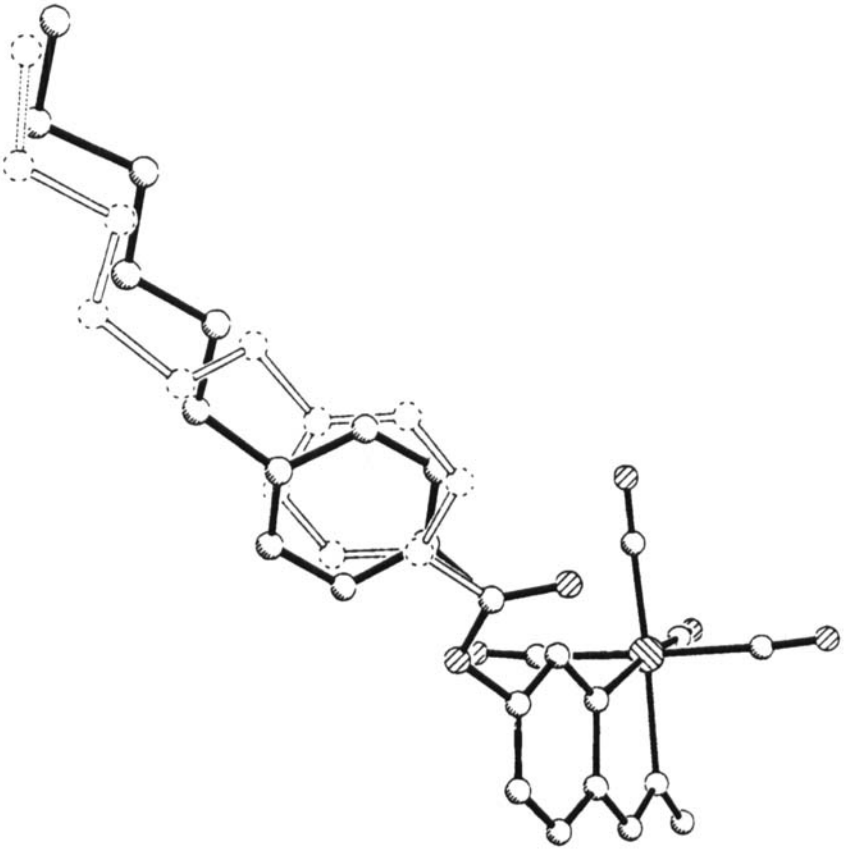


FIGURE 8 Disordered hydrocarbon fragment in the structure of **15**

gen bonding. However, the comparison would also suggest that the stabilising effect was greater for the crystal phase as the smectic A range increased with increasing chain length for the nitro compounds (from 16 to 48 °C), while the variation for the anilines was much smaller (13 to 20 °C).

The aldehydes with perfluorinated chains (**3a-d**) were also mesomorphic, showing S_A phases at temperatures broadly similar to those of the nitro compounds. No data are presented, however, for the decyl analogue which we had great difficulty purifying, although this did not affect the purity of the target imine which was subsequently obtained. The aldehyde with the alkyl chain (**5**) was non-mesomorphic, melting at 30 °C. One very obvious and immediate comparison which can be drawn at this stage is between the intermediates with a

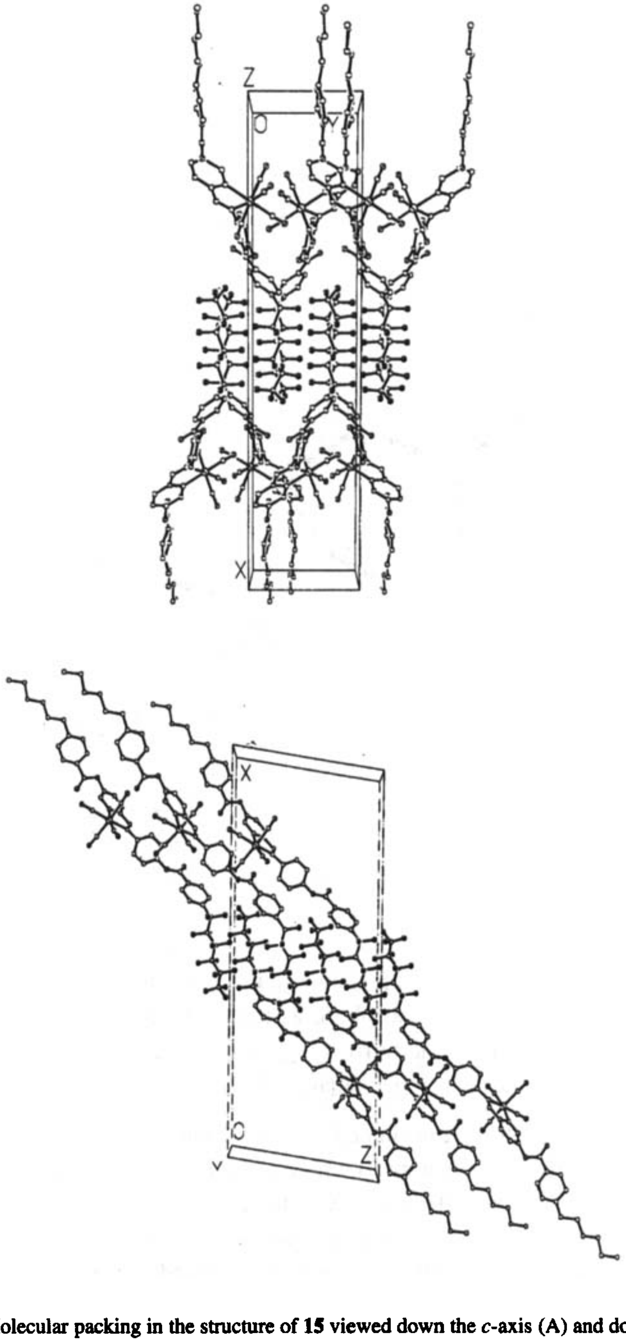


FIGURE 9 Molecular packing in the structure of **15** viewed down the *c*-axis (A) and down the *b*-axis (B)

hydrocarbon terminal chain and those with a perfluoroalkyl chain. In the former case, the intermediates are either non-mesomorphic (**5** and **8**) or show a nematic phase close to ambient temperature (**6**). However, in all of the latter compounds, the crystal phase is stabilised and the mesophase is stabilised greatly which is directly attributable to the presence of the perfluoroalkyl chain. Thus, the attractive interactions between these chains clearly contribute positively to the anisotropic dispersion forces stabilising both crystal phase and mesophase.

TABLE III Thermal data for the intermediates

m	*Transition*	*T/°C*	$\Delta H/kJ\ mol^{-1}$	$\Delta S/J\ K^{-1}\ mol^{-1}$
nitro compounds				
6	Crys – I	56	26.5	80
	(N – I)	(31)	–	–
4a	Crys – S_A	82[a]	30.2	85
	S_A – I	98[a]	2.9	8
4b	Crys – S_A	98[a]	30.8	83
	S_A – I	118[a]	2.9	7
4c	Crys – S_A	93	32.6	89
	S_A – I	133	3.0	7
4d	Crys-S_A	107[a]	37.5	97
	(S_B – S_A)	(91)[a]	(5.0)	(14)
	S_A – I	155[a]	3.7	9
amines				
8	Cr – I	70.7	27.3	78
7a	Crys – S_A	135	29.6	73
	S_A – I	148	3.3	8
7b	Crys – S_A	150	34.5	82
	S_A – I	159	4.1	9
7c	Crys – S_A	152	31.3	74
	S_A – I	170	3.8	8
7d	Crys – S_A	164	32.5	74
	S_A – I	184	5.2	11
aldehydes				
5	Cr – I	30[a]	9.66	32
3a	Crys – S_A	89	27.1	75
	S_A – I	101	2.3	6
3b	Crys – S_A	108	31.3	83
	S_A – I	123	2.2	6
3c	Crys – S_A	111	31.8	83
	S_A – I	137	2.7	8

a. These compounds have ben reported previously.[14]

TABLE IV Thermal data for the imine ligands

m	*Transition*	*T/°C*	*ΔH/kJ mol⁻¹*	*ΔS/J K⁻¹ mol⁻¹*
9	Crys – S_C	138	37.3	90
	(J – S_C)	(132)	(6.5)	(16)
	S_C – N	181	1.9	4
	N – I	320	2.7	4
10	Crys – S_C	190	46.3	100
	S_C – S_A	276	0.4	1
	S_A – I	350	–	–
11	Crys – S_C	182	39.3	86
	S_C – S_A	247	0.1	0
	S_A – I	350	12.8	20
12a	Crys – S_C	239	48.6	36
	S_C – Cub	268	2.4	5
	Cub – I	310	5.2	9
12b	Crys – S_C	240	50.5	98
	S_C – Cub	263	2.6	5
	Cub – I	317	5.8	10
12c	Crys – S_C	244	43.7	85
	S_C – Cub	254	2.3	4
	Cub – I	320	3.5	6
12d	Crys – Cub	253	76.5	146
	Cub – I (dec)	329	–	–

In looking at the mesomorphism of the imines (Table IV), we will first deal with **9** which possesses two terminal hexyl chains. This compound shows mesomorphism which is rather typical of other ligands of this type which we have investigated and melts to a S_C phase at 138 °C which gives way to a wide-range nematic phase at 181 °C which eventually clears at 320 °C. In addition, there is a monotropic J phase at 132 °C which was identified both by optical texture and by analogy with our earlier studies on related ligands. [7d] In compounds **10**, one perfluorohexyl chain has been introduced at the *C*-end (with respect to the imine) of the molecule while in **11**, the perfluorinated chain is found at the *N*-end (with respect to the imine) of the molecule. Both compounds show a S_A and S_C phase with the latter being slightly more stable in **10**, and while the transition temperatures are broadly similar in the two compounds, they are at higher temperatures than in **9**, with melting points around 180–190 °C and the S_C phase persisting to 250–270°C.

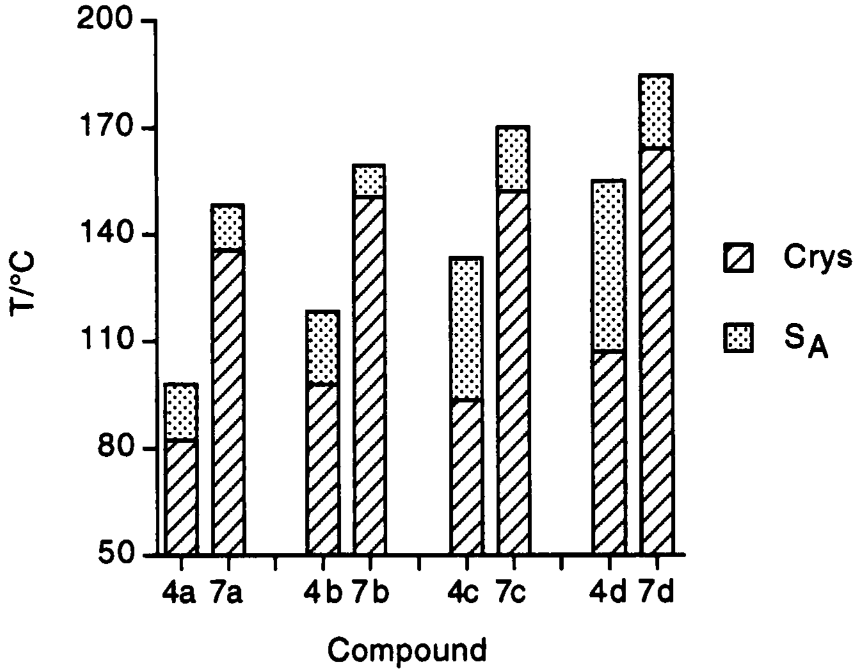


FIGURE 10 Comparsion of the mesomorphism for the nitro and amino intermediates

However, when we consider the mesomorphism of the four ligands which bear two perfluoroalkyl chains, we find rather intriguing behaviour. Thus, **12a** to **12c** melt at around 240 °C to give a S_C phase identified by its classical schlieren texture. However, on further heating, a transition occurs at 250–270 °C and the birefringent texture disappears and the sample becomes non-birefringent and viscous. Furthermore, the non-birefringence grows in across the S_C phase with sharp, square edges. At temperatures around or just above 320 °C, the sample loses its high viscosity and becomes fluid once more, although the birefringence does not return. On cooling, the high viscosity is reestablished and eventually the schlieren texture of the S_C re-appears from the non-birefringent sample. Such behaviour is entirely consistent with the formation of a cubic mesophase and this is discussed in detail below. For **12d**, the behaviour was a little different in that the crystal melted and gave way directly to the cubic phase (something we have observed before)[16] which persisted to 329 °C where it cleared with decomposition.

Mesomorphism of the Complexes

Thermal data for these complexes are collected in Table V. Let us first deal with complex **13** in which the ligand has two hexyl terminal chains. As might be expected from our previous studies, this complex showed only a nematic phase with a clearing temperature lower than that of the ligand. However, when we come to consider the complexes of the fluorinated ligands (**14**, **15**, **16a-d**), the picture changes and all of these complexes show a S_A phase irrespective of whether the ligand has one or two perfluoroalkyl chains. The first, important conclusion is that we now know that the complexes *will* form a S_A phase, although clearly, the driving force we have had to provide has been quite substantial. It is also of interest to note that the S_A phase is seen with complexes **14** and **15** where there is only one perfluoroalkyl chain.

TABLE V Thermal data for the rhenium complexes

m	*Transition*	*T/°C*	*ΔH/kJ mol⁻¹*	*ΔS/J K⁻¹ mol⁻¹*
13	Crys – N	129	25.3	61
	N – I	167	1.5	3
14	Crys – S_A (dec)	190	44.4	97
15	Crys – S_A (dec)	171	24.6	56
16a	Crys – S_A (dec)	212	51.4	105
16b	Crys – S_A (dec)	206	–	–
16c	Crys – S_A (dec)	209	–	–
16d	Crys – S_A (dec)	220	–	–

As far as the thermal behaviour is concerned, the only trend which can be seen is in melting point which increases steadily with increasing terminal chain length in the complexes with two perfluoroalkyl chains. However, the melting points for these complexes (**16a-d**) are relatively high at over 200 °C and while it is straightforward to see that they form a S_A phase, the materials decompose rather quickly at these elevated temperatures.

One of the interesting points to consider in thinking about these materials is what the S_A phase might look like in terms of the packing of the molecules, as the significant perturbation of the $Re(CO)_4$ group would probably act to prevent the molecules lining up too easily side by side. This is illustrated in Figure 11 which shows a space-filling model of two molecules of **15** side by side and indicates that the molecules would not be able to approach so closely together and so a side-to-side separation of more than 4.5 Å would be expected. However, another possibility could be that the layers are interdigitated which would more

FIGURE 11 Space-filling model of **15**

naturally allow space for the Re(CO)$_4$ groups as indicated in Figure 12, although there is still a good deal of free volume associated with such an arrangement. Unfortunately, the fact that the materials decompose upon entering the S$_A$ phase precludes a structural study by X-rays and so for now, we may only speculate.

On the Formation of the Cubic Phase in the Ligands

While it is interesting that we have been able to promote a S$_A$ phase in what are clearly strongly nematogenic metal complexes, perhaps the most interesting point in the paper is the observation of the cubic phase in the ligands with two perfluorinated chains. Cubic phases formed in simple calamitic mesogens bear-

FIGURE 12 Schematic diagram to show possible packing arrangements in the mesophase of the complexes

ing perfluorinated chains have not previously been observed and so it is instructive to consider why they might form.

Cubic phases are relatively well known in the mesomorphism of polycatenar mesogens where they are often observed as a sort of "halfway house" between the S_C phase seen at shorter chain lengths and the columnar phase seen at longer chain length. It is, we believe, possible to explain this behaviour simply on the basis of the interfacial curvature which exists at the aromatic/paraffinic interface using arguments such as those which would be advanced when discussing lyotropic systems. However, when more simple calamitic mesogens are considered,[17] it is possible to identify five main groups of materials which form a cubic mesophase,[1,8] namely:

i) Gray's biphenylcarboxylic acids;
ii) Demus' hydrazines;
iii) carbohydrates/diols (most of which possess two terminal chains at one end of the molecule and might possibly be classified as polycatenar if it is assumed that they dimerise);
iv) amides, all of which possess terminal 3,4-disubstituted phenyl rings;
v) silver salts (Figure 13).

What all of these species have in common is that they possess some mechanism for a lateral, intermolecular interaction either through a hydrogen bond or an ionic interaction and these arguments are developed in more details in references.[18–19] However, the ligands in the present work do not fit this criterion, at least at first look, as there are no functions in the centre of the molecule which lend themselves to such interactions. However, perhaps we are looking in the wrong place. Thus, in the examples above, we have been considering molecules with the ability to form specific, non-covalent interactions which stabilise lateral interactions. However, one way to consider these ligands with fluorinated chains is as molecules where side-to-side correlations are promoted as a result of the strong driving force for microphase separation – *i.e.* through non-specific interactions. That such interactions exist is without question as these ligands form exclusively smectic (and cubic) phases (*e.g.* **12a**) when hydrocarbon analogues (*e.g.* **9**) form smectic and nematic phases. Thus, it is possible to argue that these ligands are conceptually little different from the five classes above in that lateral arrangement is promoted – in this case by the terminal chains, giving some consistency to the arguments we have advanced. Such a model may well also be consistent with the observation of cubic phase formation in the so-called rod-coil molecules described by Lee *et al.*.[20]

Why this arrangement should lead to the formation of cubic phases is still something of a mystery. However, with an expanded working model to hand, it should be possible to identify many more ligands with cubic phases by using perfluoroalkyl chains and as the range of materials showing the phase increases, so gradually we will iterate to an enhanced understanding of the phase and hopefully a capability to predict its occurrence. Of course, such a thesis pre-supposes that the cubic phase is an entirely thermodynamic phenomenon and yet, as those who have worked with the phase know only too well, there are many kinetic features to its behaviour. The plot thickens!

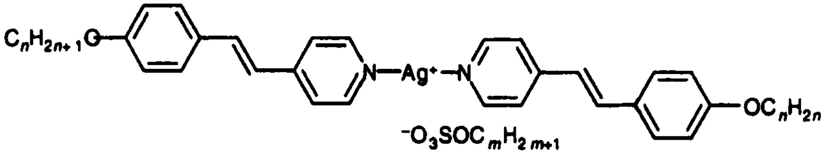


FIGURE 13 Mesomorphic silver(I) complexes which show cubic phases

EXPERIMENTAL

Elemental analyses were determined by the University of Exeter Microanalysis Service. NMR spectra were recorded on either a Bruker ACF-300 or a Bruker DRX-400 spectrometer, where the chemical shifts are reported relative to the internal standard of the deuterated solvent used. Analysis by DSC was carried out on a Perkin-Elmer DSC7 instrument using heating and cooling rates of either 5 or 10 K min^{-1}. Analysis by polarised hot-stage microscopy was carried out using an Olympus BH40 microscope equipped with a Link-Am HFS91 hot stage, TMS92 controller and LNP2 cooling unit. Solvents were purified by standard methods before use.

Perfluorohexylbenzoic acid **1a**, Perfluoroheptylbenzoic acid **1b**, Perfluorooctylbenzoic acid **1c** and Perfluorodecylbenzoic acid **1d** were synthesis according to a literature method from 1-iodoperfluorohexane, 1-iodoperfluoroheptane, 1-iodoperfluorooctane and 1-iodoperfluorodecane, respectively, purchased from Lancaster. 4-Hexylbenzoic acid **2** was obtained from Aldrich.

X-ray crystal structure determination of 15

Data were collected on a Nonius Kappa CCD area-detector diffractometer at the window of a rotating anode FR591 generator (Mo-Kα radiation, $\lambda = 0.71073$ Å; $T = 150$ K) and controlled by the Collect software package.[21] Collected images were processed using Denzo.[22] Data were corrected for absorption by using the empirical method employed in Sortav.[23] The structure was solved *via* heavy atom Patterson interpretation (DIRDIF-96)[24] and refined by full-matrix least-squares refinements on F^2 (SHELXL-97).[25] The hexylphenyl fragment C32...C43 was found to be disordered over two positions. Refinement of the alternative conformations used 77 distance restraints (SAME instruction in SHELX-97).

Preparation of 4-perfluorohexylbenzoyloxy-4′-benzaldehyde, 3a. 4

(Perfluorohexyl)benzoic acid **1a** (0.50 g, 1.14 mmol) was added to a suspension of DCC (0.28 g, 1.37 mmol), 4-hydroxybenzaldehyde (0.14 g, 1.14 mmol) and DMAP (4 mg) in CH_2Cl_2 (50 cm^3) and stirred under nitrogen for 18 h. The colourless precipitate was filtered and the filtrate evaporated to give an off-white solid. The crude product was purified by column chromatography (SiO_2, eluant: CH_2Cl_2) and the solvent evaporated to give a pure white solid. Yield : 0.49 g (88 %). Found:C, 44.0; H, 1.5. Calc. for $C_{20}H_9F_{13}O_2$, C, 44.1; H, 1.6 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (AA'XX', 2, $J = 9.0$ Hz), 7.78 (AA'XX', 2, $J = 8.5$ Hz), 7.99 (AA'XX', 2, $J = 8.5$), 8.35 (AA'XX', 2, $J = 8.9$ Hz), 10.04 (s, 1, CHO).

Compounds **3b, 3c, 3d**, and **5** were similarly prepared in yields of 68, 70, 77 and 73%, respectively. Analytical data are collected in Table VI.

TABLE VI Analytical data for the new ligands and complexes

Compound	*Yield*	*Calculated (Found)*		
		C	*H*	*N*
Imines				
9	85	79.4 (79.6)	7.3 (7.4)	2.3 (2.3)
10	84	56.9 (56.4)	3.7 (3.6)	1.7 (1.6)
11	69	56.9 (56.8)	3.7 (3.6)	1.7 (1.5
12a	83	44.3 (44.5)	1.6 (1.4)	1.3 (1.3)
12b	83	42.5 (42.2)	1.5 (1.3)	1.2 (1.1)
12c	80	41.0 (40.7)	1.4 (1.3)	1.1 (1.1)
12d	80	38.7 (38.5)	1.2 (0.9)	1.0 (0.9)
Rhenium Complexes				
13	16	58.2 (57.9)	4.8 (4.8)	1.5 (1.6)
14	36	46.0 (45.8)	2.7 (2.4)	1.2 (1.2)
15	27	46.0 (45.9)	2.7 (2.4)	1.2 (1.2)
16a	53	38.1 (37.7)	1.2 (1.0)	1.0 (1.0)
16b	30	37.1 (36.7)	1.1 (0.8)	1.0 (1.0)
16c	37	36.3 (36.2)	1.0 (1.0)	0.9 (0.9)
16d	17	34.8 (34.5)	0.9 (0.7)	0.8 (0.8)

Preparation 4-perfluorohexylbenzoyloxy-4′-nitrobenzene, 4a

4-(Perfluorohexyl)benzoic acid **1a** (0.80 g, 1.82 mmol) was added to a suspension of DCC (0.45 g, 2.18 mmol), *p*-nitrophenol (0.25 g, 1.82 mol) and DMAP (5 mg) in CH_2Cl_2 (50 cm^3) and stirred under nitrogen for 18 h. The precipitate was filtered and the solvent evaporated to give a yellow powder. The crude product was purified by column chromatography (SiO_2, eluant: CH_2Cl_2) and the solvent evaporated to give a pure white powderl.. Yield: 0.87 g (85 %). Found: C, 40.4; H, 1.3; N, 2.3. Calc. for $C_{19}H_8F_{13}NO_4$, C, 40.6; H, 1.4; N, 2.5 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (AA′XX′, 2, *J* = 9.0 Hz), 7.79 (AA′XX′, 2, *J* = 8.4 Hz), 8.35 (2 AA′XX′ overlapping, 4, *J* = 9.0 Hz).

Compounds **4b, 4c, 4d** and **6** were similarly prepared in yields of 69, 82, 50 and 82 %, respectively.

Preparation 4-perfluorohexylbenzoyloxy-4′-aniline, 7a

In a Fischer-Porter bottle, 4-(perfluorohexyl)benzoyloxy-4′-nitrobenzene **4a** (0.20 g, 0.35 mmol) is dissolved in a mixture of THF and ethanol (50 cm^3 2:3) and a few mg of 10 % palladium on activated carbon is added. The flask was sealed under 20 psi H_2 pressure and the solution was stirred overnight. The solution was filtered on a plug of celite, the solvent was removed. The crude product was purified by column chromatography (SiO_2, eluant: ether/hexane, 4:1) and the solvent evaporated to give a pure white powder. Yield: 0.19 g (100 %). Found: C, 42.9; H, 1.8; N, 2.5. Calc. for $C_{19}H_{10}F_{13}NO_2$, C, 42.9; H, 1.9; N, 2.6 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.69 (br.s. 2, NH_2), 6.72 (AA′XX′, 2, *J*= 8.9 Hz), 7.01 (AA′XX′, 2, *J* = 8.9 Hz), 7.74 (AA′XX′, 2, *J* = 8.4 Hz), 8.32 (AA′XX′, 2, *J* = 8.7 Hz).

Compounds **7b, 7c, 7d** and **8** were similarly prepared in yields of 70, 77, 88 and 89 %, respectively.

Preparation of the imines

Preparation of 10

To a suspension of 4-hexylbenzoyloxy-4′-benzaldehyde **5** (0.175 g, 0.56 mmol) 4-(perfluorohexyl)benzoyloxy-4′-aniline **7a** (0.300 g, 0.56 mmol) in ethanol (40 cm^3, absolute) were added a few drops of acetic acid (glacial). The mixture was stirred overnight at room temperature. The solid was filtered, crystallised from CH_2Cl_2 / hexane and dried to yield a pure off-white solid. Yield 0.32 g (69 %). ^{1}H NMR (400 MHz, CD_2Cl_2) δ: 0.92 (t, 3, J_{HH} = 7.0 Hz, CH_3), 1.36 (m, 6, 3 CH_2), 1.68 (m, 2, CH_2), 2.75 (t, 2, J_{HH} = 7.0, CH_2), 7.27 (AA′XX′, 2, *J*= 8.4 Hz), 7.33

(AA'XX', 2, $J = 8.0$ Hz), 7.37 (AA'XX', 2, $J = 8.0$ Hz), 7.41 (AA'XX',4, $J = 8.8$ Hz), 7.82 (AA'XX',4, $J = 8.4$ Hz), 8.05 (AA'XX', 2, $J = 8.8$ Hz), 8.12 (AA'XX', 2, $J = 8.0$ Hz), 8.57 (s, 1, C<u>H</u>=N).

Imines **9, 11** and **12a-d** was similarly prepared in yields of 85 and 84, 83, 83, 80 and 80% respectively, except note that **12a-d** were not purified by crystallisation, rather by washing with CH_2Cl_2 and then hexane to give samples which were insoluble in standard NMR solvents.

Preparation of the rhenium(I) complexes

Preparation of complex 14

To a suspension of imine **10** (50 mg, 0.043 mmol) in toluene (20 cm^3) was added pentacarbonylmethylrhenium(I) (16 mg, 0.047 mmol). The reaction mixture was stirring at reflux for 20 hours under a nitrogen atmosphere and then cooled to room temperature and the solvent removed. The yellow solid was dissolved in $CH_2Cl_2$and purified by column chromatography on alumina with CH_2Cl_2 as eluant. The solution was concentrated and hexane was added to give the pure yellow solid. Yield 0.34 g (53 %). NMR (400 MHz, CD_2Cl_2) δ: 0.92 (t, 3, $J_{HH} = 7.0$ Hz, CH_3), 1.35 (m, 6, 3 CH_2), 1.69 (m, 2, CH_2), 2.75 (t, 2, $J_{HH}= 7.8$ Hz, CH_2), 7.12 (dd, 1, $^3J_{HH}= 8.0$ Hz, $^4J_{HH} = 4.0$ Hz, Hb), 7.38 (3 AA'XX' overlapping, 6), 7.82 (d, 1, $^3J_{HH} = 8.4$ Hz, Ha), 7.85 (AA'XX', 2, $J = 8.4$ Hz), 7.85 (d overlapping with AA'XX', 1, Hc), 8.13 (AA'XX', 2, $J = 8.4$ Hz), 8.37 (AA'XX', 2, $J = 8.4$ Hz), 8.68 (s, 1, C<u>H</u>=N).

Rhenium complexes **13** and **15** were similarly prepared in yields of 16 and 36 % respectively.

Preparation of complex 16a

To a suspension of imine **12a** (55 mg, 0.076 mmol) in toluene (20 cm^3) was added pentacarbonylmethylrhenium(I) (57 mg, 0.167 mmol). The reaction mixture was stirring under reflux for 20 hours, under a nitrogen atmosphere and then was cooled to room temperature and the solvent removed. The yellow solid was dissolved in ethyl acetate and purified by column chromatography on alumina with ethyl acetate as eluant. The solution was concentrated and hexane was added to give the pure yellow solid. Yield 0.34 g (53 %). ^{1}H NMR (400 MHz, CD_2Cl_2)) δ: 7.11 (dd, 1, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 4.0$ Hz, Hb), 7.41 (2 AA'XX' overlapping, 2), 7.82 (AA'XX', 2, $J = 6.4$ Hz), 7.86 (d, 1, $^3J_{HH} = 6.4$ Hz, Ha), 7.87 (d, 1, $^3J_{HH} = 4.4$ Hz, Hc), 8.38 (AA'XX', 2, $J = 8.0$ Hz), 7.39 (AA'XX', 2, $J = 8.0$ Hz), 8.68 (s, 1, C<u>H</u>=N).

Rhenium complexes **16b, 16c** and **16d** were similarly prepared in yields of 30, 37 and 17 %, respectively.

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