Synthesis and Liquid-Crystalline Properties of Diazabutadiene Complexes of Rhenium(I)

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New *N,N′*-bis(4-((4-alkoxybenzoyl)oxy)phenyl)-1,4-diaza-1,3-butadiene (L) ligands, obtained by condensation of 4-((alkoxybenzoyl)oxy)anilines and glyoxal, were complexed to different $[ReX(CO)_3]$ fragments to give the complexes $[ReX(L)(CO)_3]$ (X = Cl, Br, I) and $[Re(CF_3SO_3)(L)(CO)_3]\cdot THF$. The chloro and bromo complexes were obtained by direct reaction of the ligands with $[ReX(CO)_5]$ (X = Cl, Br), while the iodo and triflato derivatives were obtained *via* metathesis of the chloro or bromo precursors with potassium iodide or silver triflate respectively. The liquid-crystalline behavior of the ligands and the related rhenium complexes has been studied by means of optical microscopy, differential scanning calorimetry, and small angle X-ray diffraction. Nematic and smectic C phases were observed when the coordinated counteranions were Cl, Br, and I, respectively; the triflato derivatives were not mesomorphic.

Introduction

For several years, the mesomorphic properties of metal-containing liquid crystals[1] have mostly been associated with square planar or linear coordination at the metal center. This seemed to be an essential requisite to reproduce the anisotropic shape of conventional organic mesogens and therefore to obtain mesophases. Certainly, this approach led to the synthesis of a large variety of liquid-crystalline complexes and defined some structural criteria necessary to obtain low melting materials, for example introducing structural asymmetry. Typical examples are the lower transition temperatures obtained for the P-shaped palladium complexes in comparison with H-shaped analogues,[1b] replacing hard coligands with softer ones,[2] increasing the number of hydrocarbon tails by analogy with polycatenar organic mesogens,[3] and introducing one or more chiral centers in the periphery of the molecules.[4] These developments allowed the study of the peculiar physical properties[5] of metal-containing liquid crystals (a combination of the underlying properties of the mesophases and of the metal contribution in terms of color, polarizability, magnetism, electronic properties, chirality, redox behavior) even if the complexes remained within the range of transition metals with a d^8-d^{10} configuration.

Notable examples of rodlike, metal-containing liquid crystals based on penta- or hexacoordination were vanadyl[6] or ferrocene-based metallomesogens.[7] An important turning point in the understanding of the relation between molecular structure and mesomorphism in metal-containing liquid crystals was the discovery of liquid-crystalline properties in octahedral metal complexes. For example, columnar thermotropic mesophases were observed in tris(β-diketonato)iron(III) systems[8] and metal tricarbonyl complexes of 1,4,7-triazacyclononanes.[9] Thermotropic, calamitic mesophases (i.e. mesophases derived from rodlike molecules) of octahedral species were observed for the first time by us in Mn^I and Re^I complexes of orthometalated imines (Figure 1).[10]

Our orthometalated Mn and Re systems may be considered alongside Deschenaux's ferrocene systems[7] because the structural perturbation (the $M(CO)_4$ group and the ferrocene unit respectively) is found at the center of the molecule. In both cases, it was observed that at least four aromatic rings in the organic backbone were necessary to preserve the overall molecular anisotropy and therefore obtain calamitic mesophases (Figure 2).

Having shown that octahedrally-based, rodlike liquid crystals were possible, we were keen to extend the scope of such systems by the synthesis of mesomorphic diazabutadienes[11] (Figure 3), and their related metal complexes in order to find new metal−ligand combinations for octahedral metallomesogens and to achieve a more general understanding of how ligands can be arranged around a high coordination number metal center in order to promote liquid-crystalline behavior.

Transition-metal complexes of diazabutadienes, which, along with bipyridine and pyridinecarbaldimines, belong to the family of α-diimines, have been widely investigated.[12] They play an important rôle in homogeneous catalysis. For example, iron diazabutadiene complexes are effective as catalysts for the cyclodimerization of 1,3-dienes;[13] ruthenium diazabutadienes

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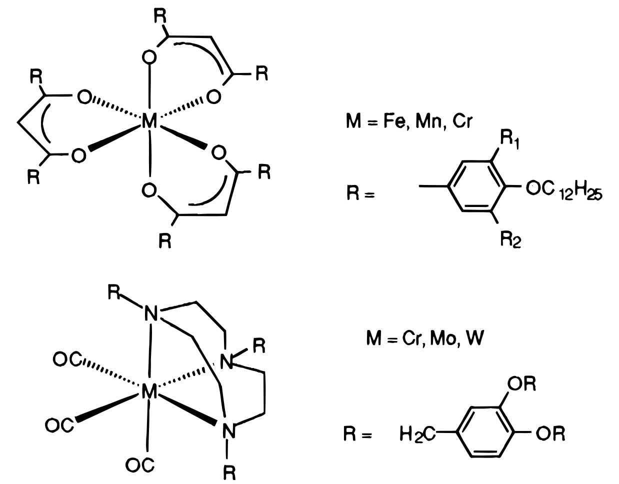

Figure 1. Octahedral-based metal-containing liquid crystals showing columnar mesophases.

were used as catalysts in the hydrogenation, hydrosilation, and isomerization of alkenes,[14] and complexes of Ni,[15] Rh,[16] and Pd[17,18] were used as catalysts for oligomerization and hydrogenation processes.

Halotricarbonyl(α-diimine)rhenium complexes have been extensively studied because they are efficient photosensitizers for energy- and electron-transfer.[19] Luminescence properties have been detected in *fac*-[ReX(α-diimine)(CO)$_3$] complexes where X can be varied from the simple halo and cyano group[19] to organic ligands such as pyridine[19] and acetylide.[20]

Diazabutadienes have never been used as *building blocks* for mesogenic complexes and, as far as α-diimines are concerned, only few papers reporting the liquid-crystalline thermotropic properties of ligands containing the bipyridine[21] and pyridinecarbaldimine unit[22] have been reported. Some simple, two-ring diazabutadienes were reported at the beginning of the century by Vorländer.[23]

We have previously reported[11] our initial findings that complexes of diazabutadienes with [ReBr(CO)$_3$] were mesomorphic. Now, in order to extend the range of this work, we wish to present the results of the synthesis of a family of such ligands and their complexes with various [ReX(CO)$_3$] groups.

Results and Discussion

Synthesis. The ligands were obtained as previously described by us,[11] except that the condensation reaction between the ((4-alkoxybenzoyl)oxy)anilines and glyoxal was better achieved using a mixture of dry THF and absolute ethanol as solvent. The diamagnetic complexes, *fac*-[ReBr(L)(CO)$_3$] and *fac*-[ReCl(L)(CO)$_3$], were easily obtained by reacting the *N,N′*-bis(4-((4-alkoxybenzoyl)oxy)phenyl)-1,4-diaza-1,3-butadiene (L) with bromopentacarbonylrhenium(I) or chloropentacarbonylrhenium(I) in a mixture of toluene and heptane, adapting the method reported by Vrieze and co-workers.[24] All compounds were purified by crystallization from suitable solvents or by column chromatography on silica gel or neutral alumina (see Experimental Section).

The iodo complexes were obtained *via* metathesis from the *fac*-[ReCl(L)(CO)$_3$] using an excess of potassium iodide. The triflate derivatives, *fac*-[Re(CF$_3$SO$_3$)(L)(CO)$_3$]·THF(*vide infra*), were synthesized in anhydrous and anaerobic conditions either from the chloro or the bromo precursors by reaction with silver triflate. The silver cation acts as scavenger for the coordinated chloride or bromide ions, and the resultant complexes were hygroscopic when isolated. The complex is written as a solvate as evidence from ^{1}H NMR in CDCl$_3$ showed that the THF was not coordinated, although integration and elemental analysis show inclusion of exactly 1 mol of THF/mole complex. It is, however, interesting to note that in the presence of adventitious water, complexes with coordinated triflate and coordinated water can be observed by ^{1}H and ^{19}F NMR. Here, it is interesting to note that the difference in ^{19}F chemical shifts between the coordinated and ionic triflates is very small (δ 87, δ 85.6, respectively), implying that the triflate is rather weakly bound.

NMR and IR spectroscopy gave information on the stereochemistry of the complexes in solution. As already found for the bromo complexes, only one set of signals was observed in the ^{1}H NMR spectra of the chloro and iodo complexes, indicating that only facial isomers were formed. This is also in agreement with the crystal structure determination for the structurally related complexes chlorotricarbonyl(*N,N″*-diisopropylethylenediimine)rhenium(I)[25] and methyltricarbonyl(*N,N′*-diisopropylethylenediimine)rhenium(I)[26] which both displayed an octahedral geometry with C$_s$ symmetry, the three carbonyls being coordinated in a *fac* geometry. All the IR spectra showed the three characteristic bands (one strong and two of medium intensity) for the carbonyl groups in a complex with C_s symmetry (*fac*-isomer).[27] Furthermore the IR spectra of the chloro derivatives showed the characteristic band for the Re−Cl stretching ($\nu_{\mathrm{Re-Cl}} = 290$ cm^{-1});[28] this band was missing in the spectra of bromo, iodo, and triflate complexes.

The change in the nature of the halo group was reflected in the NMR spectra by the upfield shift of the singlet assigned to the imino proton of the diazabutadiene in the order Cl > Br > I (δ 8.72 (X = Cl) and δ 8.68 (X = I)) and, in the infrared spectra, by the shift of the A′ carbonyl stretching mode (assigned according to ref 24) toward lower frequencies in the order I > Br > Cl (from 1920 cm^{-1} (X = I) to 1914 (X = Cl)). These

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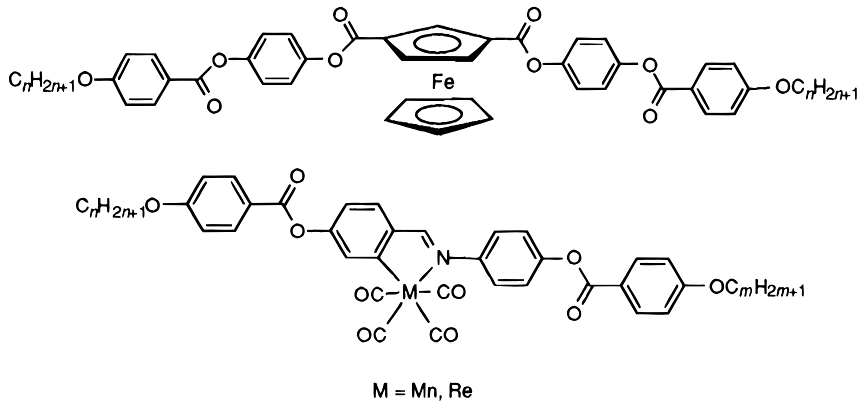


Figure 2. Hexacoordinated and octahedral-based metal-containing liquid crystals showing calamitic mesophases.

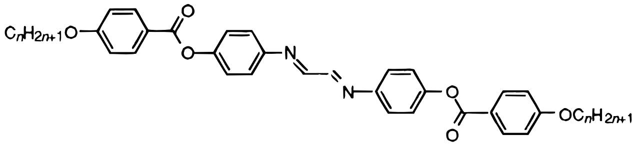
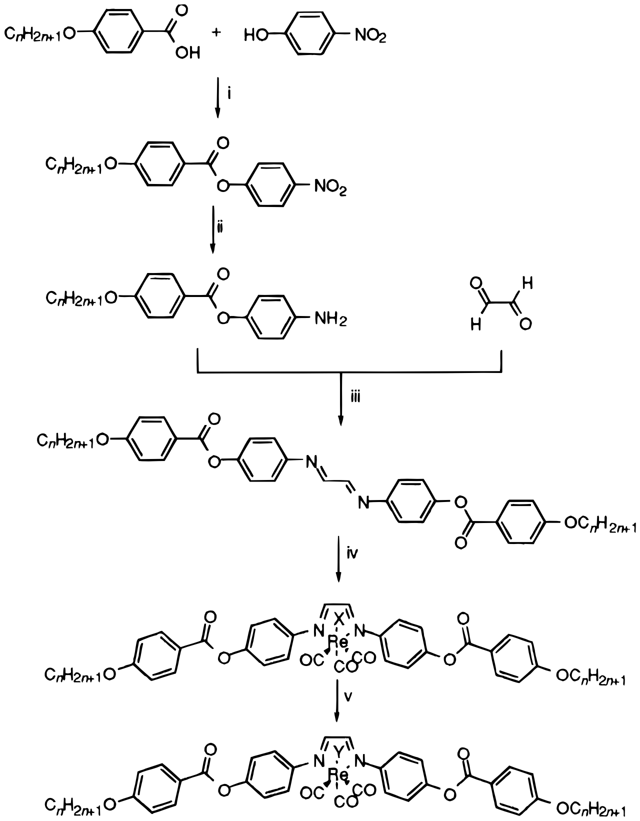


Figure 3. Structure of the *N*,*N*′-bis(4-((4-alkoxybenzoyl)oxy)phenyl)-1,4-diaza-1,3-butadienes.

Scheme 1. Synthesis of the [ReX(L)(CO)$_3$] Complexes[a]



[a] Key: (i) 1,3-dicyclohexylcarbodiimide, 4-dimethylaminopyridine, CH_2Cl_2; (ii) $SnCl_2 \cdot 2H_2O$, EtOH; (iii) THF/EtOH; (iv) [ReX(CO)$_5$], toluene, heptane (X = Cl, Br); (v) AgOTf (Y = OTf), KI (Y = I).

trends cannot be related to the decreasing electron-withdrawing nature of the substituent group, and we therefore suppose that they reflect the ability of the halides as π-donors in these systems.

Table 1. UV–Vis Spectral Data for [Re(X)L(CO)$_3$] in THF at Room Temperature (λ_{max} in nm; ϵ in M^{-1} cm^{-1})

compound	λ_{max} (ϵ)	
L_1		344 (19600)
L_2		342 (17000)
L_3		344 (21000)
[Re(Otf)(L_1)(CO)$_3$]·THF[a]		388 (15200)
[Re(Otf)(L_2)(CO)$_3$]·THF		388 (15200)
[Re(Otf)(L_3)(CO)$_3$]·THF		387 (16600)
[ReCl(L_1)(CO)$_3$]	498 (3595)	379 (11900)
[ReCl(L_2)(CO)$_3$]	497 (3892)	378 (13000)
[ReCl(L_3)(CO)$_3$]	497 (3837)	379 (12600)
[ReBr(L_1)(CO)$_3$]	504 (3779)	378 (12700)
[ReBr(L_2)(CO)$_3$]	503 (3567)	377 (12200)
[ReBr(L_3)(CO)$_3$]	503 (3607)	378 (12400)
[ReI(L_1)(CO)$_3$]	519 (2269)	370 (12500)
[ReI(L_2)(CO)$_3$]	519 (2517)	371 (13800)
[ReI(L_3)(CO)$_3$]	520 (2325)	372 (13000)

[a] Otf = $CF_3SO_3^-$.

The UV–vis absorption spectra of [ReX(L)(CO)$_3$] (X= Cl, Br, I) in THF were characterized by two bands at about 500 and 380 nm respectively. The exchange of the halo group in the order Cl, Br, and I led to a bathochromic shift of the lower energy band, while the higher energy band was quite unaffected (see Table 1). The triflato derivatives showed only the higher energy band. These data are similar to those reported by Stufkens *et al.*[29] for the related complex [ReXL′(CO)$_3$] (L′ = *p*-tolyl-1,4-diaza-1,3-butadiene, X = Br, CF_3SO_3) in which a strong resonance Raman effect on the Re–Br bond upon irradiation in the lower energy band seemed to indicate that the highest filled molecular orbital of the [ReBrL′(CO)$_3$] complexes has strongly mixed metal–halide character (the orbitals involved in the mixing being the Re-d_π and the halide-p_π) and that the lower energy transition is therefore not a pure MLCT transition. On this basis, and also on the basis of the fact that the bathochromic shift of the low-energy band in our [ReX(L)(CO)$_3$] is in accordance with the decreasing electron donor capacity of the X ligand, I > Br > Cl, we can tentatively say that also in our systems a similar mixing occurs in the MLCT state. The fact that the triflate complexes show only the high-energy band would seem to confirm this assignment.

We also measured the electronic spectra in solvents of increasing polarity (toluene, dichloromethane, tetrahydrofuran, and dimethylformamide), revealing a solvatochromic effect as expected due to the molecules possessing a polar ground state (Table 2). The red shift in absorption energies observed for the low-energy band, from dimethylformamide to toluene in order of decreasing polarity, is in accordance with the charge transfer nature of this transition.[30]

Mesomorphism. All the diazabutadiene ligands, (L_1–L_3), and the related complexes with halotricarbonylrhenium(I), [ReX(L)(CO)$_3$] (X = Cl, Br, I), were mesomorphic, but no meso-

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Table 2. UV−Vis Spectral Data for the MLCT Band for $[Re(X)L(CO)_3]$ (X = Cl, Br, I) in Different Solvents at Room Temperature (λ_{max} in nm; ϵ in $M^{-1}\ cm^{-1}$)

complex	solvent	λ_{max} (ϵ)	$\Delta E_{DMF-toluene}$ (cm^{-1})
$[ReCl(L_3)(CO)_3]$	dimethylformamide	459 (4080)	853
	tetrahydrofuran	497 (3840)	
	dichloromethane	509 (5340)	
	toluene	519 (3470)	
$[ReBr(L_3)(CO)_3]$	dimethylformamide	467 (4720)	905
	tetrahydrofuran	503 (3610)	
	dichloromethane	514 (3560)	
	toluene	527(4490)	
$[ReI(L_3)(CO)_3]$	dimethylformamide	495 (3240)	916
	tetrahydrofuran	520 (2330)	
	dichloromethane	533 (2960)	
	toluene	546 (2710)	

Table 3. Mesomorphic Behavior of $[ReX(L)(CO)_3]$ Complexes (X = Cl, Br, I)[a]

compound	transition	*T* (°C)	Δ*H* (kJ mol^{-1})
L_1[§]	C−S_C	138.0	33.62
n = 8	S_C−N	154.0	1.78
	N−d	215.0[d]	
L_2[§]	C−S_C	123.0	35.9
n = 10	S_C−N	184.0	*b*
	N−d	235.0[d]	
L_3[§]	C−S_C	126.0	39.2
n = 12	S_C−N	227.0	*b*
	N−d	250.0[d]	
$[ReCl(L_1)(CO)_3]$	C−C′	167.5	28.5
	C′−N	189.9	35.1
	N−I	269.0	*b*
$[ReCl(L_2)(CO)_3]$	C−C′	137.1	29.0
	C′−N	193.5	39.6
	N−I	258.0	*b*
$[ReCl(L_3)(CO)_3]$	C−N	189.8	25.9
	N−I	241.0	*b*
	(N−S_C)[e]	188.1	*b*
$[ReBr(L_1)(CO)_3]$[c]	C−N	194.1	75.0
	N−I	252.0	*b*
$[ReBr(L_2)(CO)_3]$[c]	C−N	181.3	81.1
	N−I	235.0	*b*
$[ReBr(L_3)(CO)_3]$	C−S_C	148.6	26.0
	S_C−N	157.0	0.3
	N−I	221.0	0.6
$[ReI(L_1)(CO)_3]$	C−N	189.4	62.7
	N−I	219.0	1.1
$[ReI(L_2)(CO)_3]$	C−I	191.8	67.3
	(I−N)	189.0	0.5
$[ReI(L_3)(CO)_3]$	C−N	144.6	18.7
	N−I	172.8	*b*

[a] C = crystal, S_C = smectic C, N = nematic, I = isotropic, d = decomposition. [b] Not detected by DSC. [c] From ref 12. [d] This temperature corresponds to the end of the decomposition process observed by microscopy; the DSC shows a broad exothermic peak. [e] Parentheses indicate a monotropic transition.

phases were observed in the triflato derivatives (Table 3). The complexes were highly colored (deep red) which sometimes made the identification of the mesophases difficult.

The ligands formed smectic C and nematic phases characterized by the typical schlieren textures with transition bars observed at transitions from smectic C to nematic. The N−I transition was accompanied by a rapid decomposition which prevented the formation of mesophases on cooling. The mesomorphic metal complexes were more thermally stable than the parent ligands and mesophases (nematic and smectic) were observed both on heating and on cooling (see Table 3). However, in the chloro derivatives, the clearing temperatures tended to be lower (10−20 °C) after one thermal cycle, indicating a slight decomposition due to the very high clearing point (241 °C for *n* = 12; 269 °C for *n* = 8); the bromo and the iodo complexes were stable over several heating and cooling cycles. Curiously, the nematic phases observed in the chloro complexes (see Table 3) had a strong tendency to show homeotropic textures (completely extinguished under crossed polarisers) on cooling from the isotropic liquid, while the bromo and iodo complexes showed threaded and schlieren nematic textures.

The nematic mesophase was the only phase observed in the octyloxy and decyloxy homologues, irrespective of the halo group, and also in the iodo complexes. The situation was somewhat different in the dodecyloxy derivatives. Thus, $[ReCl(L_3)(CO)_3]$ gave a monotropic S_C phase which showed only the typical four-brushes schlieren texture, in addition to the higher temperature nematic mesophase. The bromo complex, $[ReBr(L_3)(CO)_3]$, showed two enantiotropic mesophases with a very subtle change in the texture at the transition temperatures. The behavior of $[ReBr(L_3)(CO)_3]$ was, at first sight, difficult to characterize. Thus, in order to elucidate the nature of the two mesophases we made a contact preparation between $[ReBr(L_2)(CO)_3]$, which shows only a nematic mesophase, and $[ReBr(L_3)(CO)_3]$. The high-temperature mesophase of $[ReBr(L_3)(CO)_3]$ was miscible with the nematic phase seen in $[ReBr(L_2)(CO)_3]$. The low-temperature mesophase, which was not miscible with the nematic phase, showed a texture which was indicative of a layered, tilted phase, and by analogy with the chloro complexes, $[ReCl(L_3)(CO)_3]$, we were inclined to think that it was a smectic C phase.

Small-angle X-ray scattering experiments performed on the entire series of compounds confirmed the optical microscopy observation (X-ray diffraction patterns for $[ReBr(L_2)(CO)_3]$ and $[ReBr(L_3)(CO)_3]$ are reported in Figure 5 as representative examples). In the X-ray diffraction of liquid crystals, small angle signals correspond to apparent layer spacings for smectic phases, and to the apparent molecular length for nematic phases. In the high angle region, a broad peak is normally seen which reflects the molten nature of the alkyl chains (4.5 Å spacing); any information concerning symmetry within the layers is also usually found in this region. Thus, Figure 5A shows an X-ray pattern for the nematic phase of $[ReBr(L_2)(CO)_3]$ which shows a broad signal at low angle corresponding to an apparent molecular length of 55 Å, and a signal at high angle representative of the molten alkoxy chains. In Figure 5B, the low angle peak is much sharper, showing a more correlated arrangement of the molecules into layers, consistent with a smectic phase. In this way, the smectic C phases observed in $[ReCl(L_3)(CO)_3]$ and $[ReBr(L_3)(CO)_3]$, which have calculated lengths in their full elongated conformation of ∼56 Å, had layer spacings of 46 and 36 Å respectively corresponding to a tilt angle of 35 and 49°, if it is assumed that the layers are not interdigitated. These measurements were carried out at 180 and 155 °C respectively; further, the layer spacing of $[ReBr(L_3)(CO)_3]$ was found to be effectively temperature-independent in the range 150−160 °C.

Several features of these materials are noteworthy. Figure 4 shows the variation in the clearing points of the complexes (T_{NI}, or T_{Crys-I} for X = OTf) as a function of X; the decrease associated with the increase in the size of X is clearly seen and is as expected, representing the decrease in structural anisotropy with increased size of the halide. It may be that this explains the fact that only nematic phases are seen in the iodo complexes, as the iodide ligand may be so large as to prevent the lateral interactions necesary for smectic phase formation. However, the triflate group is so large that the structural anisotropy is reduced to the point where mesomorphism is suppressed. The

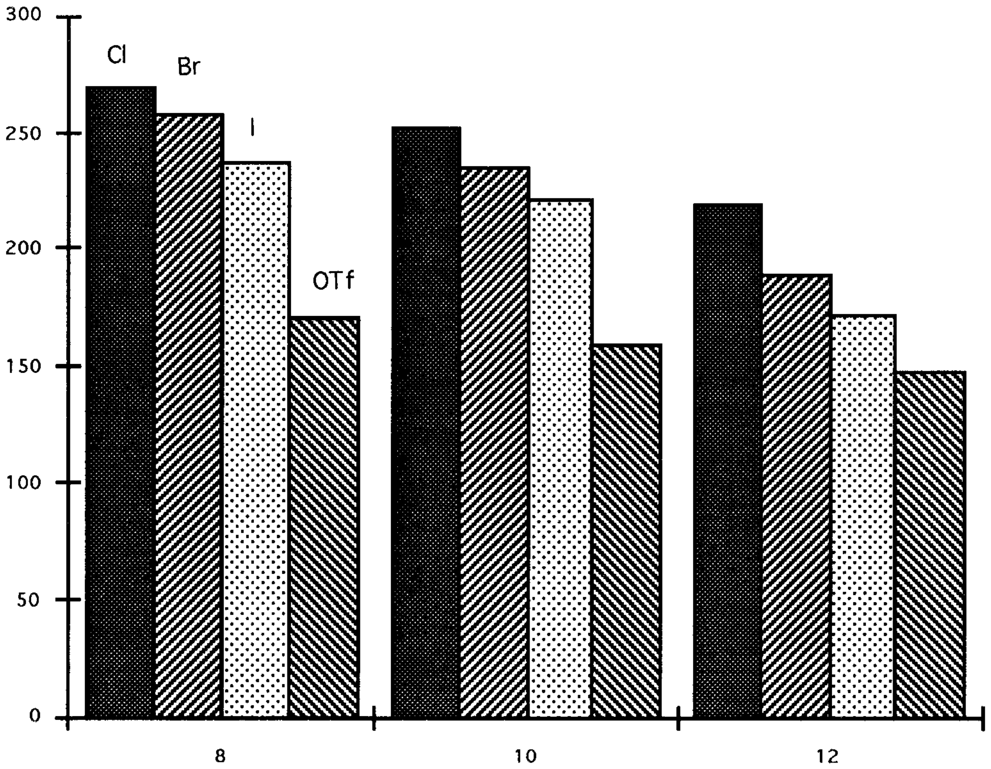

Figure 4. Plot of the clearing temperatures vs the chain length for the [ReX(L)(CO)$_3$] complexes.

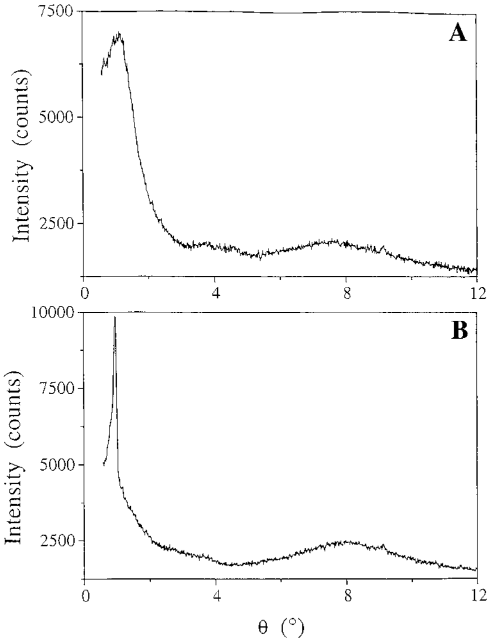

Figure 5. X-ray diffraction patterns of [ReBr(L$_2$)(CO)$_3$] (A) and [ReBr(L$_3$)(CO)$_3$] (B) complexes in the nematic and smectic C phase respectively.

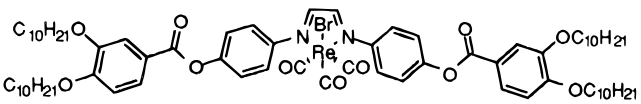

Figure 6. Structure of the bromotricarbonyl(*N,N*′-bis(4-((4-(decyloxy)benzoyl)oxy)phenyl)-1,4-diaza-1,3-butadiene)rhenium(I) complex

thermal stability of the ligands is enhanced on complexation to the Re center so that mesophases are generally seen at higher temperatures. This is particularly true for the chloro and bromo species, but complexation to the [ReI(CO)$_3$] fragment did not result in an increase of the clearing temperature when compared with those of the ligands (see Table 3).

An interesting comparison can also be made between these compounds and the Re^I and Mn^I complexes of the Schiff bases.[10] In the Schiff base complexes, the clearing points of the ligands were substantially reduced on complexation due to the presence of the bulky, lateral M(CO)$_4$ group. One would expect a similar situation for these complexes of diazabutadienes, but in these systems, the clearing point increases on complexation. If it is (reasonably) assumed that the free diazabutadiene ligands exist in a transoid form, then, on complexation, isomerization to the cisoid form must occur. This cisoid form is structurally similar to the cisoid form of 2,2′-bipyridine which has a (calculated) dipole moment of 3.8 D.[31]

In addition, there is a dipole moment associated with the Re−X bond, and so it is expected that the resulting complexes will be very dipolar in nature, leading to a stabilization of the crystal phase. The stabilization of the nematic phase is more difficult to explain at first sight, but it is possible that the dipolar nature of the complex is important here too. In, for example the cyanobiphenyl liquid crystals, the mesophases are more stable than might otherwise be expected due to the presence of antiparallel correlations of the dipolar cyanogroup. The dipole moment of these Re complexes would be expected to be across the long molecular axis, and thus a negative dielectric anisotropy is predicted for the materials. Dunmur and Toriyama[32] have shown that, in several nematic liquid crystals of negative dielectric anisotropy, local ferroelectric associations are present. It may therefore be the case that, in these systems, similar associations are present, contributing to an enhancement of nematic-phase stability. Such conclusions are consistent with our findings for mesomorphic 2,2′-bipyridines, where complexation to [ReBr(CO)$_3$] does not lead to any appreciable lowering in mesophase temperatures.[33]

We extended the series of complexes by the synthesis of a diazabutadiene ligand bearing four decyloxy chains, arranged

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in the 3- and 4-positions of the terminal phenyl rings (figure 6). Despite the fact that many so-called polycatenar mesogens of this general type are known to show mesophases,[34] none was observed in this case, a fact we attributed to a large destabilization induced by the extra chains.

Further, complexes of ligand L_1 ($n = 8$) were synthesized using the following fragments: $[Mo(CO)_4]$, $[MnBr(CO)_3]$, $PdCl_2$ and CuX (X= Cl, Br, CN). Unfortunately, the molybdenum, palladium, and copper complexes decomposed at high temperature, while the manganese complexes decomposed very quickly under natural light, being rather photosensitive.

Conclusions

Using properly tailored diazabutadiene ligands, we have synthesized new mesomorphic, octahedral halorheniumtricarbonyl complexes, $[ReX(L)(CO)_3]$, which show nematic and smectic C mesophases. Once again we demonstrated that a strong structural anisotropy of the ligand was essential to bring about calamitic mesophases in such high coordination number complexes.

The bound X group plays an important rôle in determining both the nature and the stability of the mesophases, so that increasing the size of the halo group from Cl to I lowers the transition temperatures for a given alkoxy chain length. The bulky triflate group however, which in silver complexes based on *trans*-4-(alkyloxy)-4-stilbazoles[35] had a stabilizing effect on the mesomorphism, induced a complete destabilization of the liquid-crystalline phase in this case. The nature of the halide seemed also to determine the mesophase formed, so that the formation of a layered phase (smectic C) was well tolerated for X = Cl or Br, but only a nematic phase, irrespective of the chain length, was observed when the bulkier iodo group was employed.

In contrast to other calamitic, octahedral systems which we have studied,[10] the ligand mesophases were not strongly destabilized on complexation. Indeed, not only were they thermally stabilized (with respect to decomposition) on complexation, but in some cases the mesophases appeared to be stabilized. This behavior may be attributable to the strongly dipolar nature of the complexes.

Experimental Section

Toluene and tetrahydrofuran were distilled over sodium and benzophenone prior to use, and dichloromethane was stored over calcium chloride, followed by anhydrous magnesium sulfate, followed by basic alumina, all for at least 24 h prior to use. All chemicals were used as received unless otherwise specified. Microanalyses were performed at the Department of Chemistry, University of Sheffield. Infrared spectra were recorded on Perkin-Elmer 684 (400−200 cm^{-1}) and PE1710 (4000−600 cm^{-1}) infrared spectrometers. Spectra were recorded as Nujol mulls between polythene plates, or as CH_2Cl_2 solution, or KBr disks. UV−vis spectra were recorded on a Unicam UV/vis UV4 spectrometer. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker WM250 and AM400 spectrometers; proton chemical shifts are quoted relative to an internal deuterium lock, and fluorine chemical shifts are quoted to C_6F_6. Mesomorphism was studied by heated stage polarizing microscopy using a Zeiss Labpol microscope equipped with a Linkam TH600 hot stage and PR600 temperature controller. Calorimetric measurement were performed on a Perkin-Elmer DSC 7 equipped with liquid nitrogen cooling at a rate of 5 °C min^{1}. At least two heating−cooling cycles were performed. The 4-alkoxybenzoic acids, $[Re_2(CO)_{10}]$,[36] $[ReX(CO)_5]$[37] (X = Cl, Br) were prepared as reported in the literature. In each case, one detailed preparation is given; in the related species, very similar quantites were used and so the detail is omitted in the interests of economy.

The measurement by X-rays of the periodicities were performed by using a linear monochromatic Cu Kα_1 beam obtained with a sealed-tube generator and a bent quartz monochromator. The diffraction patterns were registered on films; the cell parameter were calculated from the position of the reflection at the smallest Bragg angle, which was in all cases the most intense. Periodicities up to 90 Å could be measured and the sample temperature was controlled within ±0.3 °C.

In order to check the existence of additional reflections at very small angles, patterns were registered for all samples, by using a linear Cu Kα beam obtained with a rotating anode and passing trough a Ni filter. In the geometry used, periodicities up to 200 Å could be measured. The diffraction patterns were registered on films, and the sample temperature was controlled within ±0.3 °C.

((4-(Octyloxy)benzoyl)oxy)-4-nitrobenzene. A mixture of 4-(octyloxy)benzoic acid (5g, 0.0199 mol), 4-nitrophenol (2.8 g, 0.0199 mol), *N*,*N*′-dicyclohexylcarbodiimide (DCC) (4.10 g, 0.0199 mol), and dimethylaminopyridine (0.243 g, 0.00199 mol) in dichloromethane (80 cm^3) was stirred at room temperature for 12 h. The reaction mixture was filtered off and the solution evaporated under reduced pressure. The solid was crystallized from ethanol, filtered, and dried under vacuum. A colorless solid was obtained (6.7 g), yield 91%.

Anal. Calcd for $C_{21}H_{25}NO_5$: C, 67.9; H, 6.8; N, 3.8. Found: C, 67.7; H, 6.6; N, 3.7.

^{1}H NMR ($CDCl_3$): δ 0.90 (3H, t, CH_3−CH$_2$−, J = 6.3 Hz), 1.30 (10H, bm, CH$_3$−(CH_2)$_5$−CH$_2$−), 1.80 (2H, m, CH$_3$−(CH$_2$)$_5$−CH_2−CH$_2$−), 4.04 (2H, t, −CH_2−O−Ph, J = 6.6 Hz), 6.97 (2H, H^a, d, AA′XX′, aromatic H; J = 8.8 Hz), 8.12 (2H, H^b, d, AA′XX′, aromatic H, J = 8.8 Hz), 7.37 (2H, H^c, d, AA′XX′, aromatic H, J = 8.8 Hz); 8.30 (2H, H^d, d, AA′XX′, aromatic H, J = 8.9 Hz).

((4-(Decyloxy)benzoyl)oxy)-4-nitrobenzene was prepared similarly. Yield: 85%.

Anal. Calcd for $C_{23}H_{29}NO_5$: C, 69.1; H, 7.3; N, 3.5. Found: C, 68.8; H, 7.2; N, 3.5.

^{1}H NMR ($CDCl_3$): δ 0.87 (3H, t, CH_3−CH$_2$−, J = 6.3 Hz), 1.30 (14H, bm, CH$_3$−(CH_2)$_7$−CH$_2$−), 1.80 (2H, m, CH$_3$−(CH$_2$)$_5$−CH_2−CH$_2$−), 4.02 (2H, t, −CH_2−O−Ph, J = 6.6 Hz), 6.95 (2H, H^a, d, AA′XX′, aromatic H; J = 8.8 Hz), 8.10 (2H, H^b, d, AA′XX′, aromatic H, J = 8.8 Hz), 7.37 (2H, H^c, d, AA′XX′, aromatic H, J = 8.8 Hz), 8.30 (2H, H^d, d, AA′XX′, aromatic H, J = 8.9 Hz).

((4-(Dodecyloxy)benzoyl)oxy)-4-nitrobenzene was prepared similarly. Yield: 50%.

Anal. Calcd for $C_{25}H_{33}NO_5$: C, 70.2; H, 7.8; N, 3.3. Found: C, 69.9; H, 7.9; N, 3.1.

^{1}H NMR ($CDCl_3$): δ 0.86 (3H, t, CH_3−CH$_2$−, J = 6.3 Hz), 1.30 (18H, bm, CH$_3$−(CH_2)$_9$−CH$_2$−), 1.80 (2H, m, CH$_3$−(CH$_2$)$_5$−CH_2−CH$_2$−), 4.01 (2H, t, −CH_2−O−Ph, J = 6.6 Hz), 6.97 (2H, H^a, d, AA′XX′, aromatic H; J = 8.8 Hz), 8.12 (2H, H^b, d, AA′XX′, aromatic H, J = 8.8 Hz), 7.38 (2H, H^c, d, AA′XX′, aromatic H, J = 8.8 Hz), 8.29 (2H, H^d, d, AA′XX′, aromatic H, J = 8.9 Hz).

((4-(Octyloxy)benzoyl)oxy)-4-aniline. To a suspension of ((4-(octyloxy)benzoyl)oxy)-4-nitrobenzene (5 g, 0.0135 mol) in ethanol (100 cm^3, absolute) were added 5 equiv of $SnCl_2{\cdot}2H_2O$ (15.2 g, 0.0673 mol). The mixture was refluxed for 6 h, cooled to room temperature, and poured onto ice. The pH was adjusted to 8 using NaOH (2 mol L^{-1}) and the colorless mixture was extracted with ethyl acetate (200 cm^3). The ethyl acetate layer was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The brownish solid was crystallized from an ethanol−water mixture (4:1 v/v), filtered, and vacuum dried. The whitish solid obtained after recrystallization is 2.5 g, yield 54%.

Anal. Calcd for $C_{21}H_{27}NO_3$: C, 73.9; H, 8.0; N, 4.1. Found: C, 73.7; H, 8.0; N, 4.1.

^{1}H NMR ($CDCl_3$): δ 0.76 (3H, t, CH_3−CH$_2$−, J = 6.3 Hz), 1.30 (10H, bm, CH$_3$−(CH_2)$_5$−CH$_2$−), 1.80 (2H, m, CH$_3$−(CH$_2$)$_5$−CH_2−CH$_2$), 4.00 (2H, t, −CH_2−O−Ph−, J = 6.6Hz), 6.94 (2H, H^a, m, AA′XX′, aromatic H, J = 8.8 Hz), 8.08 (2H, H^b, d, AA′XX′, aromatic

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H, $J = 8.8$ Hz), 6.94 (2H, H^c, m, AA′XX′, aromatic H); 6.69 (2H, H^d, d, AA′XX′, aromatic H, $J = 8.1$ Hz), 3.58 (2H, bs, $-Ph-NH_2$).

((4-(Decyloxy)benzoyl)oxy)-4-aniline was prepared similarly. Yield: 47%

Anal. Calcd for $C_{23}H_{31}NO_3$: C, 74.8; H, 8.5; N, 3.8. Found: C, 74.6; H, 8.6; N, 4.1%.

^{1}H NMR ($CDCl_3$): δ 0.76 (3H, t, CH_3-CH_2-, $J = 6.3$ Hz); 1.30 (14H, bm, $CH_3-(CH_2)_7-CH_2-$), 1.80 (2H, m, $CH_3-(CH_2)_5-CH_2-CH_2$), 4.00 (2H, t, $-CH_2-O-Ph-$, $J = 6.6$Hz), 6.94 (2H, H^a, m, AA′XX′, aromatic H, $J = 8.8$ Hz), 8.08 (2H, H^b, d, AA′XX′, aromatic H, $J = 8.8$ Hz), 6.94 (2H, H^c, m, AA′XX′, aromatic H), 6.69 (2H, H^d, d, AA′XX′, aromatic H, $J = 8.1$ Hz), 3.58 (2H, bs, $-Ph-NH_2$).

((4-(Dodecyloxy)benzoyl)oxy)-4-aniline was prepared similarly. Yield: 58%

Anal. Calcd for $C_{25}H_{35}NO_3$: C, 75.; H, 8.9; N, 3.5. Found: C, 74.8; H, 9.0; N, 3.5.

^{1}H NMR ($CDCl_3$): δ 0.76 (3H, t, CH_3-CH_2-, $J = 6.3$ Hz), 1.30 (18H, bm, $CH_3-(CH_2)_9-CH_2-$), 1.80 (2H, m, $CH_3-(CH_2)_5-CH_2-CH_2$), 4.00 (2H, t, $-CH_2-O-Ph-$, $J = 6.6$ Hz), 6.94 (2H, H^a, m, AA′XX′, aromatic H, $J = 8.8$ Hz), 8.08 (2H, H^b, d, AA′XX′, aromatic H, $J = 8.8$ Hz), 6.94 (2H, H^c, m, AA′XX′, aromatic H), 6.69 (2H, H^d, d, AA′XX′, aromatic H, $J = 8.1$ Hz), 3.58 (2H, bs, $-Ph-NH_2$).

***N,N′*-Bis(4-((4-(octyloxy)benzoyl)oxy)phenyl)-1,4-diaza-1,3-butadiene (L_1).** In a typical preparation, ((4-(octyloxy)benzoyl)oxy)-4-aniline (2.9 mmol) was dissolved in dry THF (20 cm^3) and a warm ethanolic solution of monohydrated glyoxal (1.4 mmol in 30 cm^3, absolute) was added. The solution was stirred at room temperature for 4 days. After this period of time a pale yellow solid was filtered off, washed with diethyl ether, recrystallized from dichloromethane−diethyl ether, and vacuum dried. Yield: 841 mg, 85%.

Anal. Calcd for $C_{44}H_{52}N_2O_6$: C, 75.0; H, 7.4; N, 4.0. Found: C, 74.4; H, 7.4; N,3.9.

IR (KBr): ν_{CO} 1730 cm^{-1}, $\nu_{C=N}$ 1608 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 0.88 (6H, t, CH_3-CH_2-, $J = 6.6$ Hz), 1.30 (20H, bm, $CH_3-(CH_2)_5-CH_2-$), 1.85 (4H, m, $CH_3-(CH_2)_5-CH_2-CH_2-$), 4.04 (4H, t, $-CH_2-O-Ph-$, $J = 6.9$ Hz), 6.98 (4H, H^a, d, AA′XX′, aromatic H, $-CH_2-O-Ph-CO_2-$, $J = 9.4$ Hz), 8.13 (4H, H^b, d, AA′XX′, aromatic H, $J = 8.8$ Hz), 7.37 (4H, H^c, d, AA′XX′, aromatic H, $J = 8.8$ Hz), 7.27 (4H, H^d, d, AA′XX′, aromatic H, $J = 8.8$ Hz), 8.41 (2H, s, $-CH{=}N-$).

^{13}C NMR ($CDCl_3$): δ 159.72 ($-C{=}N-$), 164.86 ($-CO_2-$).

***N,N′*-Bis(4-((4-(decyloxy)benzoyl)oxy)phenyl)-1,4-diaza-1,3-butadiene, L_2,** was prepared similarly. Yield: 59%.

Anal. Calcd for $C_{48}H_{60}N_2O_6$: C, 75.8; H, 7.9; N, 3.7. Found: C, 76.0; H, 8.1; N, 3.2.

IR (KBr): ν_{CO} 1730 cm^{-1}, $\nu_{C=N}$ 1608 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 0.85 (6H, t, CH_3-CH_2-, $J = 6.6$ Hz), 1.30 (28H, bm, $CH_3-(CH_2)_7-CH_2-$), 1.85 (4H, m, $CH_3-(CH_2)_5-CH_2-CH_2-$), 4.02 (4H, t, $-CH_2-O-Ph-$, $J = 6.9$ Hz), 6.94 (4H, H^a, d, AA′XX′, aromatic H; $-CH_2-O-Ph$-CO_2-, $J = 9.4$ Hz), 8.09 (4H, H^b, d, AA′XX′, aromatic H, $J = 8.8$ Hz), 7.35 (4H, H^c, d, AA′XX′, aromatic H, $J = 8.8$ Hz), 7.26 (4H, H^d, d, AA′XX′, aromatic H, $J = 8.8$ Hz), 8.41 (2H, s, $-CH{=}N-$).

^{13}C NMR ($CDCl_3$): δ 159.70 ($-C{=}N-$), 164.86 ($-CO_2-$).

***N,N′*-Bis(4-((4-(dodecyloxy)benzoyl)oxy)phenyl)-1,4-diaza-1,3-butadiene, L_3,** was prepared similarly. Yield: 66%.

Anal. Calcd for $C_{52}H_{68}N_2O_6$: C, 76.4; H, 8.4; N, 3.4. Found: C, 76.3; H, 8.2; N, 3.2.

IR (KBr): ν_{CO} 1730 cm^{-1}, $\nu_{C=N}$ 1608 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 0.85 (6H, t, CH_3-CH_2-, $J = 6.6$ Hz), 1.30 (36H, bm, $CH_3-(CH_2)_9-CH_2-$), 1.85 (4H, m, $CH_3-(CH_2)_5-CH_2-CH_2-$), 4.02 (4H, t, $-CH_2-O-Ph-$, $J = 6.9$ Hz), 6.94 (4H, H^a, d, AA′XX′, aromatic H; $-CH_2-O-Ph-CO_2-$, $J = 9.4$ Hz), 8.09 (4H, H^b, d, AA′XX′, aromatic H, $J = 8.8$ Hz), 7.35 (4H, H^c, d, AA′XX′, aromatic H, $J = 8.8$ Hz), 7.26 (4H, H^d, d, AA′XX′, aromatic H, $J = 8.8$ Hz), 8.41 (2H, s, $-CH{=}N-$).

^{13}C NMR ($CDCl_3$): δ 159.72 ($-C{=}N-$), 164.86 ($-CO_2-$).

[ReBr(L_1)(CO)$_3$]. Equimolar quantities of **L_1** (100 mg, 0.142 mmol) and bromopentacarbonylrhenium (I) (57 mg, 0.142 mmol), suspended in a mixture of toluene (4 cm^3) and heptane (6 cm^3), were stirred at 80 °C for 3 h under a nitrogen atmosphere. Cooling of the red solution to room temperature gave a microcrystalline reddish-brown solid which was filtered off, dissolved in a minimum amount of dichloromethane, chromatographed on a neutral alumina column, and eluted with the same solvent. The solid obtained after evaporation of the solvent was washed with pentane (1 cm^3) and vacuum dried. Yield: 118 mg, 79%.

Anal. Calcd for $C_{47}H_{52}N_2BrO_9Re$: C, 53.5; H, 5.0; N, 2.7; Br, 7.6. Found: C, 53.5; H, 5.0; N, 2.5; Br, 7.6.

IR (CH_2Cl_2 solution) ν_{CO}: 2031 cm^{-1} (s), 1943 cm^{-1} (s), 1917 cm^{-1} (s).

^{1}H NMR ($CDCl_3$): δ 0.84 (6H, t, CH_3-CH_2-, $J = 6.6$ Hz), 1.30 (20H, bm, $CH_3-(CH_2)_5-CH_2-$), 1.85 (4H, m, $CH_3-(CH_2)_5-CH_2-CH_2-$), 3.98 (4H, t, $-CH_2-O-Ph-$, $J = 6.9$ Hz), 6.98 (4H, H^a, d, AA′XX′, aromatic H; $J = 8.8$ Hz), 8.15 (4H, H^b, d, AA′XX′, aromatic H, $J = 8.8$ Hz), 7.32 (4H, H^c, d, AA′XX′, aromatic H, $J = 8.8$ Hz), 7.56 (4H, H^d, d, AA′XX′, aromatic H, $J = 9.1$ Hz), 8.72 (2H, s, $-CH{=}N-$).

^{13}C NMR ($CDCl_3$): δ 162.98 ($-C{=}N-$), 194.64 (2CO, trans to L_1), 182.23 (CO, trans to Br).

[ReBr(L_2)(CO)$_3$] was prepared similarly. Yield: 71%

Anal. Calcd for $C_{51}H_{60}N_2BrO_9Re$: C, 55.1; H, 5.4; N, 2.5; Br, 7.2. Found: C, 55.0; H, 5.2; N, 2.4; Br, 7.4.

Ir (CH_2Cl_2 solution): ν_{CO} 2031 cm^{-1} (s), 1943 cm^{-1} (s), 1917 cm^{-1}(s).

^{1}H NMR ($CDCl_3$): δ 0.84 (6H, t, CH_3-CH_2-, $J = 6.6$ Hz), 1.30 (28H, bm, $CH_3-(CH_2)_7-CH_2-$), 1.85 (4H, m, $CH_3-(CH_2)_5-CH_2-CH_2-$), 3.98 (4H, t, $-CH_2-O-Ph-$, $J = 6.9$ Hz), 6.90 (4H, H^a, d, AA′XX′, aromatic H; $J = 8.8$ Hz), 8.07 (4H, H^b, d, AA′XX′, aromatic H, $J = 8.8$ Hz), 7.32 (4H, H^c, d, AA′XX′, aromatic H, $J = 8.8$ Hz), 7.56 (4H, H^d, d, AA′XX′, aromatic H, $J = 9.1$ Hz), 8.72 (2H, s, $-CH{=}N-$).

^{13}C NMR ($CDCl_3$): δ 163.10 ($-C{=}N-$), 194.73 (2CO, trans to L_1), 182.28 (CO, trans to Br).

[ReBr(L_3)(CO)$_3$] was prepared similarly. Yield: 58%.

Anal. Calcd for $C_{55}H_{68}N_2BrO_9Re$: C, 56.6; H, 5.9; N, 2.4; Br, 6.8. Found: C, 56.6; H, 5.7; N, 2.4; Br, 7.0.

Ir (CH_2Cl_2 solution): ν_{CO} 2031 cm^{-1}(s), 1943 cm^{-1}(s), 1918 cm^{-1}(s).

^{1}H NMR ($CDCl_3$): δ 0.87 (6H, t, CH_3-CH_2-, $J = 6.6$ Hz), 1.30 (36H, bm, $CH_3-(CH_2)_9-CH_2-$), 1.85 (4H, m, $CH_3-(CH_2)_5-CH_2-CH_2-$), 3.99 (4H, t, $-CH_2-O-Ph-$, $J = 6.9$ Hz), 6.90 (4H, H^a, d, AA′XX′, aromatic H; $J = 8.8$ Hz), 8.07 (4H, H^b, d, AA′XX′, aromatic H, $J = 8.8$ Hz), 7.32 (4H, H^c, d, AA′XX′, aromatic H, $J = 8.8$ Hz), 7.56 (4H, H^d, d, AA′XX′, aromatic H, $J = 9.1$ Hz), 8.72 (2H, s, $-CH{=}N-$).

^{13}C NMR ($CDCl_3$): δ 163.18 ($-C{=}N-$), 194.73 (2CO, trans to L_1), 182.30 (CO, trans to Br).

[ReCl(L_1)(CO)$_3$]. Equimolar quantities of **L_1** (200 mg, 0.28 mmol) and chloropentacarbonylrhenium (I) (57 mg, 0.142 mmol), suspended in a mixture of toluene (8 cm^3) and heptane (12 cm^3), were stirred at 80 °C for 4 h under a nitrogen atmosphere. The red suspension was allowed to cool down and filtered off. The solid was dissolved in a minimum amount of dichloromethane and chromathographed on a neutral alumina column using dichloromethane as eluent. The brick red solid obtained after evaporation of the solvent was crystallized from dichloromethane−diethyl ether and vacuum dried. Yield: 260 mg, 89%.

Anal. Calcd for $C_{47}H_{52}N_2ClO_9Re$: C, 55.9; H, 5.2; N, 2.8; Cl, 3.5. Found: C, 56.0; H, 5.1; N, 2.7; Cl, 3.2.

IR (CH_2Cl_2 solution): ν_{CO} 2031 cm^{-1} (s), 1941 cm^{-1} (m), 1914 cm^{-1} (m).

IR (polythene plates): ν_{Re-Cl} 290 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 0.87 (6H, t, CH_3-CH_2-, $J = 6.6$ Hz), 1.30 (20H, bm, $CH_3-(CH_2)_5-CH_2-$), 1.82 (4H, m, $CH_3-(CH_2)_5-CH_2-CH_2-$), 4.04 (4H, t, $-CH_2-O-Ph-$, $J = 6.7$ Hz), 6.96 (4H, H^a, d, AA′XX′, aromatic H; $J = 9.2$ Hz), 8.11 (4H, H^b, d, AA′XX′, aromatic H, $J = 9.1$ Hz), 7.37 (4H, H^c, d, AA′XX′, aromatic H, $J = 8.8$ Hz), 7.56 (4H, H^d, d, AA′XX′, aromatic H, $J = 8.8$ Hz), 8.71 (2H, s, $-CH{=}N-$).

^{13}C NMR ($CDCl_3$): δ 163.59 ($-C{=}N-$), 195.23 (2CO, trans to L_1), 182.83 (CO, trans to Cl).

[ReCl(L_2)(CO)$_3$] was prepared similarly. Yield: 85%.

Anal. Calcd for $C_{51}H_{60}N_2ClO_9Re$: C, 57.4; H, 5.7; N, 2.6; Cl, 3.3. Found: C, 57.5; H, 5.7; N, 2.7; Cl, 3.2.

IR (CH_2Cl_2 solution): ν_{CO} 2031 cm^{-1} (s), 1941 cm^{-1} (m), 1914 cm^{-1} (m).

IR (polythene plates): ν_{Re-Cl} 290 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 0.88 (6H, t, CH_3-CH_2-, J = 6.6 Hz), 1.30 (28H, bm, $CH_3-(CH_2)_7-CH_2-$), 1.82 (4H, m, $CH_3-(CH_2)_7-CH_2-CH_2$-), 4.04 (4H, t, $-CH_2-O-Ph-$, J = 6.7 Hz), 6.97 (4H, H^a, d, AA′XX′, aromatic H; J = 9.2 Hz), 8.12 (4H, H^b, d, AA′XX′, aromatic H, J = 9.1 Hz), 7.37 (4H, H^c, d, AA′XX′, aromatic H, J = 8.8 Hz), 7.57 (4H, H^d, d, AA′XX′, aromatic H, J = 8.8 Hz), 8.71 (2H, s, $-CH{=}N-$).

^{13}C NMR ($CDCl_3$): δ 163.57 ($-C{=}N-$), 195.22 (2CO, trans to L_1), 182.85 (CO, trans to Cl).

[ReCl(L$_3$)(CO)$_3$] was prepared similarly. Yield: 74%.

Anal. Calcd for $C_{55}H_{68}N_2ClO_9Re$: C, 58.8; H, 6.1; N, 2.5; Cl, 3.2. Found: C, 58.4; H, 6.1; N, 2.4; Cl, 3.5.

IR (CH_2Cl_2 solution): ν_{CO} 2031 cm^{-1} (s), 1941 cm^{-1} (m), 1914 cm^{-1} (m).

IR (polythene plates): ν_{Re-Cl} 290 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 0.88 (6H, t, CH_3-CH_2-, J = 6.6 Hz), 1.30 (36H, bm, $CH_3-(CH_2)_9-CH_2-$), 1.82 (4H, m, $CH_3-(CH_2)_9-CH_2-CH_2-$), 4.04 (4H, t, $-CH_2-O-Ph-$, J = 6.7 Hz), 6.97 (4H, H^a, d, AA′XX′, aromatic H; J = 9.2 Hz), 8.12 (4H, H^b, d, AA′XX′, aromatic H, J = 9.1 Hz), 7.37 (4H, H^c, d, AA′XX′, aromatic H, J = 8.8 Hz), 7.57 (4H, H^d, d, AA′XX′, aromatic H, J = 8.8 Hz), 8.71 (2H, s, $-CH{=}N-$).

^{13}C NMR ($CDCl_3$): δ 163.54 ($-C{=}N-$), 195.21 (2CO, trans to L_1), 182.82 (CO, trans to Cl).

[ReI(L$_1$)(CO)$_3$]. To a solution of **[ReCl(L$_1$)(CO)$_3$]** (100 mg, 0.097 mmol) in 10 cm^3 of dry THF was added 10 equiv of KI (162 mg, 0.97 mmol). The suspension was stirred at 50 °C in the dark for 4 days and it was successively filtered on Celite. The dark red solution was evaporated under reduced pressure, and the resulting dark red solid was purified by chromathography on silica gel using dichloromethane as eluent. The first band corresponds to the iodo complex, while the second band is the unreacted chloro complex. Yield: 75%.

Anal. Calcd for $C_{47}H_{52}N_2IO_9Re$: C, 51.2; H, 4.7; N, 2.5; I, 11.5. Found: C, 51.0; H, 4.6; N, 2.6; I, 11.6.

IR (CH_2Cl_2 solution): ν_{CO} 2031 cm^{-1} (s), 1945 cm^{-1} (m), 1921 cm^{-1} (m).

^{1}H NMR ($CDCl_3$): δ 0.89 (6H, t, CH_3-CH_2-, J = 6.4 Hz), 1.30 (20H, bm, $CH_3-(CH_2)_5-CH_2-$), 1.82 (4H, m, $CH_3-(CH_2)_5-CH_2-CH_2-$), 4.05 (4H, t, $-CH_2-O-Ph-$, J = 6.4 Hz), 6.98 (4H, H^a, d, AA′XX′, aromatic H; J = 8.8 Hz), 8.14 (4H, H^b, d, AA′XX′, aromatic H, J = 8.8 Hz), 7.37 (4H, H^c, d, AA′XX′, aromatic H, J = 8.8 Hz), 7.61 (4H, H^d, d, AA′XX′, aromatic H, J = 8.8 Hz), 8.69 (2H, s, $-CH{=}N-$).

^{13}C NMR ($CDCl_3$): δ 162.36 ($-C{=}N-$), 194.03 (2CO, trans to L_1), 182.00 (CO, trans to I).

[ReI(L$_2$)(CO)$_3$] was prepared similarly. Yield: 70%.

Anal. Calcd for $C_{51}H_{60}N_2IO_9Re$: C, 52.9; H, 5.2; N, 2.4; I, 11.0. Found: C, 53.2; H, 5.3; N, 2.3; I, 11.1.

IR (CH_2Cl_2 solution): ν_{CO} 2031 cm^{-1} (s), 1945 cm^{-1} (m), 1921 cm^{-1} (m).

^{1}H NMR ($CDCl_3$): δ 0.87 (6H, t, CH_3-CH_2-, J = 6.4 Hz), 1.30 (28H, bm, $CH_3-(CH_2)_7-CH_2-$), 1.82 (4H, m, $CH_3-(CH_2)_5-CH_2-CH_2-$), 4.04 (4H, t, $-CH_2-O-Ph-$, J = 6.7 Hz), 6.97 (4H, H^a, d, AA′XX′, aromatic H; J = 8.8 Hz), 8.13 (4H, H^b, d, AA′XX′, aromatic H, J = 8.8 Hz), 7.36 (4H, H^c, d, AA′XX′, aromatic H, J = 8.8 Hz), 7.60 (4H, H^d, d, AA′XX′, aromatic H, J = 8.8 Hz), 8.68 (2H, s, $-CH{=}N-$).

^{13}C NMR ($CDCl_3$): δ 162.35 ($-C{=}N-$), 194.03 (2CO, trans to L_2), 182.00 (CO, trans to I).

[ReI(L$_3$)(CO)$_3$] was prepared similarly. Yield: 68%.

Anal. Calcd for $C_{51}H_{60}N_2IO_9Re$: C, 54.4; H, 5.7; N, 2.3; I, 10.4. Found: C, 54.7; H, 5.8; N, 2.1; I, 10.8.

IR (CH_2Cl_2 solution): ν_{CO} 2031 cm^{-1} (s), 1945 cm^{-1} (m), 1921 cm^{-1} (m).

^{1}H NMR ($CDCl_3$): δ 0.87 (6H, t, CH_3-CH_2-, J = 6.4 Hz), 1.30 (36H, bm, $CH_3-(CH_2)_9-CH_2-$), 1.82 (4H, m, $CH_3-(CH_2)_5-CH_2-CH_2-$), 4.04 (4H, t, $-CH_2-O-Ph-$, J = 6.7 Hz), 6.97 (4H, H^a, d, AA′XX′, aromatic H; J = 8.8 Hz), 8.13 (4H, H^b, d, AA′XX′, aromatic H, J = 8.8 Hz), 7.36 (4H, H^c, d, AA′XX′, aromatic H, J = 8.8 Hz), 7.60 (4H, H^d, d, AA′XX′, aromatic H, J = 8.8 Hz), 8.68 (2H, s, $-CH{=}N-$).

^{13}C NMR ($CDCl_3$): δ 162.64 ($-C{=}N-$), 194.11 (2CO, trans to L_3), 182.06 (CO, trans to I).

[Re(CF$_3$SO$_3$)(L$_1$)(CO)$_3$]·THF. The reaction was conducted under anhydrous and anaerobic conditions using the standard Schlenk technique.

To a solution of [ReBr(L$_1$)(CO)$_3$] (200 mg, 0.189 mmol) in 10 cm^3 of dry THF was added an equimolar quantity of $AgCF_3SO_3$ (48.56 mg, 0.189 mmol) previously dissolved in 5 cm^3 of dry THF. The solution was stirred at room temperature in the dark for 1 h. After this period of time the solvent was evaporated, the residue dissolved in dichloromethane and filtered on Celite. The solvent was evaporated and the orange solid dried *in vacuo* and stored on silica. Yield: 60%. Mp: 170 °C.

Anal. Calcd for $C_{52}H_{60}N_2O_{13}SF_3Re$: C, 52.2; H, 5.0; N, 2.3. Found: C, 51.8; H, 4.9; N, 2.5.

IR (CH_2Cl_2 solution): ν_{CO} 2044 cm^{-1} (s), 1953 cm^{-1} (m), 1935 cm^{-1} (m).

^{1}H NMR ($CDCl_3$): δ 0.89 (6H, t, CH_3-CH_2-, J = 6.4 Hz), 1.30 (20H, bm, $CH_3-(CH_2)_5-CH_2-$), 1.85 (4H, m, $CH_3-(CH_2)_5-CH_2-CH_2-$), 1.85 (2H, m, β-CH_2-, THF), 3.74 (2H, m, α-CH_2-, THF), 4.07 (4H, t, $-CH_2-O-Ph-$, J = 6.7 Hz), 7.00 (4H, H^a, d, AA′XX′, aromatic H; J = 8.8 Hz), 8.15 (4H, H^b, d, AA′XX′, aromatic H, J = 8.8 Hz), 7.45 (4H, H^c, d, AA′XX′, aromatic H, J = 8.8 Hz), 7.60 (4H, H^d, d, AA′XX′, aromatic H, J = 8.8 Hz), 8.79 (2H, s, $-CH{=}N-$).

^{13}C NMR ($CDCl_3$): δ 165.56 ($-C{=}N-$), δ 193.68 (2CO, trans to L_3), 184.84 (CO, trans to the coordinated solvent).

^{19}F NMR ($CDCl_3$): δ 87.02 (3 F, s, CF_3SO_3)

[Re(CF$_3$SO$_3$)(L$_2$)(CO)$_3$]·THF was prepared similarly. Mp: 159 °C. Yield: 67%.

Anal. Calcd for $C_{56}H_{68}N_2O_{13}SF_3Re$: C, 53.7; H, 5.5; N, 2.2. Found: C, 54.2; H, 5.2; N, 2.3.

IR (CH_2Cl_2 solution): ν_{CO} 2044 cm^{-1} (s), 1953 cm^{-1} (m), 1934 cm^{-1} (m).

^{1}H NMR ($CDCl_3$): δ 0.89 (6H, t, CH_3-CH_2-, J = 6.4 Hz), 1.30 (28H, bm, $CH_3-(CH_2)_7-CH_2-$), 1.85 (4H, m, $CH_3-(CH_2)_5-CH_2-CH_2-$), 1.85 (2H, m, β-CH_2-, THF), 3.74 (2H, m, α-CH_2-, THF), 4.07 (4H, t, $-CH_2-O-Ph-$, J = 6.7 Hz), 7.00 (4H, H^a, d, AA′XX′, aromatic H; J = 8.8 Hz), 8.15 (4H, H^b, d, AA′XX′, aromatic H, J = 8.8 Hz), 7.45 (4H, H^c, d, AA′XX′, aromatic H, J = 8.8 Hz), 7.60 (4H, H^d, d, AA′XX′, aromatic H, J = 8.8 Hz), 8.79 (2H, s, $-CH{=}N-$).

^{13}C NMR ($CDCl_3$): δ 165.60 ($-C{=}N-$), 193.68 (2CO, trans to L_3), 184.84 (CO, trans to the coordinated solvent).

^{19}F NMR ($CDCl_3$): δ 87.02 (3 F, s, CF_3SO_3)

[Re(CF$_3$SO$_3$)(L$_3$)(CO)$_3$]·THF was prepared similarly. Mp: 148 °C. Yield: 65%.

Anal. Calcd for $C_{60}H_{76}N_2O_{13}SF_3Re$: C, 55.1; H, 5.8; N, 2.1. Found: C, 54.6; H, 5.5; N, 2.2.

IR (CH_2Cl_2 solution): ν_{CO} 2041 cm^{-1} (s), 1947 cm^{-1} (m), 1931 cm^{-1} (m).

^{1}H NMR ($CDCl_3$): δ 0.89 (6H, t, CH_3-CH_2-, J = 6.4 Hz), 1.30 (36H, bm, $CH_3-(CH_2)_9-CH_2-$), 1.85 (4H, m, $CH_3-(CH_2)_5-CH_2-CH_2-$), δ 1.85 (2H, m, β-CH_2-, THF), δ 3.74 (2H, m, α-CH_2-, THF), 4.07 (4H, t, $-CH_2-O-Ph-$, J = 6.7 Hz), 7.00 (4H, H^a, d, AA′XX′, aromatic H; J = 8.8 Hz), 8.15 (4H, H^b, d, AA′XX′, aromatic H, J = 8.8 Hz), 7.45 (4H, H^c, d, AA′XX′, aromatic H, J = 8.8 Hz), 7.60 (4H, H^d, d, AA′XX′, aromatic H, J = 8.8 Hz), 8.79 (2H, s, $-CH{=}N-$).

^{13}C NMR ($CDCl_3$): δ 165.65 ($-C{=}N-$), 193.68 (2CO, trans to L_3), 184.84 (CO, trans to the coordinated solvent).

^{19}F NMR ($CDCl_3$): δ 87.00 (3 F, s, CF_3SO_3).

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