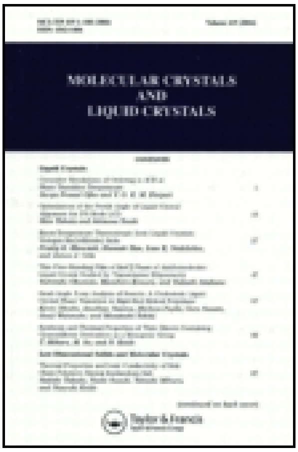
This article was downloaded by: [University of California, San Diego]
On: 07 August 2012, At: 12:18
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Preparation and Single Crystal Structure of a Dirhenium(I) Complex of a Bent-Core Mesogen

Deborah M. Huck [a], Laurent Omnès [a], Mark E. Light [b] & Duncan W. Bruce [a]

[a] Department of Chemistry, University of York, Heslington, York YO10 5DD (UK)

[b] EPSRC Crystallographic Service, Department of Chemistry, University of Southampton, Southampton So17 1BJ (UK)

Version of record first published: 07 Oct 2011

To cite this article: Deborah M. Huck, Laurent Omnès, Mark E. Light & Duncan W. Bruce (2011): Preparation and Single Crystal Structure of a Dirhenium(I) Complex of a Bent-Core Mesogen, Molecular Crystals and Liquid Crystals, 549:1, 19-28

To link to this article: http://dx.doi.org/10.1080/15421406.2011.581121

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst., Vol. 549: pp. 19–28, 2011
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.581121

Downloaded by [University of California, San Diego] at 12:18 07 August 2012

Preparation and Single Crystal Structure of a Dirhenium(I) Complex of a Bent-Core Mesogen

DEBORAH M. HUCK,[1] LAURENT OMNÈS,[1]
MARK E. LIGHT,[2] AND DUNCAN W. BRUCE[1,*]

[1]Department of Chemistry, University of York, Heslington,
York YO10 5DD (UK)
[2]EPSRC Crystallographic Service, Department of Chemistry, University
of Southampton, Southampton So17 1BJ (UK)

Dinuclear complexes of Re^I are prepared by functionalising a symmetric, bent-core mesogen containing two imine groups. The resulting complex is characterised by single crystal X-ray diffraction and presents the expected geometry, but unfortunately the introduction of the two Re(CO)$_4$ moieties suppresses the mesomorphism of the parent ligand.

Introduction

Since the report of spontaneous symmetry breaking in bent-core mesogens in 1995[1] and the identification of the origin of the chirality soon afterwards, there has been a great deal of interest in the preparation and properties of large families of bent-core mesogens. Arguably, bent-core mesogens were reported in the early part of the 20th century by Vorländer, but more systematic work originated from papers by Matsunaga and co-workers in the early 1990s.[2] An insightful review into bent-core materials was published in 2006 by Reddy and Tschierscke,[3] while their implication in the biaxial nematic phase forms part of a recent critical review by Tschierscke and Photinos.[4]

Of the variables in bent-core materials, the literature shows that the compounds are sensitive (of course) to their chemical composition and subtle changes thereof (*e.g.* the direction of esters or imine functions), to the angle at the 'elbow' of the compound and to dipole moment. Indeed, the combination of bend angle and dipole moment are crucial factors in discussions of the N_B phase of bent-core materials.[5]

However, another factor that can be of significance is shown by some of our work on mesogenic terpyridines. We prepared examples (Figure 1) of 5,5′-disubstituted terpyridines (**4**) using inverse electron demand Diels-Alder chemistry with 1,2,4-triazine substrates (**3**) prepared from hydrozone oximes (**1**) and pyridine-2,6-dicarboxaldehyde (**2**). Compounds **5**, which are derivatives of **4**, were found to show one of the SmC_aP_A or SmC_sP_F (B_2) phases, as optical microscopy showed them to exist in a chiral mesophase. However, compound **6**, which is also obtained from **3**, showed an entirely different behaviour, exhibiting both a SmC and a N phase. While there was a small difference in the bend angle between **5** and

---

[*]Corresponding author. E-mail: duncan.bruce@york.ac.uk

Downloaded by [University of California, San Diego] at 12:18 07 August 2012

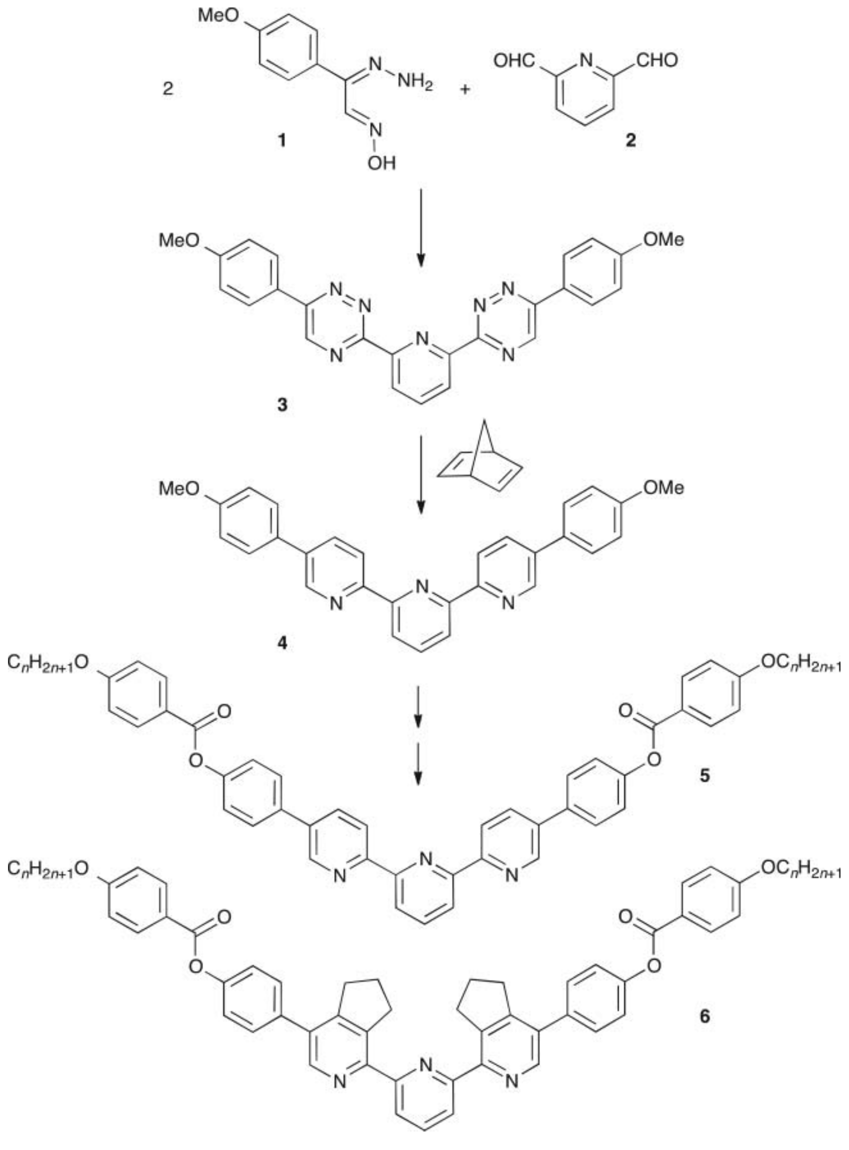


Figure 1. Synthetic route to mesomorphic, bent-core terpyridines **5** and **6**.

6, it is likely somehow that ‘filling in’ of the elbow is a significant factor in changing the mesomorphism.[6]

Such effects can be seen in other ways, too, so that long-chain derivatives of **4** are not mesomorphic, while on complexation to Zn^{II} the resulting material shows a columnar mesophase.[7] Similarly, related hexacatenar 1,3-dipyridylbenzenes (**7**) are not liquid crystalline, while their chloroplatinum(II) complexes (**8**) are.[8] Here, it seems that rigidification (from complexation) and the introduction of a dipole moment (reorientation of the pyridine nitrogen atoms on complexation) contribute to the induction of mesomorphism. However, it is possible for rigidification and even dipole moment to work in different ways for,

Downloaded by [University of California, San Diego] at 12:18 07 August 2012

as stated, long-chain analogues of **4** are not liquid crystalline and yet, as five-ring, bent-core molecules, mesomorphism could reasonably be expected. However, as we reported, preparation of the ester derivatives, **5**, leads to materials showing one of the chiral B_2 modifications. Addition of the ester function adds both a dipole moment and flexibility and mesomorphism is induced.

In considering the incorporation of metals, the study of metallomesogens in the last 25 years has shown the possibilities offered by different metal-ligand combinations, and these are collected in several reviews.[9] Many metals have been used in this way and all major areas of the periodic table are represented. For example, they are known to affect linear polarisability and birefringence, to introduce paramagnetic properties, to modulate photophysical and mesophase properties due to intermolecular interactions, to be emissive and to act as templates for heterogeneous catalysts.[10] Therefore, it is of interest to consider the possibilities offered if a metal were incorporated into a bent-core structure.

Results and Discussion

Metallomesogenic, bent-core materials are little studied. Abe *et al.*[11] reported 4,4'-disubstituted derivatives of metal-salen complexes, but the core of these materials is too small to be considered alongside classical bent-core materials. Similarly, Pucci *et al.*[12] reported on zinc(II) complexes (**10**) of dimeric salicylaldimato ligands linked by a flexible spacer (Figure 2). Šepelj *et al.*[13] had reported the mesomorphic properties of the isolated ligands (**9**) and had shown that when the number of linking methylene groups, *m*, was an even number, the compounds behaved as conventional mesogens showing SmC and N phases, while when *m* was odd, the behaviour changed markedly and Col_r and N_{col} phases were seen—behaviour often associated with bent-core materials.

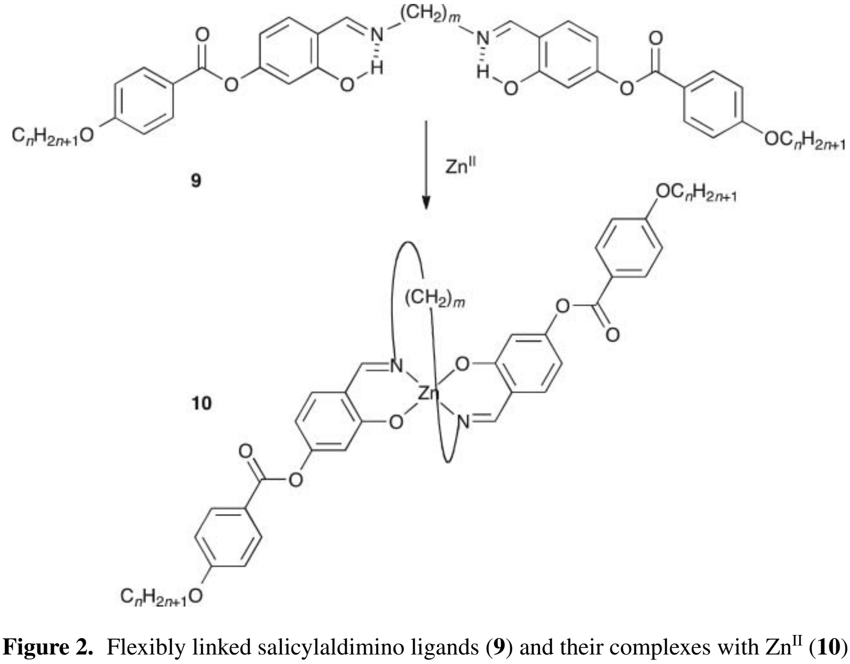


Figure 2. Flexibly linked salicylaldimino ligands (**9**) and their complexes with Zn^{II} (**10**).

Downloaded by [University of California, San Diego] at 12:18 07 August 2012

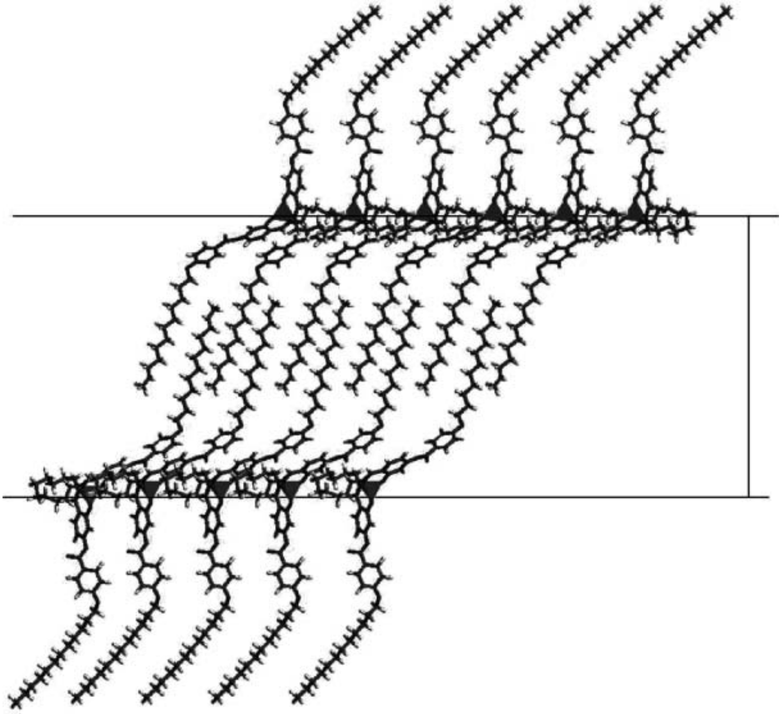


Figure 3. Proposed arrangement of Zn salicylaldimine complexes in the $SmC_{intercal}$ (B_6) phase. Reproduced with permission from reference 12; copyright Wiley-VCH Verlag GmbH & Co. KGaA.

When complexed to tetrahedral Zn^{II}, it was proposed that the flexible linker was held in a fly-over arrangement and that the whole complex had an overall bent structure, consistent with the observation of a $SmC_{intercal}$ phase, Figure 3 (also known as a B_6 phase), although the extensive hysteresis at the clearing point does give some cause for concern in attributing the thermal behaviour.[12]

Some time ago, we had shown that the Group 7 elements Mn and Re could react with benzylideneanilines as their $[MMe(CO)_5]$ complexes to give *ortho*-metallated tetracarbonyl complexes that were mesomorphic (Figure 4). Design of these complexes required that the

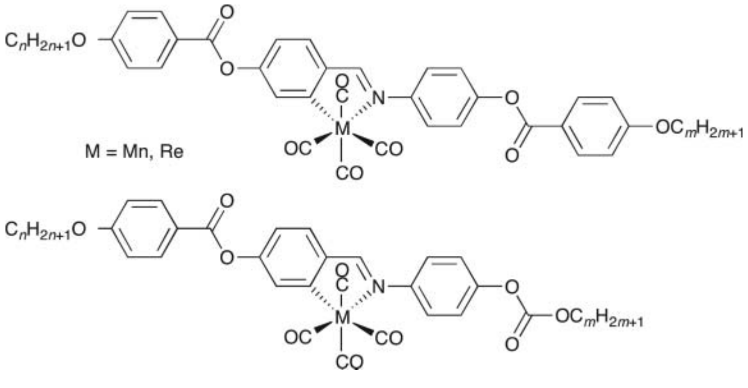
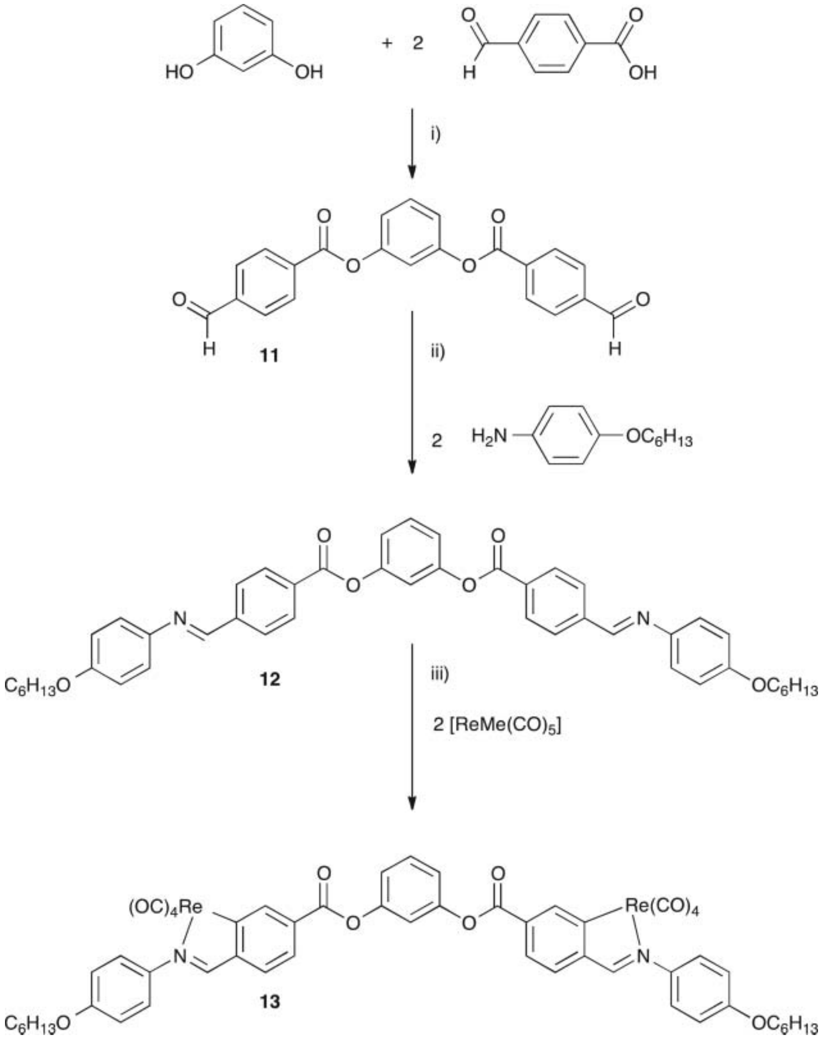


Figure 4. Three- and four-ring *ortho*metallated imine complexes of Mn^I and Re^I.

imine ligands were sufficiently anisotropic to compensate for the destabilising effect of the [M(CO)$_4$] moiety, so that four-ring imine ligands led to complexes with enantiotropic mesomorphism, while three-ring ligands resulted in monotropic behaviour.[14]

Imine links are also a common feature of bent-core mesogens, and so in the light of the discussion above, it was of interest to attempt the preparation of bent-core, imine-containing materials and to investigate the possible *ortho*-metallation using rhenium (which, in general, gives more thermally stable complexes compared to manganese). The ligand identified is compound **12**, whose preparation is shown in Scheme 1.



Scheme 1. Preparation of the target complexes. i) DCC/DMAP/CH_2Cl_2, rt, N_2; ii) H^+ (cat.), toluene/rt/N_2; iii) toluene (anhyd.), N_2, reflux.

While the ligand is a known material prepared by esterification of resorcinol with the appropriate carboxylic acid,[15] in this work we obtained the material in a different way in order to allow for subsequent convergent synthesis of analogues. Thus, resorcinol was esterified with benzaldehyde-4-carboxylic acid using a DCC/DMAP coupling to give aldehyde **11**, which was then condensed with hexyloxyaniline under acid catalysis to give

Downloaded by [University of California, San Diego] at 12:18 07 August 2012

target ligand **12**. We were able to confirm the published mesomorphism of **12** as:

$$\text{Cr} \bullet 144 \bullet \text{B}_4 \bullet 159 \bullet \text{B}_1 \bullet 174 \bullet \text{Iso}$$

Ligand **12** was then doubly metallated by reaction with [ReMe(CO)$_5$] (itself from [Re$_2$(CO)$_{10}$] by reaction with Na/Hg and then MeI[16]) in anhydrous toluene under reflux and the yellow/orange product was obtained by separation from excess of ligand using column chromatography in dichloromethane. Crystallisation was achieved from the same solvent by layering hexane on top and gave the product, **13**, in 69% yield for this last step.

Crystal and Molecular Structure of 13

Careful crystallisation of **13** from CH$_2$Cl$_2$/hexane yielded crystals that were analysed using single-crystal X-ray crystallography. The complex crystallised in the $P\bar{1}$space group with an *R*-factor that is acceptable, particularly given the fact that the data were acquired at ambient temperature. Essential crystallographic data are collected in Table 1.

Table 1. Crystallographic data for **13**

CCDC Deposition Number	806600	
Empirical formula	$C_{54}H_{46}N_2O_{14}Re_2$	
Formula weight/g mol^{-1}	1319.33	
Temperature/K	293(2)	
Wavelength/Å	0.71073	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions (Å)/angles (°)	$a = 13.6293(10)$ Å	$\alpha = 111.817(5)°$
	$b = 14.9561(12)$ Å	$\beta = 91.913(4)°$
	$c = 16.6900(18)$ Å	$\gamma = 115.516(3)°$
Volume/Å^3	2773.3(4)	
Z	2	
Density (calculated)/Mg m^{-3}	1.580	
Absorption coefficient/mm^{-1}	4.424	
F(000)	1292	
Crystal size/mm^3	$0.20 \times 0.10 \times 0.05$	
θ range for data collection/°	$2.92 - 24.71$	
Index ranges	$-16 \le h \le 16, -17 \le k \le 16, -19 \le l \le 19$	
Reflections collected	23336	
Independent reflections	9284 [$R_{int} = 0.1141$]	
Completeness to $\theta = 24.71°$	98.2%	
Absorption correction	Multiscan, SORTAV	
Max. and min. transmission	0.8091 and 0.4715	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	9284/266/627	
Goodness-of-fit on F^2	0.937	
Final *R* indices [$F^2 > 2\sigma(F^2)$]	$R1 = 0.0623$, $wR2 = 0.1279$	
R indices (all data)	$R1 = 0.1711$, $wR2 = 0.1687$	
Largest diff. peak and hole/e Å^{-3}	1.363 and -0.951	

Downloaded by [University of California, San Diego] at 12:18 07 August 2012

Downloaded by [University of California, San Diego] at 12:18 07 August 2012

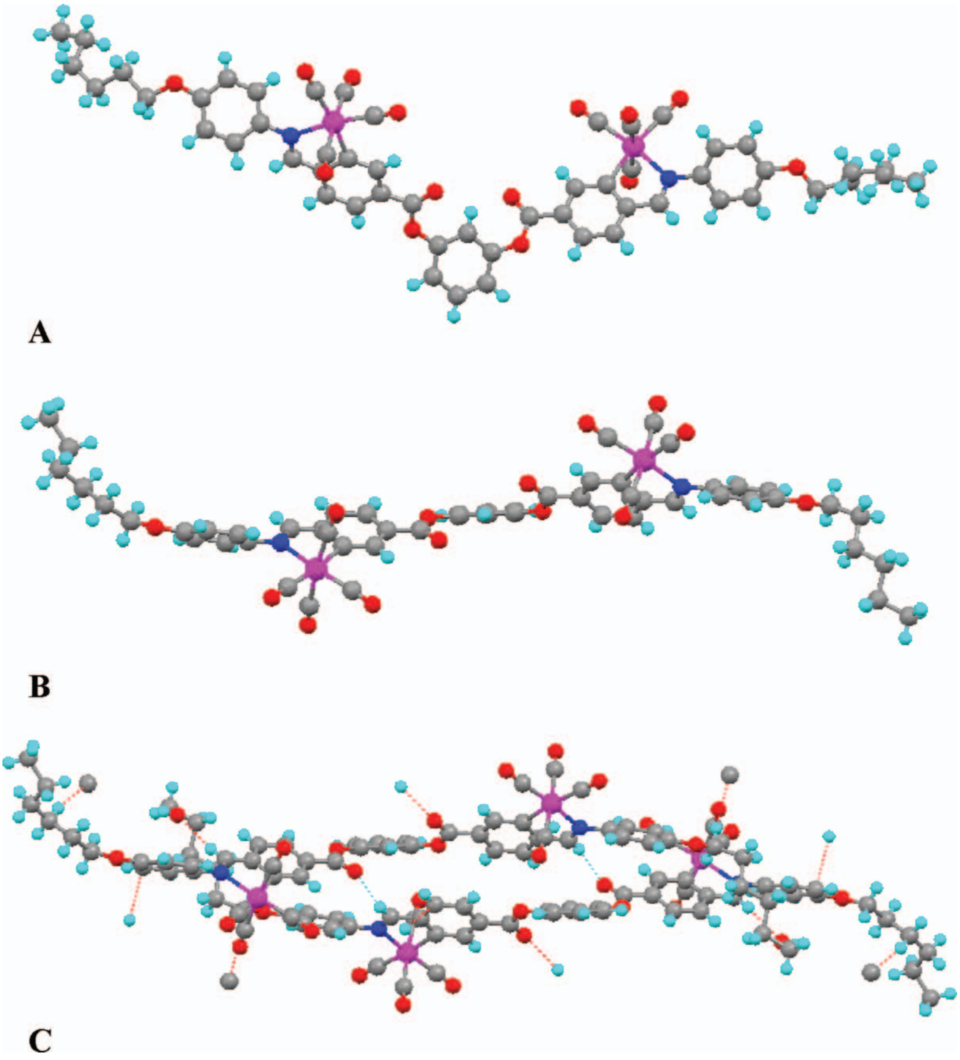


Figure 5. Three views of the molecular structure of complex **13**. Views **A** and **B** are general views, while view **C** shows short intermolecular contacts.

The structure (Figure 5) shows clearly the incorporation of two Re^{I} centres and, within the bounds of statistical factors, the two centres are identical in terms of bond lengths and angles. The rings of the complex are not co-planar. Thus, the central benzene ring makes angles of 38.11° and 33.82° with the adjacent rings to which it is joined *via* ester functionality and these are in opposite senses so that one Re centre appears above the plane of the central resorcinol ring, while the other appears below it. The two rings that are involved in the metallation make a mutual angle of 47.10° at Re(1) and 43.86° at Re(2). Statistically, there is no change in the Re–CO bond lengths that depends on whether the carbonyl is *trans* to nitrogen or carbon.

In terms of intermolecular contacts at the level of 0.1 Å less than the sum of the van der Waals' radii, contacts (3.277 Å) are identified between the carbonyl oxygen of an ester function and an imino hydrogen, although it is difficult to say with any certainty if these are in any way structure directing. This interaction is shown in Figure 5C. In the pair of molecules shown in this figure, the two benzene rings in the centre of the figure, one from each complex, are formally parallel with a plane-to-plane separation of 3.407 Å, although there is no evidence for intermolecular π-π interactions. These planes do not perpetuate in the structure.

Thermal Behaviour

Unfortunately, complex **13** proved not to be mesomorphic and heating the crystalline solid resulted in a melting event to an isotropic fluid at 98 °C. Cooling this liquid either slowly or quickly showed no evidence of a birefringent texture, even under mechanical disturbance, although the high viscosity of the fluid at lower temperatures suggested the formation of a glass.

Thus, the disruption of the already reduced anisotropy of the ligand (most mesogens can be approximated to be $C_{\infty v}$, while bent-core mesogens are approximated as C_{2v}) by the inclusion of two, octahedral centres is incommensurate with forming an organised, fluid structure. At the present time it is unclear whether preparation of an unsymmetric ligand containing a single metallated octahedral rhenium centre would support mesomorphism or whether a much more extended structure would be necessary. However, it is also not entirely clear whether any disruption to the bent-core motif would be tolerated, for example by the introduction of a square-planar metal centre such as that which may be obtained using Pd^{II} or Pt^{II}, marking this area as one required detailed further investigation.

Experimental

X-Ray Structure Determination

The diffractometer was a Nonius Kappa with CCD area detector, using φ scans and ω scans to fill the asymmetric unit sphere. The cell determination used DirAx software,[17] while data collection used Collect software.[18] Data reduction and cell refinement employed Denzo,[19] while absorption corrections used SORTAV.20 Structure solution and refinement used SHELXS97[21] and SHELXL97,[22] respectively.

Compound 11

1,3-Dicyclohexylcarbodiimide (DCC) (6.71 g, 32.7 mmol) was dissolved in CH_2Cl_2 (100 cm^3) to give a colourless solution. To this, a solution of resorcinol (3.00 g, 27.2 mmol) dissolved in THF (22 cm^3) was added followed by 4-formylbenzoic acid (7.55 g, 50.3 mmol) giving an off-white milky solution due to the incomplete dissolution of the benzaldehyde. Finally 4-(*N*,*N*-dimethylamino)pyridine (DMAP) (0.79 g, 6.1 mmol) was added giving a slightly exothermic reaction. The mixture was stirred at room temperature under nitrogen for 15 h giving a cloudy white precipitate, which was recovered by filtration. The product was extracted into hot DCM in which the excess starting materials are insoluble and then crystallised from THF to give the product **11** in a yield of 36.5% (3.71 g, 9.9 mmol).

Synthesis of Compound 12

Compound **11** (0.50 g, 1.30 mmol) and distilled 4-hexyloxyaniline (0.52 g, 2.7 mmol) were placed in a flask along with toluene (100 cm^3) in which the 4-hexyloxyaniline dissolved

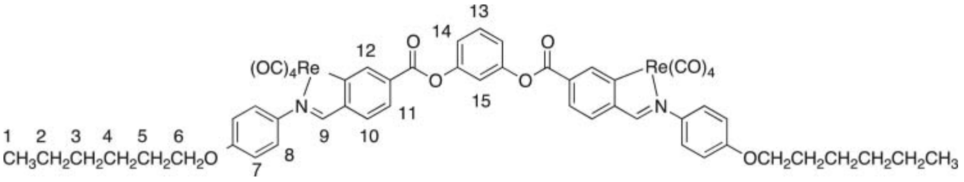
Downloaded by [University of California, San Diego] at 12:18 07 August 2012

straight away to give a brown solution. The mixture was heated gently for 10 minutes to dissolve **11** and acetic acid (glacial, 2 drops) was added. The mixture was stirred at room temperature under nitrogen for 15 hours. After cooling in the fridge, an off-white solid precipitated and was recovered by filtration and then crystallised from DCM and ethanol in a 4:1 ratio (30 cm^3). A second crystallisation was performed from the same solvent giving compound **12** in a yield of 11.7% (0.11 g, 0.15 mmol).

CHN % Expected (% Obtained) C: 76.2 (75.8) H: 6.7 (6.7) N: 3.9 (3.6)

Synthesis of Compound 13

Compound **12** (0.093 g, 0.13 mmol) and methylpentacarbonylrhenium(I) (0.88 g, 0.26 mmol) were dissolved in anhydrous toluene (20 cm^3) and heated at reflux under N_2 for 15 h. The solvent of the resulting brown solution was evaporated off leaving a yellow/orange solid. ^{1}H-NMR spectroscopy indicated the presence of excess **12**. A chromatography column using CH_2Cl_2 was performed with the first band being the product. This was further purified by precipitation where the solid was dissolved in CH_2Cl_2 (1 cm^3) and a layer of hexane (3 cm^3) was added. The two layers were left to mix slowly and were placed in the fridge for 3 d to ensure full precipitation. Orange needle-like crystals of compound **13** were filtered off in a yield of 69.2% (0.12g, 0.09 mmol). It is accepted that the N analysis below is outside of normal limits, but both C and H are within and all other data are consistent with a pure material.



^{1}H NMR ($CDCl_3$) δ: 0.84–0.93 (6H, m, H_1), 1.22–1.52 (8H, m, H_2, H_3) 1.76–1.81 (8H, m, H_4, H_5), 4.00 (4H, t, $^3J_{HH} = 8.3$ Hz, H_6), 6.97 (4H, AA′XX′ system, $J = 7.92$ Hz, H_7), 7.20–7.28 (7H, m, H_8, H_{14}, H_{15}), 7.53 (1H, m, H_{13}), 7.8 (2H, d, $^3J_{HH} = 7.97$ Hz, H_{10}), 7.96 (2H, dd, $^4J_{HH} = 1.90$ Hz, $^3J_{HH} = 7.97$ Hz, H_{11}), 8.64 (2H, s, H_9), 7.74 (2H, d, $^4J_{HH} = 1.90$ Hz, H_{12}).

% Expected (% Obtained) C: 49.2 (49.0) H: 2.9 (3.2) N: 3.9 (3.0)

Acknowledgements

We are grateful to the EU and NEDO for funding (LO) and H.C. Stark for a generous gift of ammonium tetraoxorhenate(VII).

References

[1] T. Niori, T. Sekine, J. Watanabe, T. Furukawa, and H. Takezoe, *J. Mater. Chem.*, 1996, **6**, 1231.

[2] H. Matsuzaki and Y. Matsunaga, *Liq. Cryst.*, 1993, **14**, 105; Y. Matsunaga and S. Miyamoto, *Mol. Cryst., Liq. Cryst.*, 1993, **237**, 311.

[3] R. A. Reddy and C. Tschierske, *J. Mater. Chem.*, 2006, **16**, 907.

Downloaded by [University of California, San Diego] at 12:18 07 August 2012

[4] C. Tschierscke and D. J. Photinos, *J. Mater. Chem.*, 2010, **20**, 4263.

[5] J. Peláez and M. R. Wilson, *Phys. Rev. Lett.*, 2006, **97**, 267801.

[6] V. N. Kozhevnikov, A. C. Whitwood, and D. W. Bruce, *Chem. Commun.*, 2007, 3826

[7] V. N. Kozhevnikov and D. W. Bruce, *unpublished results*.

[8] V. N. Kozhevnikov, B. Donnio, and D. W. Bruce, *Angew. Chem. Int. Ed.*, 2008, **47**, 6286.

[9] D. W. Bruce, R. Deschenaux, B. Donnio, and D. Guillon, in *Comprehensive Organometallic Chemistry III*; Eds. R. H. Crabtree and D. M. P. Mingos, Elsevier: Oxford, UK, 2006, Vol. 12. Chapter 12.05, pp 195–294; B. Donnio, D. Guillon, R. Deschenaux, and D. W. Bruce in *Comprehensive Coordination Chemistry II*; Eds. J. A. McCleverty and T. J. Meyer, Elsevier: Oxford, UK, 2003, Vol. 7, Chapter 7.9, pp 357–627.

[10] K. Binnemans in *Molecular Materials*, Eds D. W. Bruce. D. O'Hare and R. I. Walton, Wiley, Chichester, 2010, Chapter 2, pp 61–143.

[11] a) Y. Abe, H. Akao, N. Nakajima, T. Tanase, S. Katano, H. Mukai, and K. Ohta, *Mol. Cry. Liq. Cry.* 2007, **466**, 129; b) Y. Abe, H. Akao, Y. Yoshida, H. Takashima, T. Tanase, H. Mukai, and K. Ohta, *Inorg. Chim. Acta.* 2006, **359**, 3147.

[12] D. Pucci, I. Aiello, A. Bellusci, A. Crispini, M. Ghedini, and M. La Deda, *Eur. J. Inorg. Chem.*, 2009, 4274.

[13] M. Šepelj, A. Lesac, U. Baumeister, S. Diele, D. W. Bruce, and Z. Hameršak, *Chem. Mater.*, 2006, **18**, 2050.

[14] D. W. Bruce and X.-H. Liu, *J. Chem. Soc., Chem. Commun.*, 1994, 729; X.-H. Liu, B. Heinrich, I. Manners, D. Guillon, and D. W. Bruce, *J. Mater. Chem.*, 2000, **10**, 637; M.-A. Guillevic and D. W. Bruce, *Liq. Cryst.*, 2000, **27**, 153; M.-A. Guillevic, T. Gelbrich, M. B. Hursthouse, and D. W. Bruce, *Mol. Cryst., Liq. Cryst.*, 2001, 362, 147; X.-H. Liu, I. Manners, and D. W. Bruce, *J. Mater. Chem.*, 1998, **8**, 1555; D. W. Bruce and X.-H. Liu, *Liq. Cryst.*, 1995, **18**, 165.

[15] T. Sekine, T. Niori, M. Sone, J. Watanabe, S. W. Choi, Y. Takanishi, and H. Takezoe, *Jpn. J. Appl. Phys.*, 1997, **36**, 6455

[16] R. L. Bennett, M. I. Bruce, B. L. Goodall, M. Z. Iqbal, and F. G. A. Stone, *J Chem Soc, Dalton Trans*, 1992, 1787.

[17] A. J. M. Duisenberg, *J. Appl. Cryst.*, 1992, **25**, 92.

[18] Collect: Data collection software, R. Hooft, Nonius B.V., 1998.

[19] Z. Otwinowski and W. Minor in, *Methods in Enzymology*, Vol. **276**: *Macromolecular Crystallography*, part A, pp 307–326; C. W. Carter, Jr. and R. M. Sweet, Eds., Academic Press, New York, 1997.

[20] R. H. Blessing, *Acta Cryst.*, 1995, **A51**, 33; R. H. Blessing, *J. Appl. Cryst.*, 1997, 30, 421.

[21] G. M. Sheldrick, *Acta Cryst.*, 1990, **A46** 467.

[22] G. M. Sheldrick, University of Göttingen, Germany, 1997.

Downloaded by [University of California, San Diego] at 12:18 07 August 2012