Square-planar rhodium(I) complexes with aromatic bent terdentate nitrogen ligands as candidates for rod-like extended materials†

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The crystal structure of 2,6-bis(1-methylbenzimidazol-2-yl)pyridine (L^4) evidenced a quasi *trans-trans* conformation of the unsubstituted nitrogen atoms of the aromatic rings which is maintained in solution on the NMR timescale. Reactions of L^4, or of its lipophilic analogue 2,6-bis(1-octylbenzimidazol-2-yl)pyridine (L^5), with [Rh(NBD)Cl]$_2$ (NBD = bicyclo[2.2.1]hepta-2,5-diene) produced poorly soluble dimetallic complexes [{Rh(NBD)Cl}$_2$L^i] (i = 4 or 5). The crystal structure of [{Rh(NBD)Cl}$_2$L^5] revealed that the terdentate aromatic unit adopts a distorted *trans-trans* conformation and acts as a bridging ligand connecting two [Rh(NBD)Cl] units through the nitrogen atoms of the benzimidazole side arms. Solution studies (ES-MS, NMR) indicate that (i) the dimetallic structure is maintained in solution, (ii) the complicated fluxional behaviour observed at room temperature is blocked at 210 K on the NMR timescale and (iii) the bent aromatic core cannot act as a meridional terdentate chelate toward Rh^I. The consequences of this co-ordination behaviour on the molecular anisometry of extended complexes is discussed.

Introduction

Until 1996,[1] no example of calamitic metallomesogens (*i.e.* metal-containing liquid crystals) involving terdentate binding units had been reported, while only few discotic metallomesogens with terdentate 1,3,5-triketonate,[2] 1,4,7-triazacyclonane[3] and pyridine-2,6-dimethanol[4] ligands have been described. Recently, two concomitant approaches have been developed for introducing bent terdentate binding units into rod-like receptors exhibiting mesomorphism. The first approach uses the connection of semi-rigid lipophilic long chains connected to the 4 position of the central pyridine unit in 6′-phenyl-2,2′-bipyridine,[5] pyridine-2,6-dicarboxylic acids and pyridine-2,6-dithiocarboxylic acids[6] in order to induce significant molecular anisometry compatible with calamitic mesomorphism. Nematic,[5] smectic and columnar[6] mesophases have been detected at high temperature for the ligands and for their rigid tabular complexes with square-planar Pd^{II} in which partial or complete charge compensation results from orthometallation[5] or deprotonation.[6] On the other hand, neutral aromatic bent terdentate binding units incorporated into extended aromatic receptors offer fascinating perspectives for the preparation of fast-switching ferro- or antiferro-electric mesophases.[7] Rod-like (L^1)[8] and banana-shaped (L^2)[9] receptors (see Scheme 1) containing bent 2,6-bis(1-ethylbenzimidazol-2-yl)pyridine cores display respectively calamitic (smectic and nematic)[8] and columnar mesomorphism,[10] but meridional three-co-ordination of the central binding unit to Ln(NO$_3$)$_3$
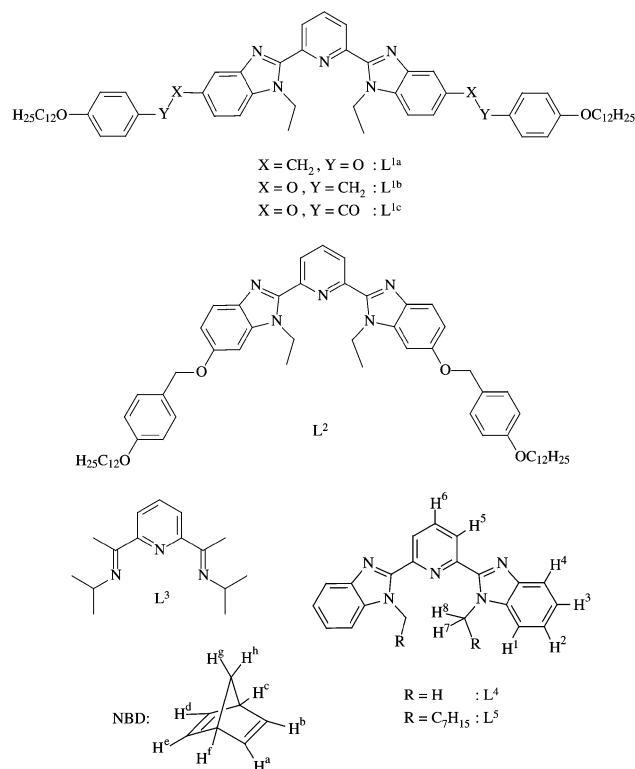
Scheme 1

and Ln(CF$_3$CO$_2$)$_3$ (Ln = La to Lu) provides non-mesogenic rod-like [Ln(L^2)(NO$_3$)$_3$] and [Ln(L^2)(CF$_3$CO$_2$)$_3$]$_2$ and U-shaped [Ln(L^1)(NO$_3$)$_3$] complexes.[8,9] We tentatively assign this dramatic

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change to the large spatial expansion induced by co-ordination of anions and/or solvent molecules on both sides of the plane defined by the meridionally three-co-ordinated binding unit and the metal ion in the complexes. In order to test the potential use of L[1] and L[2] for producing calamitic metallomesogens, we have launched into a research project aiming at introducing metal ions and counter anions producing controlled anisometry and predictable steric characteristics in the final complexes. Although five-co-ordinated and tetrahedral complexes with Rh[I] have been reported,[11] the strong stereochemical preference of Rh[I] for square-planar complexes[11,12] together with its single positive charge are compatible with the design of neutral square-planar complexes in which Rh[I] is meridionally three-co-ordinated by a neutral terdentate chelating nitrogen ligand, the fourth position being occupied by a co-ordinating anion (Cl^{−}, Br^{−}). Contrary to the rich literature reporting rhodium(I) complexes with π-acid ligands,[11] the complexation of Rh[I] with terdentate aromatic N-donor ligands has poorly been explored and we are aware of a single report describing the structure of the highly reactive complex [Rh(L[3])Cl] in which Rh[I] is meridionally three-co-ordinated by a complexing unit analogous to that found in L[i] (i = 1 or 2).[13] Detailed studies of this complex in solution show that (i) complicated intra- and intermolecular exchange processes involve the imine side arms on the NMR timescale at room temperature and (ii) only weakly bound alkenes can be replaced by the nitrogen atoms of L[3].[14] To the best of our knowledge, no study involving 2,2′:6′,2″ terpyridine (terpy) or its derivatives has been reported and this paper describes the complexation behaviour of Rh[I] with the analogous ligands 2,6-bis(1-alkylbenzimidazol-2-yl)pyridine L[4] and L[5] which are (i) slightly better π-accepting ligands compared with terpy[15] and (ii) considered as simple models of the co-ordination sites found in L[1] and L[2].

Results and discussion

Structure of ligands L[4] and L[5]

Theoretical calculations using semi-empirical EHMO[16] and ZINDO (INDO/S developed by Zerner)[9] methods suggest that the *trans-trans* conformation (*i.e.* the nitrogen atom of the pyridine ring is *trans* to the unsubstituted nitrogen atoms of the benzimidazole rings) corresponds to the most stable geometry in the gas phase and in solution as demonstrated by the predicted electronic spectra which closely match those recorded in acetonitrile–dichloromethane. ^{1}H NMR studies of L[1], L[2], L[4] and L[5] confirm that the ligands display an average C_{2v} symmetry in solution in agreement with a *trans-trans* conformation on the NMR timescale which is ascertained by the lack of NOE effects between H[7,8] and H[5].[8,9,16] Finally, crystal structures of L[1a] and L[1b] unambiguously establish that approximate *trans-trans* conformations are also adopted in the solid state,[8] but severe distortions occur when one benzimidazole side arm is protonated in [L[4]+H]ClO[4].[17] In order to assess the relative and subtle effects of (i) protonation, (ii) crystal packing forces and (iii) steric constraints induced by the substituents borne by the benzimidazole rings on the exact conformation of the terdentate core, we have solved the crystal structure of L[4]. Fig. 1 shows the atomic numbering scheme and Fig. 2 a comparison of the molecular structures of L[4] and [L[4]+H][+]. Selected bond distances and bond angles are given in the ESI supporting information (Table S1).

The molecular structure of L[4] in the solid state confirms the approximate *trans-trans* conformation of the bis(benzimidazolyl)pyridine binding unit (N1 is *trans* with respect to N2 and N4), and the C–C and C–N bond distances and bond angles are within standard values[18] in complete agreement with those found in L[1a], L[2a] and [L[4] + H][+]. The only significant differences between the conformations of these terdentate binding units result from variable interplanar angles between the connected
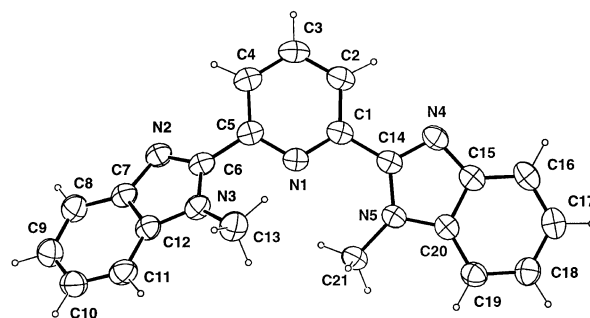

Fig. 1 Numbering scheme for the ligand L[4]. Ellipsoids are represented at the 50% probability level.
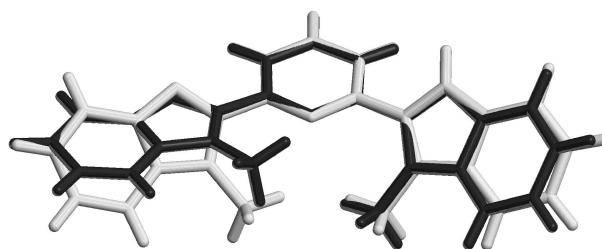

Fig. 2 Superimposed representation of the molecular structures of L[4] (black) and [L[4] + H][+] (grey).[17]

pyridine and benzimidazole units. In L[4] the benzimidazole ring N4,N5 is almost coplanar with the pyridine ring (interplanar angle: 7.11(3)°), while a larger torsion (36.80(3)°) is observed between the pyridine ring and the second benzimidazole side arm (N2,N3). Similar geometries are observed for L[1a] (interplanar angles: 3.2°, 20.9°)[8] and L[1b] (interplanar angles: 12.3°, 35.6°),[8] while a larger distortion from planarity characterises the arrangement of the aromatic rings in [L[4] + H][+] (interplanar angles: 30.5, 45.3°, Fig. 2).[17] This strongly suggests that (i) the increased steric constraints when going from *N*-methyl- (L[4]) to *N*-ethyl-benzimidazole rings (L[1a], L[1b]) have only minor effects on the conformation of the tridentate core and (ii) intermolecular interactions (dipolar, hydrogen bonds, π stacking) mainly control the fine arrangement of the terdentate core in the solid state. These hypotheses are supported by the contact distances between the carbon atoms of the alkyl substituents directly connected to the benzimidazole rings (C13···C21 for L[4]) which display no straightforward relationship with the nature of the substituents (3.81 (L[4]), 3.75 (L[1a]), 3.94 (L[1b]) and 3.61 Å ([L[4] + H][+])), but which depend on specific intermolecular interactions. In L[4] and L[1a] the almost coplanar pyridine–benzimidazole moieties of one ligand strongly interact with the identical moiety of a second molecule related by an inversion centre (1 − x, 1 − y, 1 − z), thus producing head-to-head π-stacked pairs whose average interplanar distance (3.41(7) for L[4], 3.50 Å for L[1a],[8] ESI Fig. S1) can be compared to that found in graphite (3.35 Å).[19] In L[1b] the terdentate core is not involved in significant intermolecular stacking interactions[8] and a complicated network of hydrogen bonds involving the protonated benzimidazole ring controls the packing in [L[4] + H]ClO[4].[17]

Synthesis and characterisation of the complexes

Attempts to use [Rh(C[2]H[4])[2]Cl][2] containing weakly bound alkenes as starting material[20] produce intricate mixtures of fluxional complexes with L[4] or L[5] on the NMR timescale between 210 and 333 K in CDCl[3]. Reactions in DMSO-d[6] show the appearance of solvated ethylene in agreement with its low affinity for Rh[I],[14] but we were not able to isolate pure complexes in solution or in the solid state. Reaction of L[4] (1.0 equivalent) with the alternative starting complex [Rh(NBD)-Cl][2] (1.0 equivalent; NBD = bicyclo[2.2.1]hepta-2,5-diene) in

dichloromethane produces a yellow precipitate which is insoluble in most organic and inorganic solvents. The IR spectrum displays absorption bands in the 1200–1600 cm^{-1} domain typical of the terdentate ligand (1460, 1560, 1580 cm^{-1}; v(C=C) + v(C=N)) and of the co-ordinated norbornadiene (NBD) fragment (1375 cm^{-1}; v(C=C)). Elemental analyses are compatible with the formulation [{Rh(NBD)Cl}$_2$L^4]·3H$_2$O **1** in agreement with the formation of a dimetallic complex. Positive mode ESI-MS spectra recorded for a highly diluted solution of **1** in THF show only two peaks corresponding to [Rh$_2$(NBD)$_2$-Cl(L^4)]$^+$ (m/z = 764.2) and [Rh(NBD)(L^4)]$^+$ (m/z = 534.2) and MS-MS experiments demonstrate that [Rh$_2$(NBD)$_2$Cl(L^4)]$^+$ fragments to give [Rh(NBD)(L^4)]$^+$ with concomitant loss of one [Rh(NBD)Cl] unit. We thus conclude that the charged complex [Rh$_2$(NBD)$_2$Cl(L^4)]$^+$ observed in the gas phase originates from dissociation of chloride from the neutral dimetallic precursor [{Rh(NBD)Cl}$_2$L^4]. Unfortunately, we were unable to obtain X-ray quality crystals of **1** as a result of its poor solubility and have repeated these experiments with the lipophilic analogue L^5. Reaction of L^5 with [Rh(NBD)Cl]$_2$ in acetonitrile for stoichiometric ratios 1:1 or 2:1 gives good yields (calculated for the limiting reactant) of a microcrystalline yellow powder. The elemental analyses, IR and ESI-MS spectra ([Rh$_2$(NBD)$_2$Cl(L^5)]$^+$ (m/z = 960.1) and [Rh(NBD)(L^5)]$^+$ (m/z = 730.3)) are compatible with the formulation as a dimetallic complex [{Rh(NBD)Cl}$_2$L^5] **2** which is more soluble in organic solvent than **1**. Recrystallisation from hot acetonitrile provides crystals suitable for X-ray diffraction studies.

Crystal and molecular structure of [{Rh(NBD)Cl}$_2$L^5] 2

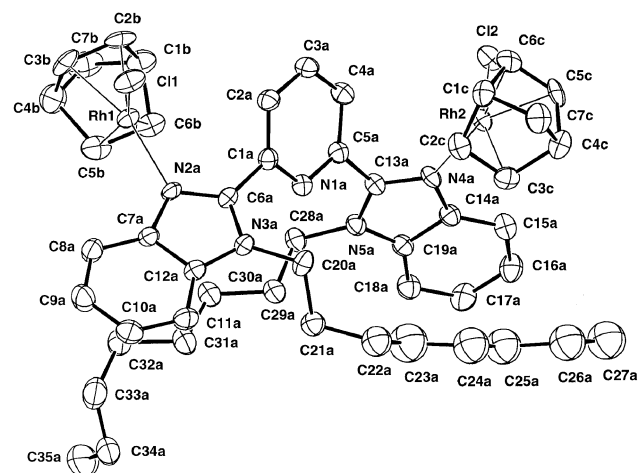The molecular structure of **2** consists of a dimetallic complex in which L^5 acts as a bis-monodentate bridging ligand, one nitrogen atom of each benzimidazole ring being co-ordinated to a [Rh(NBD)Cl] unit. Selected bond distances and bond angles are collected in Table 1; Fig. 3 displays the atomic numbering scheme and a stereoview of the complex is shown in Fig. 4.

The terdentate core of the complex adopts a distorted *trans-trans* conformation similar to that found in the molecular structure of the ligand L^4, but it evidences larger interplanar angles between the non-co-ordinating central pyridine ring and the benzimidazole side arms (48.58(3) and 55.25(3)°, ESI Table S2), thus producing a significant helical twist of L^5. The contact distance between the carbon atoms bound to the benzimidazole rings C20a···C28a 5.412(6) Å is significantly larger than those found in L^{1a}, L^{1b}, L^4 and [L^4 + H]$^+$ which strongly suggests that only minor repulsion occurs between the divergent lipophilic octyl chains. Each rhodium atom is four-co-ordinated by one nitrogen atom of a benzimidazole ring, one chloride and one chelating norbornadiene. The latter diene is considered as a bidentate ligand with the double bonds connected through their midpoints to the rhodium atom (Table 1, Fig. 3). The two resulting distorted square-planar metallic co-ordination spheres are very similar with Rh^I located slightly out of the plane of the four-co-ordinating centres (deviation: 0.057(1) Å for Rh1 and 0.011(1) Å for Rh2). The Rh–Cl distances (2.360–2.366 Å, Table 1) are standard[22] and can be compared to 2.3488(5) Å found in [Rh(L^3)Cl].[13] The Rh–C distances (2.102–2.124 Å, average 2.11(1) Å) are slightly shorter than those found in other rhodium complexes containing NBD or 1,5-cyclooctadiene (2.156 Å), but they are close to those observed in rhodium complexes with ethylene (2.129 Å).[22] The Rh–N distances (2.110–2.113 Å) are also standard[22]

Fig. 3 Numbering scheme for the complex [{Rh(NBD)Cl}$_2$L^5] **2**. Ellipsoids are represented at the 40% probability level.

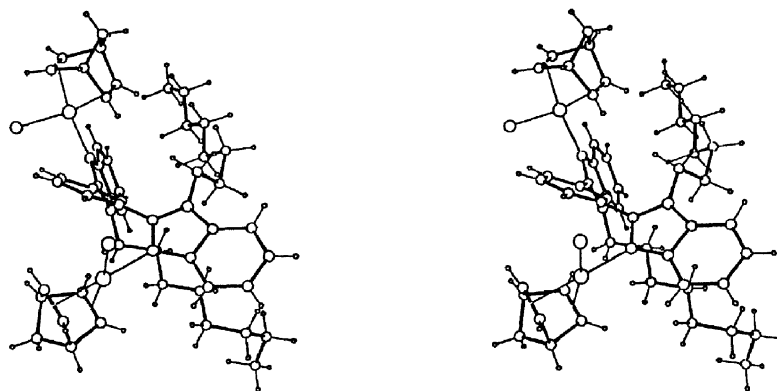**Table 1** Selected bond distances (Å) and angles (°) for [{Rh(NBD)-Cl}$_2$L^5] **2**

Rh1···Rh2	8.4218(6)		
Rh1–Cl1	2.366(1)	Rh2–Cl2	2.360(1)
Rh1–N2a	2.113(4)	Rh2–N4a	2.110(3)
Rh1–C2b	2.118(5)	Rh2–C2c	2.106(5)
Rh1–C3b	2.124(6)	Rh2–C3c	2.116(5)
Rh1–P1b^a	2.0051(4)	Rh2–P1c^a	1.9922(3)
Rh1–C5b	2.108(6)	Rh2–C5c	2.118(4)
Rh1–C6b	2.102(5)	Rh2–C6c	2.121(5)
Rh1–P2b^a	1.9876(4)	Rh2–P2c^a	2.0010(3)
N2a–Rh1–Cl1	88.2(1)	N4a–Rh2–Cl2	90.75(9)
N2a–Rh1–P1b^a	172.0(1)	N4a–Rh2–P1c^a	99.42(9)
N2a–Rh1–P2b^a	100.9(1)	N4a–Rh2–P2c^a	171.1(1)
Cl1–Rh1–P1b^a	98.55(4)	Cl2–Rh2–P1c^a	169.76(3)
Cl1–Rh1–P2b^a	170.56(4)	Cl2–Rh2–P2c^a	97.79(3)
P1b–Rh1–P2b^a	72.15(1)	P1c–Rh2–P2c^a	72.11(1)

^{a} P1i is the midpoint between the carbon atoms C2i and C3i and P2i that between C5i and C6i (i = b or c); the uncertainties of P_{ji} are set to 0 (j = 1 or 2 and i = b or c).

Fig. 4 ORTEP[21] stereoview of complex **2** along the helically twisted terdentate binding unit.

and similar to that found in [Rh(NBD)Cl(dmap)] (2.106 Å; dmap = 4-(*N*,*N*-dimethylamino)pyridine).[23] The pseudo-square-planar units [Rh1, N2a, Cl1, P1b, P2b] and [Rh2, N4a, Cl2, P1c, P2c] adopt almost orthogonal arrangements with respect to the benzimidazole ring to which they are connected (81.14(3)° for Rh1 and 77.23(3)° for Rh2) together with a relative antiparallel orientation of the Rh1–Cl1 and Rh2–Cl2 vectors located respectively above and below the least-square plane passing through the twisted terdentate bridging ligand (Fig. 4). Although no crystallographic symmetry is observed for the dimetallic complex [{Rh(NBD)Cl}$_2$L^5], the non-aliphatic part of the structure shows a pseudo-C_2 axis passing through N1a and C3a. The observed and refined olefinic hydrogen atoms of the NBD units severely deviate (0.18–0.31 Å, average 0.25(5) Å) from their expected positions in pure sp^2 hybrids consistent with steric constraints and/or efficient Rh→NBD π-back-donation which move these hydrogen atoms away from the rhodium metal. Finally, weak π-stacking interactions between the parallel benzimidazole rings N4a, N5a of two complexes related by an inversion centre (average stacking dis-tance: 3.559(8) Å) produce associations by pairs in the crystal packing of **2** (ESI Fig. S2).

Solution structure of [{Rh(NBD)Cl}$_2$L^5] 2

The ^{1}H NMR spectra of complex **2** in CDCl$_3$ or CD$_2$Cl$_2$ at room temperature display only broad signals resulting from slow intra- and/or inter-molecular exchange processes as previously observed for related rhodium complexes with bi-dentate and terdentate nitrogen ligands.[13,14] At low temperature (210 K) a series of resolved signals corresponding to a single species in slow exchange on the NMR timescale (>90% of the ligand speciation according to the integration of the signals) can be assigned by using {^{1}H–^{1}H}-COSY spectra and NOE measurements (Fig. 5). The AX$_2$ spin system observed for the protons H^{5,6}, together with the equivalence of the two benzimidazole side arms, point to the existence of a symmetry element (a mirror plane or a twofold axis) bisecting the central pyridine ring. The 1:2 ratio of the integrals of the signals for protons belonging to L^5 and NBD respectively indicates that the dimetallic structure found in the solid state is maintained in solution and the considerable complexation shifts observed for H^5 ($\Delta\delta = 1.70$ ppm) and H^4 ($\Delta\delta = 0.81$ ppm) confirm the co-ordination of the benzimidazole rings to [Rh(NBD)Cl]. The observation of two multiplets for the diastereotopic protons H^{7,8} precludes the existence of an average mirror plane con-taining the terdentate binding unit on the NMR timescale and the concomitant non-equivalence of H^{a,b,d,e} and H^{c,f} implies that (i) the co-ordinated norbornadienes do not rotate rapidly on the NMR timescale and (ii) the perpendicular orientation of the square-planar rhodium units with respect to the benzimidazole rings is maintained in solution. We thus conclude that the di-metallic complex adopts an average C_s- (**I**) or C_2-symmetrical structure (**II**) in solution at low temperature (Fig. 6). The latter arrangement (**II**) is closer to that found in the solid state, but NMR spectra cannot distinguish between these two structures. Finally, it is worth noting that the detected intramolecular NOE effects are systematically negative for **2** in CDCl$_3$ at 210 K consistent with a slow tumbling rate of the complex.[24] We tentatively assign this effect to the increased viscosity of the solvent (freezing point of CHCl$_3$: 209 K) and this is supported by the detection of related, but weakly positive NOE effects for **2** in CD$_2$Cl$_2$ at 210 K (freezing point of CH$_2$Cl$_2$: 178 K).

Conclusion

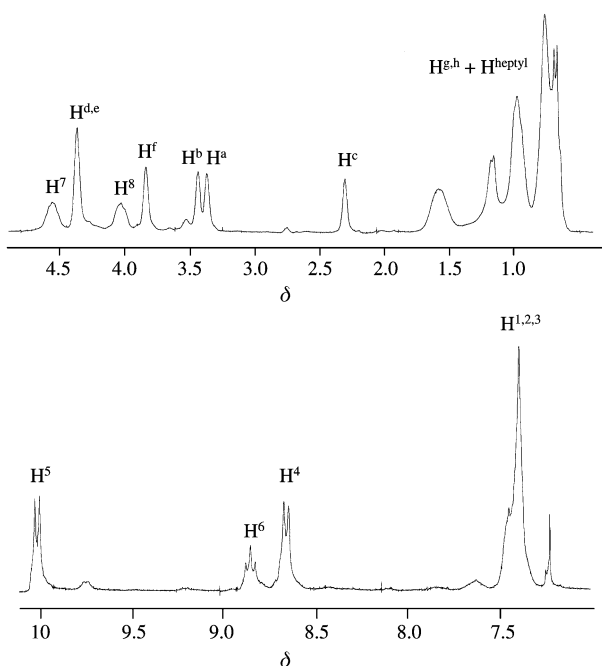The reactions of the potentially terdentate binding units L^4 and L^5 with [Rh(NBD)Cl]$_2$ produce exclusively the dimetallic

Fig. 5 ^{1}H NMR spectrum of complex **2** in CDCl$_3$ at 210 K.
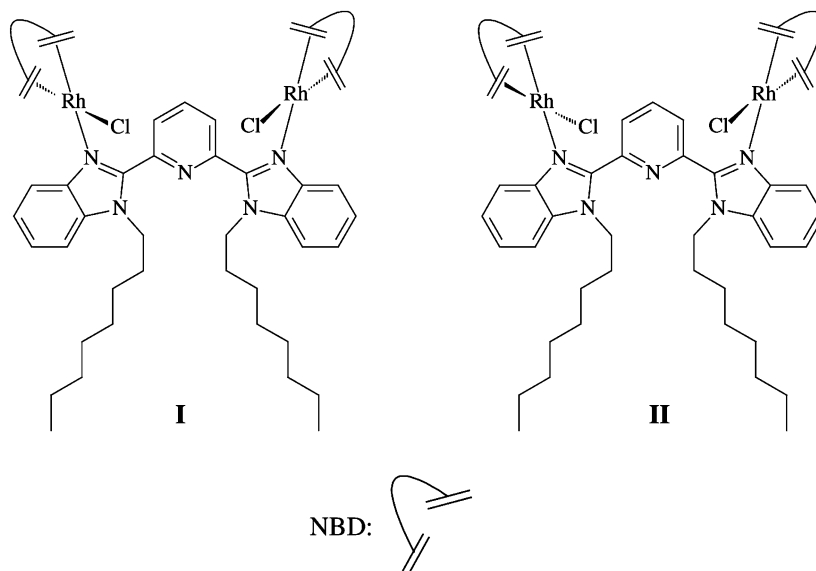
Fig. 6 Possible structures for complex **2** in solution at 210 K.

complexes [{Rh(NBD)Cl}$_2$L^i] (i = 4 or 5) in which L^4 and L^5 act as bis-monodentate bridging ligands as previously reported for the double-stranded helicates [M$_2$(L^4)$_2$]$^{2+}$ (M = Cu^I or Ag^I).[25,26] In the latter complexes the metal ions are essentially linearly co-ordinated by two benzimidazole units belonging to the different strands and theoretical calculations[25] suggest that the double-stranded helical structure results from a compromise between specific steric constraints and the electronic destabilisation of the alternative monometallic Y-shaped complexes.[26] For the larger Rh^I a less constrained T-shaped geometry is required for a monometallic complex with L^i (i = 4 or 5) and the latter argument is no longer valid since a related arrangement has been observed in [Rh(L^3)Cl].[13] We thus tentatively assign the absence of double-stranded helical structures as a result of the weak π-accepting properties of the ligands L^4 and L^5 which cannot stabilise the electron-rich Rh^I in a two-co-ordinate linear arrangement. Moreover, L^4 and L^5 are unable to displace the chelated norbornadiene which precludes meridional three-co-ordination around Rh^I, a complexation mode found for numerous complexes between L^4 and M^{II} (M = Mn, Fe, Co, Cu, Zn, Ru or Pt)[15,27] and M^{III} (M = Co[28] or Ln[29]). We conclude that the observed dimetallic complexes **1** and **2** correspond to a compromise in which Rh^I is tetragonally co-ordinated by a chelating π-accepting diene, a chloride anion and a nitrogen donor consistent with its stereoelectronic requirements. However, the resulting large spatial expansion brought by the [Rh(NBD)Cl] units co-ordinated to the terdentate core strongly limits the preparation of extended rod-like complexes with L^2 possessing minimal perpendicular anisometries compatible with calamitic mesomorphism. The alternative meridional co-ordination observed with square-planar Pd^{II} or Pt^{II} might overcome this limitation, but the increased positive charge borne by the metal is better suited for the preparation of amphiphilic aggregates such as Langmuir–Blodgett films or lyotropic metallomesogens.[27] Finally, Rh^I–diene complexes bearing amine ligands are regarded as convenient precursors of various organorhodium complexes which can be used as catalysts for the efficient polymerisation of alkynes.[30]

Experimental

Solvents and starting materials

These were purchased from Fluka AG (Buchs, Switzerland) and used without further purification unless otherwise stated. The ligands L^4 and L^5 were prepared according to literature procedures.[15] X-Ray quality crystals of L^4 were obtained by recrystallisation from dimethyl sulfoxide–acetonitrile. Hexane, dichloromethane and acetonitrile were distilled from CaH$_2$ and all experiments were carried out in a dry nitrogen atmosphere using standard Schlenk techniques.

Preparations

[{Rh(NBD)Cl}$_2$L^4]·3H$_2$O 1. 40 mg L^4 (0.12 mmol) in a dry dichloromethane solution (20 cm^3) were added under nitrogen to a dichloromethane solution (10 cm^3) of [Rh(NBD)Cl]$_2$ (54.5 mg, 0.12 mmol). The resulting solution was stirred for 30 min and the yellow precipitate was filtered off, washed with hexane (20 cm^3) and dried in vacuum to give 80% of [{Rh-(NBD)Cl}$_2$L^4]·3H$_2$O **1** (75 mg, 0.096 mmol). Calc. for C$_{49}$H$_{55}$Cl$_2$N$_5$O$_3$Rh$_2$: C, 49.20; N, 8.20; H, 4.60. Found: C, 49.38; N, 8.22; H, 4.52%. ES-MS (THF): m/z 764.2 ([M − Cl]$^+$) and 534.2 ([M − Cl − (Rh(NBD)Cl)]$^+$).

[{Rh(NBD)Cl}$_2$L^5] 2. To a solution of 46 mg L^5 (0.086 mmol) in acetonitrile (1.5 cm^3), 39.7 mg of [RhCl(C$_7$H$_8$)]$_2$ (0.086 mmol) in acetonitrile (0.5 cm^3) were added dropwise. The reaction was refluxed overnight and the yellow microcrystalline powder was filtered off, washed with hexane (3 cm^3) and dried in vacuum. The mother liquor was concentrated, cooled to 4 °C (1 day)

and a second crop of yellow microcrystals collected. The total yield of the resulting complex [{Rh(NBD)Cl}$_2$L^5] **2** amounted to 72% (62 mg, 0.062 mmol). Suitable crystals for X-ray diffraction studies were obtained by recrystallisation from hot acetonitrile. Calc. for C$_{49}$H$_{61}$Cl$_2$N$_5$Rh$_2$: C, 59.04; N, 7.03; H, 6.17. Found: C, 58.66; N, 7.04; H, 6.15%. ^{1}H NMR in CDCl$_3$ (210 K): δ 1.13–0.65 (32H, m), 2.29 (2H, s, broad), 3.35 (2H, s, broad), 3.42 (2H, s, broad), 3.83 (2H, s, broad), 4.02 (2H, m), 4.36 (4H, s, broad), 4.55 (2H, m), 7.39 (6H, m), 8.65 (2H, d, ^3J = 8), 8.86 (1H, t, ^3J = 8) and 10.00 (2H, d, ^3J = 8 Hz). ES-MS (THF): m/z 960.1 ([M − Cl]$^+$) and 730.3 ([M − Cl − (Rh-(NBD)Cl)]$^+$).

These complexes gave IR spectra compatible with their formulations.

Crystal-structure determinations

L^4. C$_{21}$H$_{17}$N$_5$, M = 339.4, orthorhombic, space group *Pbcn*, a = 18.1923(12), b = 9.1514(4), c = 20.1888(9) Å, U = 3361.1(3) Å^3, Z = 8, μ(Mo-Kα) = 0.08 mm^{-1}, T = 200 K, 39992 measured reflections, 3308 observed [|F_o| > 4σ(F_o)] and 1239 unique (R_{int} for equivalent reflections = 0.061). R = 0.036, wR = 0.040.

[{Rh(NBD)Cl}$_2$L^5] 2. C$_{49}$H$_{61}$Cl$_2$N$_5$Rh$_2$, M = 996.9, triclinic, space group, $P\bar{1}$, a = 11.2730(8), b = 12.5579(9), c = 17.6931(12) Å, α = 92.805(8), β = 105.964(8), γ = 103.756(9)°, U = 2321.5(3) Å^3, Z = 2, μ(Mo-Kα) = 0.86 mm^{-1}, T = 170 K, 22760 measured reflections, 10428 unique (R_{int} for equivalent reflections = 0.031) of which 7066 were observed [|F_o| > 4σ(F_o)]. R = 0.042, wR = 0.044. The octyl chain C21a–C27a was disordered and refined with two atomic sites for each carbon atom with population parameters of 0.5. The disordered atomic sites were refined with isotropic displacement parameters (14 atoms) and all other non-H atoms (51) with anisotropic displacement parameters.

CCDC reference numbers 152869 and 152870.

See http://www.rsc.org/suppdata/dt/b0/b009051o/ for crystallographic data in CIF or other electronic format.

Physical measurements

IR spectra were obtained from KBr pellets with a Perkin-Elmer 883 spectrometer, ^{1}H NMR spectra at 25 °C on a Broadband Varian Gemini 300 spectrometer with chemical shifts given in ppm with respect to TMS. Pneumatically assisted electrospray (ES-MS) mass spectra were recorded from THF solutions on API III or API 3000 tandem mass spectrometers (PE Sciex) by infusion at 4–10 μl min^{-1} under low up-front declustering or collision induced dissociation (CID) conditions, typically ΔV = 0–30 V between the orifice and the first quadrupole of the spectrometer. Elemental analyses were performed by Dr H. Eder from the Microchemical Laboratory of the University of Geneva.

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