Solution Equilibria of Enantiopure Helicates: The Role of Concentration, Solvent and Stacking Interactions in Self-Assembly

Christophe Provent, Elisabeth Rivara-Minten, Sujatha Hewage, Gerhard Brunner, and Alan F. Williams*[a]

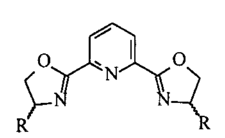
Abstract: The formation of helicates between silver(I) and a series of enantiopure ligands ($\mathbf{L_1}-\mathbf{L_4}$) containing the bis(oxazolyl) pyridine unit has been studied in solution. Ligands $\mathbf{L_1}$ and $\mathbf{L_2}$ form $[AgL_2]^+$ and double-helical $[Ag_2L_2]^{2+}$. $\mathbf{L_3}$ and $\mathbf{L_4}$ show more complicated behaviour, forming $[AgL_2]^+$, $[Ag_2L_2]^{2+}$, $[Ag_2L_3]^{2+}$ and $[Ag_3L_3]^{3+}$. The relative concentrations of the complexes may be modified by changing the total concentration or the solvent. For $\mathbf{L_3}$ the trinuclear species is believed to be stabilised by interligand π-stacking interactions which are enhanced in $\mathbf{L_4}$, leading to almost exclusive formation of $[Ag_3L_3]^{3+}$. All complexes appear to be labile on an NMR time scale at room temperature, and racemic mixtures of ligands undergo exclusive homochiral association.

Keywords: helical structures · N ligands · self-assembly · silver · supramolecular chemistry

Introduction

The formation of helicates in a self-assembly process by simple mixing of ligands and labile metal cations has been studied with great interest over the last ten years. Much work has been published on helicates since the first report by Lehn and co-workers.[1] In the earliest helicates, the helical axis passed through the metal ions, but the synthesis of circular helicates,[2] in which the ligands twist about a circle around which metal ions are disposed at regular intervals, has been reported recently. Several reviews[3–6] give an overview of these compounds and their properties.

Although helicates are chiral, the combination of achiral ligands and metal cations generally leads to racemic mixtures. To obtain selective synthesis of *P* and *M* helicates (which is an obvious challenge) chiral elements have been introduced into the ligands; if these ligands are well chosen enantioselective synthesis of helicates can be achieved, and several linear helicates have been prepared[7–14] by this strategy. A more recent development in this field has been the enantioselective synthesis of circular helicates.[15, 16] The chirality of helicates has been reviewed.[17] We have achieved enantioselective synthesis of helicates by using chiral bis(oxazolyl)pyridine ligands Bzpybox ($\mathbf{L_1}$) and Phpybox ($\mathbf{L_3}$) (Scheme 1),[15] the rhodium complexes of which were first reported by Nishiyama and co-workers in 1991 to achieve highly enantioselective hydrosilylation of ketones.[18]



$\mathbf{L_1}$: R = -CH_2-C_6H_5 (Bzpybox)
$\mathbf{L_2}$: R = -CH_3 (Mepybox)
$\mathbf{L_3}$: R = -C_6H_5 (Phpybox)
$\mathbf{L_4}$: R = -C_6H_4 -OC_2H_5 (EtOphpybox)

Scheme 1. The ligands $\mathbf{L_1}-\mathbf{L_4}$.

Both $\mathbf{L_1}$ and $\mathbf{L_3}$ form enantiopure helicates with Ag^I, but the type of helix differs. $\mathbf{L_1}$ forms a double helix, $[Ag_2(\mathbf{L_1})_2]^{2+}$ (see Figure 1); the complex has D_2 symmetry with pseudo-twofold axes passing through the silver ions and through the pyridine groups. The compound obtained with $\mathbf{L_3}$ was a circular trinuclear helix, $[Ag_3(\mathbf{L_3})_3]^{3+}$ (see Figure 3) with crystallographic C_3 symmetry, and consists of an equilateral triangle of silver(I) ions with the ligands bridging the sides of the triangle. Each ligand is bonded, through the oxazoline moieties, to one metal atom from below the plane of the silver atoms and to a second metal atom from above this plane. The structure shows strong stacking interactions between the pyridine group of one ligand and the phenyl rings of the other two. However, this trimeric cation appears to be unstable in solution, leading to an equilibrium between the different species.

Here we present studies of helicates with ligands $\mathbf{L_1}$, $\mathbf{L_2}$ (Mepybox), $\mathbf{L_3}$ and $\mathbf{L_4}$ (EtOphpybox) in solution. This work shows how the product of self-assembly can depend, as postulated previously,[19] on both external information (the solvent and concentration) and intrinsic information (the

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structure of the ligands and coordination preference of the metal). We also show how judicious use of π-stacking interactions can modify the product distribution in a predictable manner.

Results

Synthesis of the helicates: Synthesis of the ligands $\mathbf{L}_1$ and $\mathbf{L}_3$ was as described in a preliminary communication.[15] $\mathbf{L}_2$ was prepared by the same procedure as for $\mathbf{L}_1$ and $\mathbf{L}_3$. Ligand $\mathbf{L}_4$ was synthesised from pyridine-2,6-dicarboxylic acid and 4-hydroxyphenylglycine following a procedure described by Nesper and co-workers.[20] The silver helicates were prepared simply by mixing equivalent amounts of the ligands and silver(I) tetrafluoroborate in dichloromethane/methanol. After evaporation to dryness the residue was taken up in acetonitrile and crystallised by diffusion of diethyl ether or benzene.

Structures in solution

Helicates prepared with $\mathbf{L}_1$: In the solid state the silver(I) complex $[Ag_2(S,S\text{-}\mathbf{L}_1)_2](BF_4)_2$ has a double helical structure with $P(\Delta)$ helicity (Figure 1),[15] whose behaviour in solution has been determined in several studies.

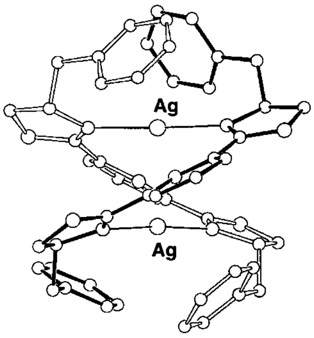


Figure 1. X-ray structure of $[Ag_2(S,S\text{-}\mathbf{L}_1)_2](BF_4)_2$.

Abstract in French: *Différents hélicates d'argent(I), préparés avec une série de ligands ($\mathbf{L}_1$–$\mathbf{L}_4$) contenant le motif bis(oxazolinyl)pyridine, ont été étudiés en solution. Avec les ligands $\mathbf{L}_1$ et $\mathbf{L}_2$, le complexe $[AgL_2]^+$ et la double hélice $[Ag_2L_2]^{2+}$ ont été observés. $\mathbf{L}_3$ et $\mathbf{L}_4$ présentent un comportement plus complexe, car selon les conditions, les espèces $[AgL_2]^+$, $[Ag_2L_2]^{2+}$, $[Ag_2L_3]^{2+}$ et $[Ag_3L_3]^{3+}$ ont été obtenues. Les proportions relatives des différents complexes peuvent être modifiées en faisant varier la concentration totale ou la nature du solvant. Dans le cas de $\mathbf{L}_3$, l'espèce trinucléaire semble être stabilisée par des interactions d'empilement de type "π stacking" qui se trouvent renforcées avec $\mathbf{L}_4$, conduisant ainsi à la formation quasi exclusive de $[Ag_3L_3]^{3+}$. A température ambiante, tous ces complexes sont labiles par rapport à l'échelle de temps RMN. Les expériences réalisées avec des mélanges racémiques des ligands ont permis d'observer exclusivement l'assemblage homochiral.*

Variable-temperature ^{1}H NMR ($-40\,^\circ C \leftarrow +50\,^\circ C$) of this complex in CD_3CN showed no modification of the spectrum. ^{1}H NMR titration of a solution of $S,S\text{-}\mathbf{L}_1$ in CD_3CN with $AgBF_4$ showed the successive formation of two species. Initially, a complex of stoichiometry $Ag^+/(S,S\text{-}\mathbf{L}_1) = 0.5{:}1$ was formed, but as more silver(I) was added the peaks broadened, sharpening again for a 1:1 metal-to-ligand ratio, after which the spectrum remained unmodified even after the addition of a large excess of silver salt. This result is in accordance with the formation of an $[Ag(S,S\text{-}\mathbf{L}_1)^+]_n$ species.

^{109}Ag NMR spectra of a concentrated solution (0.1 M in CD_3CN) of $[Ag_2(S,S\text{-}\mathbf{L}_1)_2](BF_4)_2$ with direct observation of the silver atom showed a single peak at $\delta = 512$ (reference: silver nitrate, $\delta = 0$). This peak corresponds to the silver atom in the helical compound and no trace of free silver was observed.

Electrospray mass spectrometry (ES-MS; Figure 2) of acetonitrile solutions of $[Ag(S,S\text{-}\mathbf{L}_1)^+]_n$ showed peaks at *m/z* 505.3 ($[Ag(S,S\text{-}\mathbf{L}_1)^+]_n$, base peak), 901.4 ($[Ag(S,S\text{-}\mathbf{L}_1)_2]^+$) and 1097.4 ($\{[Ag_2(S,S\text{-}\mathbf{L}_1)_2]\cdot(BF_4)\}^+$). The isotopic abundance of the peak at *m/z* 505.3 shows the typical (0.5) peak separation of a doubly charged species, which confirms the presence of the helical complex $[Ag_2(S,S\text{-}\mathbf{L}_1)_2]^{2+}$. The isotopic distribution pattern suggests that a small amount of $[Ag(S,S\text{-}\mathbf{L}_1)]^+$ was present, which has been attributed to fragmentation in the

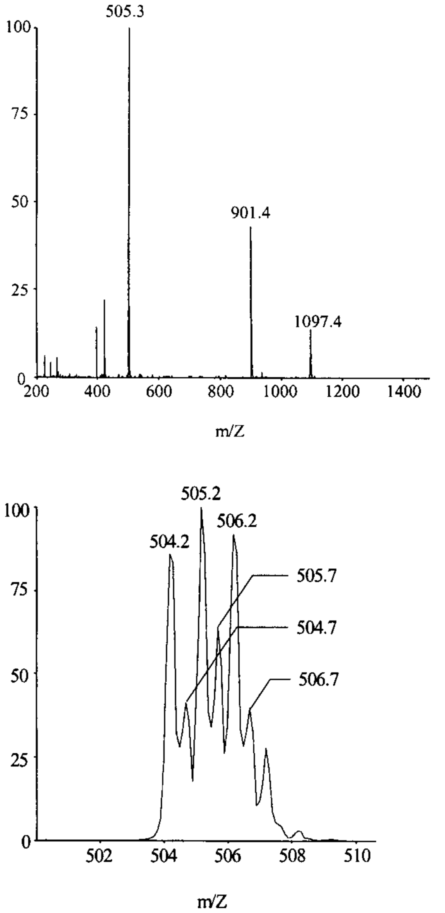


Figure 2. ES-MS of $[Ag_2(S,S\text{-}\mathbf{L}_1)_2](BF_4)_2$ in acetonitrile: whole spectrum (top); enlargement of peak corresponding to $[Ag(S,S\text{-}\mathbf{L}_1)]_2^{2+}$ (bottom).

mass spectrometer since the ^{1}H NMR spectrum shows the presence of only one product.

There are great changes in the CD spectrum of the ligand upon complex formation: the free ligand shows a weak negative band in the UV region of the spectrum ($\Delta\varepsilon_{296} = -0.4\,\text{M}^{-1}\text{cm}^{-1}$), whereas the complex shows a strong positive band ($\Delta\varepsilon_{301} = +10.15\,\text{M}^{-1}\text{cm}^{-1}$ for a one-metal centre), corresponding to a new shoulder in the UV/Vis spectrum ($\varepsilon = 1547\,\text{M}^{-1}\text{cm}^{-1}$). This CD activity can be attributed to a blocked conformation of the ligands in the helical compound, whereas the free ligand may adopt different conformations which cancel each other in the CD spectrum. This phenomenon has been explained for several organic compounds[21, 22] and metal complexes[16, 23] by the exciton theory.

The *R*,*R* enantiomer of $\mathbf{L_1}$ was synthesised in order to test chiral recognition during the self-assembly process. The two helicates Λ/*R*,*R* and Δ/*S*,*S*, each prepared with an enantiomerically pure ligand, are enantiomers and have the same ^{1}H NMR spectrum. When a racemic mixture of ligands was used, the spectrum of the product was the same as that of the pure species $[\text{Ag}_2(R,R\text{-}\mathbf{L_1})_2](\text{BF}_4)_2$ or $[\text{Ag}_2(S,S\text{-}\mathbf{L_1})_2](\text{BF}_4)_2$. No trace of the "mixed" species, which would have a different spectrum, was observed during the experiment and, logically, no CD signal was observed. This establishes that there is homochiral recognition during the self-assembly, which means that the chirality of the first ligand to be complexed induces a choice in the chirality of the second.

Helicates prepared with $\mathbf{L_2}$: The solution studies on $\mathbf{L_2}$ (Mepybox) with silver(I) led to the same results as with $\mathbf{L_1}$. The ^{1}H NMR spectrum of this complex in CD_3CN remained unchanged while the experimental temperature was gradually decreased from +50 °C to −40 °C, and clearly differed from that of the free ligand. As observed for $\mathbf{L_1}$ complexes, the use of a racemic mixture of *R*,*R*-$\mathbf{L_2}$ and *S*,*S*-$\mathbf{L_2}$ leads to the formation of species which have essentially the ^{1}H NMR spectrum observed for the pure diastereomers $[\text{Ag}_2(S,S\text{-}\mathbf{L_2})_2]^{2+}$ and $[\text{Ag}_2(R,R\text{-}\mathbf{L_2})_2]^{2+}$, confirming that homochiral self-assembly is observed with $\mathbf{L_2}$.

ES-MS of acetonitrile solutions of $[\text{Ag}(S,S\text{-}\mathbf{L_2})^+]_n$ exhibits peaks at *m/z* 351.9 ($[\text{Ag}(S,S\text{-}\mathbf{L_2})^+]_n$, 45 %), 393.1 ($[\text{Ag}(S,S\text{-}\mathbf{L_2})\text{CH}_3\text{CN}]^+$, base peak), 597.3 ($[\text{Ag}(S,S\text{-}\mathbf{L_2})_2]^+$, 60 %) and 792.8 ($\{[\text{Ag}_2(S,S\text{-}\mathbf{L_2})_2](\text{BF}_4)\}^+$, 25 %). This helicate seems to be more sensitive to fragmentation in the mass spectrometer than $[\text{Ag}_2(S,S\text{-}\mathbf{L_1})_2]^{2+}$. The abundance of $[\text{Ag}(S,S\text{-}\mathbf{L_2})\text{CH}_3\text{CN}]^+$ may indicate a partial dissociation of the complex in solution but this is not supported by the ^{1}H NMR spectrum, which shows only one species.

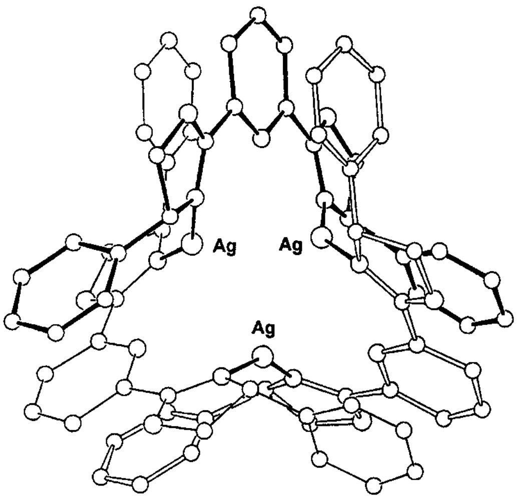


Figure 3. X-ray structure of $[\text{Ag}_3(R,R\text{-}\mathbf{L_3})]_3(\text{BF}_4)_3$.

Helicates prepared with $\mathbf{L_3}$: X-ray crystallography shows that in the solid state the silver(I) complex of $\mathbf{L_3}$ (Phpybox) has a circular helical structure (Figure 3).[15] There are strong stacking interactions between the strands, which are probably responsible for this particular structure in the solid state. In solution this trimeric circular helicate is not stable and spectroscopic studies have been performed to elucidate its behaviour.

The ^{1}H NMR spectrum of a concentrated solution (0.1 M in CD_3CN) of $[\text{Ag}_3(R,R\text{-}\mathbf{L_3})_3](\text{BF}_4)_3$ at 20 °C shows broad peaks typical of a rapid exchange on the NMR time scale. When the solution is heated to +60 °C the peaks narrow, leading to averaged signals. When it is cooled from +60 °C to −40 °C the peaks broaden around +30 °C, split into separate signals around −30 °C and eventually sharpen again at −40 °C. At −40 °C there are three distinct species (Figure 4); all the following NMR experiments have been carried out at this temperature.

^{1}H NMR titration of a solution of *R*,*R*-$\mathbf{L_3}$ in CD_3CN with AgBF_4 (Figure 5) showed the initial formation of a complex of stoichiometry $[\text{Ag}(R,R\text{-}\mathbf{L_3})_2^+]_n$; on addition of more silver(I), the peaks attributable to this compound decreased and another species appeared. Its abundance was maximal at a silver/ligand ratio around 0.7, corresponding to $[\text{Ag}_2(R,R\text{-}\mathbf{L_3})_3]^{2+}$. As the metal/ligand ratio increases, the proportion of the $[\text{Ag}_2(R,R\text{-}\mathbf{L_3})_3]^{2+}$ species decreases and two other complexes are formed. They have been identified as the double helical compound $[\text{Ag}_2(R,R\text{-}\mathbf{L_3})_2]^{2+}$ and the trimeric circular helix $[\text{Ag}_3(R,R\text{-}\mathbf{L_3})_3]^{3+}$. The NMR shifts are consistent with these structures and the pyridine and oxazoline proton shifts of the $[\text{Ag}_2(R,R\text{-}\mathbf{L_3})_2]^{2+}$ species can be compared with those of the $[\text{Ag}_2(R,R\text{-}\mathbf{L_1})_2]^{2+}$ species. Comparison of the NMR shifts of five protons in $[\text{Ag}_2(R,R\text{-}\mathbf{L_3})_2]^{2+}$ and $[\text{Ag}_2(R,R\text{-}\mathbf{L_1})_2]^{2+}$ (Table 1) shows clearly that protons expected to be little

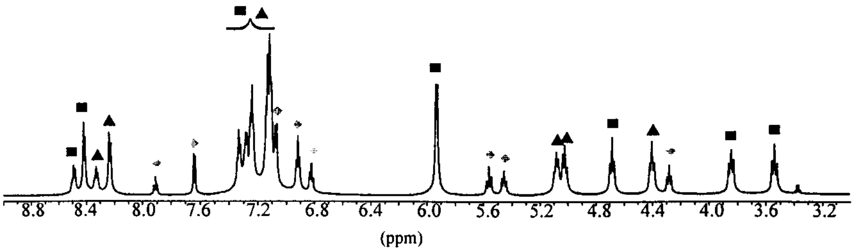


Figure 4. ^{1}H NMR spectrum (600 MHz) of *R*,*R*-$\mathbf{L_3}$ silver complex in CD_3CN at −40 °C; ■: $[\text{Ag}_2(R,R\text{-}\mathbf{L_3})_3]^{2+}$; ▲: $[\text{Ag}_2(R,R\text{-}\mathbf{L_3})_2]^{2+}$; ◆: $[\text{Ag}_3(R,R\text{-}\mathbf{L_3})_3]^{3+}$.

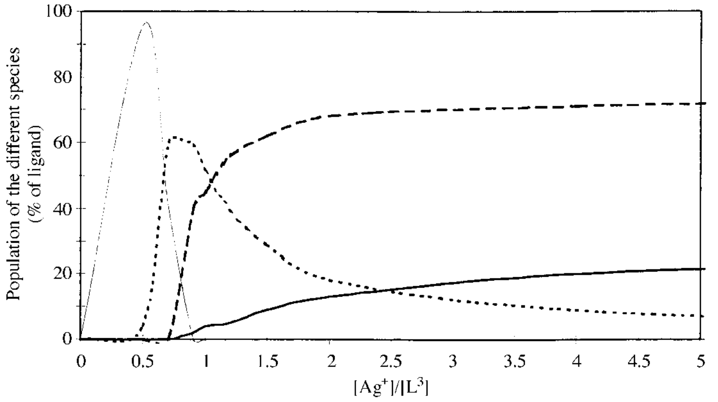
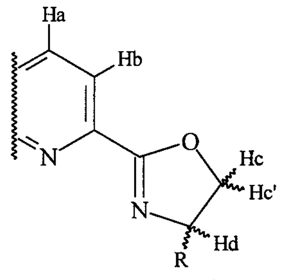


Figure 5. Species distribution as a function of stoichiometry, determined by ^1H NMR titration (CD_3CN, $-40\,^\circ C$) of a solution of R,R-$\mathbf{L_3}$ with $AgBF_4$. Solid light line: $[Ag(R,R\text{-}\mathbf{L_3})_2]^{2+}$; dotted line: $[Ag_2(R,R\text{-}\mathbf{L_3})_3]^{2+}$; broken line: $[Ag_2(R,R\text{-}\mathbf{L_3})_2]^{2+}$; solid dark line: $[Ag_3(R,R\text{-}\mathbf{L_3})_3]^{3+}$.

Table 1. Comparison of the ^1H NMR shifts of 5 protons of $[Ag_2(\mathbf{L_1})_2]^{2+}$ and $[Ag_2(\mathbf{L_3})_2]^{2+}$ (in CD_3CN at $-40\,^\circ C$). The proton assignment is given in Scheme 2.

Protons	^1H NMR shifts (ppm) in the $[Ag_2L_2]^{2+}$ species when R = Ph:$\mathbf{L_3}$	R = Bz:$\mathbf{L_1}$
Ha	8.31	8.32
Hb	8.22	8.16
Hc	5.11	5.19
Hc′	4.39	4.45
Hd	5.01	4.15

influenced by a change in the substituent of the oxazoline ring have similar NMR shifts. The shielding observed for proton H_d when the ligand is changed from $\mathbf{L_3}$ to $\mathbf{L_1}$ is due to the linkage of the carbon atom bonded to H_d with a phenyl or a benzyl moiety respectively (Scheme 2). Further arguments are given below to confirm the assignment of the three species.



Scheme 2. Proton assignment in $[Ag_2(\mathbf{L_1})_2]^{2+}$ and $[Ag_2(\mathbf{L_3})_2]^{2+}$ (R = Ph, Bz).

Influence of the solvent on the equilibrium: The ^1H NMR spectrum of the crystallised $[Ag_3(R,R\text{-}\mathbf{L_3})_3](BF_4)_3$ in a CD_3NO_2 solution shows the presence of only two species, and is well resolved even at room temperature. That $[Ag_2(R,R\text{-}\mathbf{L_3})_3]^{2+}$ is not observed can be explained by the different complexation properties of CD_3CN and CD_3NO_2. Formation of $[Ag_2(R,R\text{-}\mathbf{L_3})_3]^{3+}$ (stoichiometry = 2:3) upon dissolution of $[Ag_3(R,R\text{-}\mathbf{L_3})_3]^{3+}$ would lead to liberation of silver, which can be strongly solvated by acetonitrile but not by nitromethane. Therefore the formation of $[Ag_2(R,R\text{-}\mathbf{L_3})_3]^{2+}$ is not favourable in this solvent.

Influence of concentration on the equilibrium: The effect of concentrations between 160 mM (saturation) and 8 mM on the speciation was studied by ^1H NMR (CD_3CN, $-40\,^\circ C$) (Figure 6).

The percentage of trimer increases with concentration. $[Ag_3(R,R\text{-}\mathbf{L_3})_3]^{3+}$ represents 27% (with respect to the ligand) of the mixture for a concentration of 160 mM but disappears below 20 mM. This is logical because high concentrations favour the formation of the most polymeric species. The relative populations of the other two species, $[Ag_2(R,R\text{-}\mathbf{L_3})_2]^{2+}$ and $[Ag_2(R,R\text{-}\mathbf{L_3})_3]^{2+}$, decrease from 20 to 160 mM. Below 20 mM the double helical species population increases as rapidly as $[Ag_2(R,R\text{-}\mathbf{L_3})_3]^{2+}$ decreases. These trends are consistent with the proposed formulae, because the compound whose population increases upon dilution (to below 20 mM) is the least aggregated.

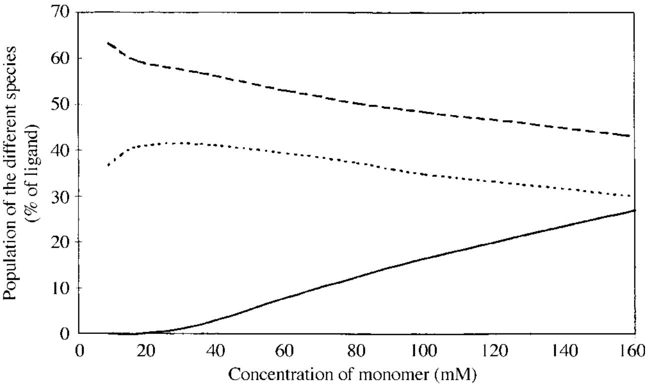


Figure 6. Speciation of the products of RR-Phpybox (R,R-$\mathbf{L_3}$) in solution with $AgBF_4$ as a function of total concentration determined by ^1H NMR spectroscopy (CD_3CN, $-40\,^\circ C$). Dotted line: $[Ag_2(R,R\text{-}\mathbf{L_3})_3]^{2+}$; broken line: $[Ag_2(R,R\text{-}\mathbf{L_3})_2]^{2+}$; solid line: $[Ag_3(R,R\text{-}\mathbf{L_3})_3]^{3+}$.

The ^{109}Ag NMR spectrum of a solution (0.1 M in CD_3CN) of the crystallised trimeric complex with direct observation of the silver atom at 20 °C is composed of a single broad peak around $\delta = 455$. When the solution is cooled to $-40\,^\circ C$, three sharp peaks are observed (δ = 501.8, 503.0 and 536.2, with respective integrals of 1.0, 0.5 and 0.2). By comparison with the proportions observed in the ^1H NMR spectrum, these peaks are assigned to correspond to $[Ag_2(R,R\text{-}\mathbf{L_3})_2]^{2+}$, $[Ag_2(R,R\text{-}\mathbf{L_3})_3]^{2+}$ and $[Ag_3(R,R\text{-}\mathbf{L_3})_3]^{3+}$ respectively. To confirm the assignment, a sample was prepared simply by mixing two equivalents of silver(I) tetrafluoroborate and three equivalents of R,R-$\mathbf{L_3}$ in CD_3CN, to generate the $[Ag_2(R,R\text{-}\mathbf{L_3})_3]^{2+}$ complex in situ. This solution at $-40\,^\circ C$ exhibits a single NMR peak at $\delta = 503.6$ corresponding to that observed in the mixture.

ES-MS of solutions of $[Ag(R,R\text{-}\mathbf{L_3})^+]_n$ in acetonitrile showed peaks at m/z 476.0 ($[Ag(R,R\text{-}\mathbf{L_3})^+]_n$, base peak), 517.3 ($[Ag(R,R\text{-}\mathbf{L_3})CH_3CN]^+$, 25%), 843.7 ($[Ag(R,R\text{-}\mathbf{L_3})_2]^+$, 60%) and 1041.2 ($\{[Ag_2(R,R\text{-}\mathbf{L_3})_2](BF_4)\cdot H_2O\}^+$, 20%). Very low-intensity peaks centred at m/z 1606.5 ($\{[Ag_3(R,R\text{-}\mathbf{L_3})_3CH_3CN](BF_4)_2\}^+$, approximately 2%) were also observed. The many peaks observed and the small amount of trimer are attributable to: 1) the equilibrium in solution; 2) the fragmentation in the spectrometer; and 3) the experimental concentration (10 mM), which is not favourable to the formation of the trimeric species.

The CD spectrum shows a strong negative band at 302 nm. Although the presence of more than one species makes quantification of the CD activity difficult, that the transition occurs at the same wavelength as the complex of $\mathbf{L}_1$ suggests that this CD activity should also be attributed to a blocked conformation of the ligand (exciton coupling).

Helicates prepared with $\mathbf{L}_4$ (EtOphpybox): Stacking interactions are probably responsible for the formation of $[Ag_3(R,R\text{-}\mathbf{L}_3)_3]^{3+}$, but, as shown above, it is not very stable in solution. One strategy to stabilise the compound would be to increase the π-stacking interactions. It has been shown that the substitution of aromatic rings can modify the π-stacking interactions between such rings.[24] Depending on whether the substituent is electron-withdrawing or -attracting, an increase in the stacking interactions may result which would lead to the stabilisation of the trimeric form. The ligand $R,R\text{-}\mathbf{L}_4$ (R,R-EtOphpybox) was therefore synthesised and its silver(I) complex was studied in solution.

The ^{1}H NMR spectrum of a 0.1 M solution of the complex in CD_3CN at 20 °C shows peaks of more than one species, with the typical broad shape of averaged signals that is observed when several species are in equilibrium in solution. On cooling from +20 to −40 °C, the peaks of the most abundant species sharpen around +10 °C, while the others remain broad. Between −30 and −40 °C, the broad peaks split and are resolved into three components: one major, $[Ag_3(R,R\text{-}\mathbf{L}_4)_3]^{3+}$ (90 %), and two minor ones, $[Ag_2(R,R\text{-}\mathbf{L}_4)_2]^{2+}$ and $[Ag_2(R,R\text{-}\mathbf{L}_4)_3]^{2+}$ (approximately 5 % each). These three species are similar to those observed in the $R,R\text{-}\mathbf{L}_3$ complex, but their proportions are different (Figure 7).

Influence of solvent on the equilibrium: As for $R,R\text{-}\mathbf{L}_3$, the ^{1}H NMR spectrum of a CD_3NO_2 solution of the crystallised complex shows only two species, $[Ag_2(R,R\text{-}\mathbf{L}_4)_2]^{2+}$ and $[Ag_3(R,R\text{-}\mathbf{L}_4)_3]^{3+}$, which are observed in equivalent quantities at room temperature. The effect of concentration on the equilibrium between the three species was followed by ^{1}H NMR (CD_3CN, −40 °C) and is shown in Figure 8.

The equilibrium is quite different from that observed with $R,R\text{-}\mathbf{L}_3$. For a monomer concentration of 160 mM there is effectively only one complex in solution, the $[Ag_3(R,R\text{-}\mathbf{L}_4)_3]^{3+}$ helix (98 %), whereas the two other species are almost undetectable. Upon dilution, the trimer proportion decreases, but remains preponderant as long as the concentration is greater than 8 mM. At this concentration the proportions of the three species are almost equal, around 30 %. At lower concentrations, $[Ag_2(R,R\text{-}\mathbf{L}_4)_2]^{2+}$ becomes dominant, while the proportion of the each of the others falls to zero for a concentration of 0.5 mM. $[Ag_2(R,R\text{-}\mathbf{L}_4)_3]^{2+}$ never constitutes more than 30 % of the species in solution; its proportion increases slowly between 160 and 5 mM and then decreases very rapidly at lower concentrations. Comparison of these results with those obtained with $R,R\text{-}\mathbf{L}_3$ (Figure 9) clearly establishes the importance of the π stacking interactions in stabilising the circular helix, and of their increase upon suitable functionalisation of the phenyl groups.

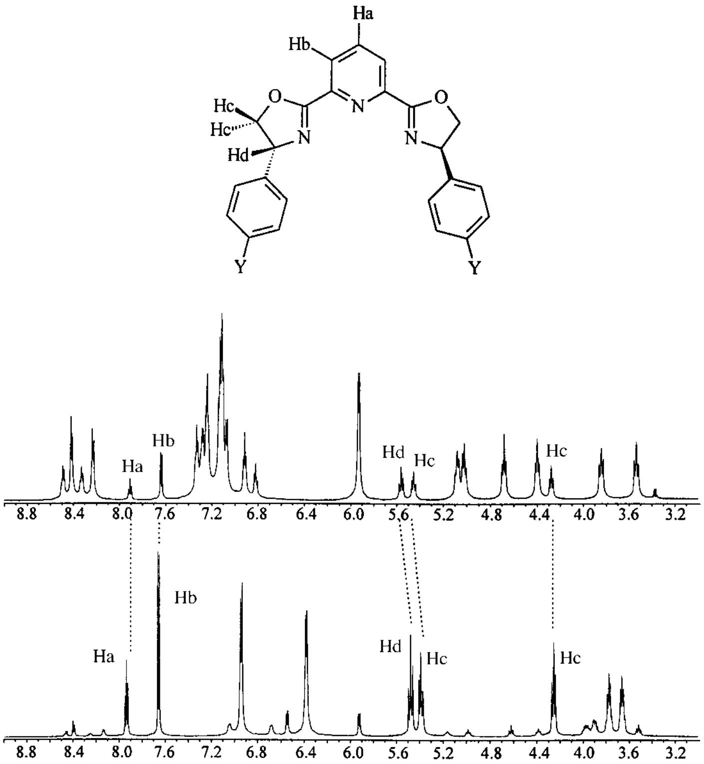


Figure 7. ^{1}H NMR spectrum of $R,R\text{-}\mathbf{L}_3$–silver (above) and $R,R\text{-}\mathbf{L}_4$–silver (below) complexes; (0.1 M; CD_3CN; −40 °C). The dotted lines join equivalent peaks for the trinuclear complexes.

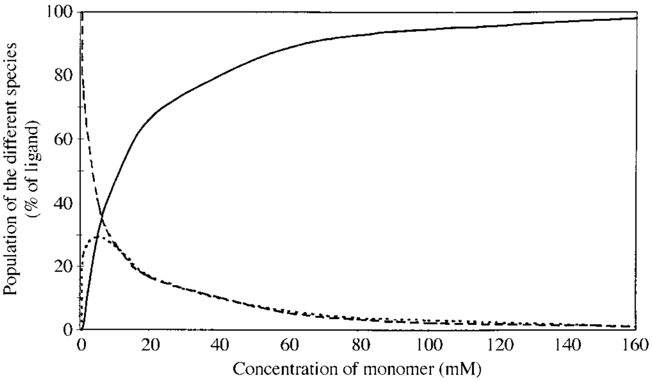


Figure 8. Speciation of $R,R\text{-}\mathbf{L}_4$–silver complex as a function of concentration. Dotted line: $[Ag_2(R,R\text{-}\mathbf{L}_4)_3]^{2+}$; broken line: $[Ag_2(R,R\text{-}\mathbf{L}_4)_2]^{2+}$; solid line: $[Ag_3(R,R\text{-}\mathbf{L}_4)_3]^{3+}$.

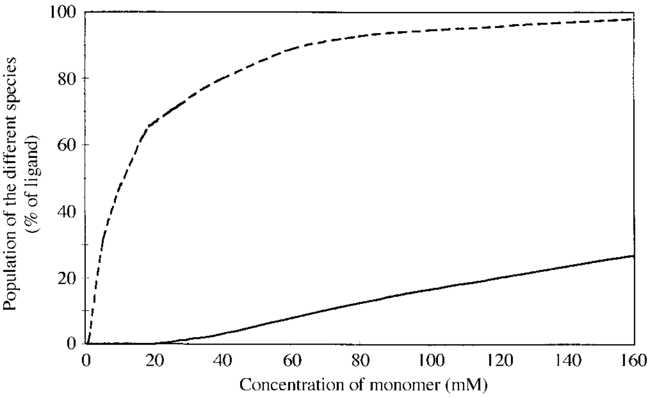


Figure 9. Proportion of Ag_3L_3 as a function of monomer concentration: solid line: $[Ag_3(R,R\text{-}\mathbf{L}_3)_3]^{3+}$; broken line: $[Ag_3(R,R\text{-}\mathbf{L}_4)_3]^{3+}$.

0947-6539/99/0512-3491 $ 17.50+.50/0

The ^{109}Ag NMR spectrum of the crystallised complex (0.1 M in CD_3CN; −40 °C) shows a single peak at $\delta = 532.5$, which corresponds to the chemical shift of the silver atom in the circular helix $[Ag_3(R,R\text{-}\mathbf{L_4})_3]^{3+}$ and which is similar to that observed for $[Ag_3(R,R\text{-}\mathbf{L_3})_3]^{3+}$. ES-MS of acetonitrile solutions of $[Ag(RR\text{-}\mathbf{L_4})^+]_n$ shows peaks at *m/z* 564.0 ($[Ag(R,R\text{-}\mathbf{L_4})^+]_n$, 80 %), 605.3 ($[Ag(R,R\text{-}\mathbf{L_4})CH_3CN]^+$, 60 %), 1023.2 ($[Ag(R,R\text{-}\mathbf{L_4})_2]^+$, base peak), 1217.1 ($\{[Ag_2(R,R\text{-}\mathbf{L_4})_2](BF_4)\}^+$, 40 %) and 1871.0 ($[[Ag_3(R,R\text{-}\mathbf{L_4})_3](BF_4)_2]^+$, 20 %). As observed for the $R,R\text{-}\mathbf{L_3}$ complexes, several species are present, for the reasons listed previously (the equilibrium in solution, the fragmentation in the spectrometer and the experimental concentration), but with the great difference that, as the trimeric species is more stable, it is now clearly detected in the mass spectrometer.

The CD spectrum of this compound shows a single band at approximately the same wavelength as those of the silver complexes of $\mathbf{L_1}$ and $\mathbf{L_3}$. This is a strongly negative band, at 308 nm ($\Delta\varepsilon_{308} = -10.2\,M^{-1}cm^{-1}$), which can be attributed to a blocked conformation of the ligands (exciton coupling). It is interesting to compare this band with that of the $(R,R\text{-}\mathbf{L_3})$–silver complex, which is expected to have, at least partially, the same circular helical structure. The intensity of the CD signal measured for the $(R,R\text{-}\mathbf{L_4})$ complex is 150 % of that observed with the $(R,R\text{-}\mathbf{L_3})$ complex. This enhancement is consistent with the NMR and MS results and provides further proof of the increase in the proportion of circular helicate observed with ligand $(R,R\text{-}\mathbf{L_4})$.

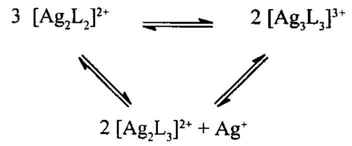
Discussion

At first sight the results reported above for the closely related ligands $\mathbf{L_1}$–$\mathbf{L_4}$ reveal a remarkable variety of behaviour, since these ligands differ only in substituents remote from the coordination site. The data give clear evidence that in all four cases the systems are at equilibrium, with rapid kinetics as shown by the ^{1}H NMR spectra. These conditions are indeed necessary for self-assembly reactions, so that mistakes can be corrected and the minimum free energy attained. In these circumstances, any effect influencing the total free energy may modify the position of the free-energy minimum, and thereby the most stable product. The metal ion coordination preferences and the disposition and nature of the ligand-binding sites are generally the primary considerations in metal-directed self-assembly reactions, but intramolecular ligand–ligand interactions, the solvation energy and the activity of the components (both their relative activities (the stoichiometry) and their total concentration) may all intervene. The results presented here involve the same ligand-binding site and, with the exception of the $[Ag_2L_3]^{2+}$ complex, all show two-coordinate Ag^I; the differences in behaviour may therefore be attributed to the last three effects.

The behaviour of $\mathbf{L_1}$ and $\mathbf{L_2}$ is essentially identical, with stepwise formation of $[AgL_2]^{2+}$ and $[Ag_2L_2]^{2+}$. The double helicate is stable, and corresponds to the structure observed in the solid state by X-ray crystallography.[15] The two ligands with phenyl substituents, $\mathbf{L_3}$ and $\mathbf{L_4}$, show quite different behaviour, which may be attributed to ligand–ligand interactions in the complexes. This is also, we suppose, the reason for the formation of the $[Ag_2L_3]^{2+}$ complex, which is not observed with $\mathbf{L_1}$ and $\mathbf{L_2}$.

The formation of $[Ag_3L_3]^{3+}$ from $[Ag_2L_2]^{2+}$ is disfavoured by entropy considerations. This entropy barrier may be overcome either by increasing the concentration of silver and ligand in solution (the activity effect) or by including a counterbalancing enthalpic term for the formation of the trinuclear species, which is achieved by the π stacking observed between phenyl groups and pyridine moieties, and confirmed by the increase in stability of the trinuclear species observed when donor groups are grafted onto the phenyl ring to augment the stacking. We believe this is the first example in which stacking interactions have been shown unambiguously to determine the structure of a metal-assembled complex, although very recent work has shown how the ratio of ML/ML_2 complexes may be changed by stacking.[26] Although many X-ray crystal structures have demonstrated the existence of π-stacking interactions, it has never been clearly established that their presence is essential to the adoption of the structure.

The equilibrium of $[Ag_3L_3]^{3+}$ and $[Ag_2L_2]^{2+}$ with $[Ag_2L_3]^{2+}$ implies liberation of free silver ions (Scheme 3), and is consequently dependent upon the solvation energy of such an ion. Acetonitrile solvates the ion well enough for significant quantities of $[Ag_2L_3]^{2+}$ to be present in a solution with an Ag/L ratio of 1:1, but nitromethane is not able to stabilise the free silver ion sufficiently. The peak broadening due to rapid exchange was less noticeable in nitromethane, suggesting that the exchange may take place by a dissociative mechanism such as that observed previously for a related dicopper helical system.[27] Constable et al. have recently reported a similar change in product for a silver–terpyridine complex upon changing from acetonitrile to dichloromethane.[28]



Scheme 3. Equilibrium of $[Ag_3L_3]^{3+}$ and $[Ag_2L_2]^{2+}$ with $[Ag_2L_3]^{2+}$.

The results presented here show again that the structure of the product crystallising from solution may correspond to only one of the products present in solution, as previously reported by Lehn et al.,[29] who found the simultaneous presence of grids, linear helicates and circular helicates in a system composed of copper(I) and a bisbidentate system. In such systems, minor changes to the ligands (intrinsic information), or to the external conditions (conditional information) may suffice to displace the equilibrium in favour of one particular product. This is indeed a prerequisite for what Lehn has termed "virtual combinatorial libraries",[31] where the inclusion of one anion or another can change the structure of the final product; Raymond and co-workers[32] have reported a similar example where a cation included in a tetrahedral adamantane structure may be exchanged rapidly, implying rapid dissociation and reassociation of the complex. These systems contain much more strongly complexing units (chelate ligands with di-, tri- or tetravalent cations) than the simple systems discussed here, yet they show equally flat potential surfaces. Constable and co-workers recently reported a copper(I)–quaterpyridine system in which a variety of helical complexes with nuclearities between 2 and 5 were observed as a function of concentration.[30] Although factors such as π-stacking, concentration and solvent might seem to add complexity, they may also be used, if they are well understood, as elements of control for the self-assembly process.

Although the results reported here show the simultaneous existence of a variety of species in solution, the experiments with racemic mixtures of the ligands demonstrate a strong preference for homochiral association.

Experimental Section

General: Dichloromethane, methanol and diethyl ether were purified according to standard procedures. Other solvents (Fluka p.a.) were used without further purification. Anhydrous silver tetrafluoroborate (Fluka) was used without purification. Melting points were recorded on a Büchi apparatus and are uncorrected. NMR solvents ([D$_3$]acetonitrile, [D$_3$]nitromethane and D_2O, isotopic purity > 99.80 atom % D) were from Dr. Glaser AG Basel. CD spectra were recorded on a Jasco J-715 spectropolarimeter with a 1 cm cell at 22 °C.

Synthesis of ligands and complexes: The syntheses of the ligands have been discussed previously.[15, 18, 20] All complexes were prepared according to the same procedure: the ligands (0.5 mmol) in dichloromethane (5 mL) were each mixed with a methanolic solution (5 mL) of silver tetrafluoroborate (0.5 mmol) and then stirred for 15–30 min at room temperature. The solution was evaporated to dryness, and the residue taken up in acetonitrile (3–5 mL). After filtration to remove insoluble material, crystals were obtained by diffusion of diethyl ether or benzene.

$[Ag_2(S,S\text{-}L_1)_2](BF_4)_2$: Crystallographic data, elemental analysis and ^1H NMR characterisation were reported previously.[15] ^{109}Ag NMR (27.93 MHz, [D$_3$]acetonitrile, 22 °C, $AgNO_3$): $\delta = 512$.

$[Ag_2(R,R\text{-}L_1)_2](BF_4)_2$: M.p. 204–210 °C (decomp); ^1H NMR (300 MHz, [D$_3$]acetonitrile, 22 °C, TMS): $\delta = 2.48$ (dd, $J = 11.5$, 14.0 Hz, 2H), 3.12 (dd, $J = 3.3$, 14.0 Hz, 2H), 4.15 (dq, 2H), 4.45 (dd, $J = 9.1$, 10.7 Hz, 2H), 5.19 (dd, $J = 9.2$, 9.4 Hz, 2H), 6.46 (t, 2H), 6.72 (t, 4H), 6.99 (d, 4H), 8.16 (d, 2H), 8.32 (t, 1H); $Ag_2C_{50}H_{46}N_6O_4B_2F_8$: calcd C 50.71, H 3.92, N 7.10; found C 50.64, H 4.05, N7.07.

Mixture of 2 $AgBF_4$, 1*R,R*-L_1 and 1*S,S*-L_1: M.p. 208–211 °C (decomp); ^1H NMR (300 MHz, [D$_3$]acetonitrile, 22 °C, TMS): $\delta = 2.44$ (dd, $J = 11.7$, 13.8 Hz, 2H), 3.10 (dd, $J = 2.6$, 13.8 Hz, 2H), 4.03 (dq, 2H), 4.43 (dd, 2H), 5.19 (dd, 2H), 6.36 (t, 2H), 6.67 (t, 4H), 6.97 (d, 4H), 8.12 (d, 2H), 8.29 (t, 1H); $Ag_2C_{50}H_{46}N_6O_4B_2F_8 \cdot 0.5\,H_2O$: calcd C 50.33, H 3.97, N 7.04; found C 50.38, H 4.00, N 7.03.

$[Ag_2(R,R\text{-}L_2)_2](BF_4)_2$: M.p. 199–202 °C (decomp); ^1H NMR (300 MHz, [D$_3$]acetonitrile, 22 °C, TMS): $\delta = 1.19$ (d, 6H), 4.10–4.25 (m, 2H), 4.25 (dd, 2H), 4.78 (dd, 2H), 8.15 (d, 2H), 8.25 (t, 1H); $Ag_2C_{26}H_{30}N_6O_4B_2F_8$: calcd C 35.49, H 3.44, N 9.55; found C 35.43, H 3.55, N 9.52.

$[Ag_2(S,S\text{-}L_2)_2](BF_4)_2$: M.p. 199–202 °C (decomp); $Ag_2C_{26}H_{30}N_6O_4B_2F_8$: calcd C 35.49, H 3.44, N 9.55; found C 35.36, H 3.57, N 9.56.

Mixture of 2 $AgBF_4$, 1*R,R*-L_2 and 1*S,S*-L_2: M.p. 197–200 °C (decomp); ^1H NMR (300 MHz, [D$_3$]acetonitrile, 22 °C, TMS): $\delta = 1.19$ (d, 6H), 4.20–4.40 (m, 4H), 4.83 (dd, 2H), 8.18 (d, 2H), 8.27 (t, 1H); $Ag_2C_{26}H_{30}N_6O_4B_2F_8$: calcd C 35.49, H 3.44, N 9.55; found C 35.46, H 3.51, N 9.55.

$[Ag_3(R,R\text{-}L_3)_3](BF_4)_3$: Crystallographic data and elemental analysis were reported previously.[15] ^1H NMR (300 MHz, [D$_3$]acetonitrile, 0.1M, −40 °C, TMS): three species: 35 % of Ag_2L_3 [$\delta = 3.54$ (t, 2H), 3.84 (t, 2H), 4.67 (t, 2H), 5.94 (d, 4H), 7.05–7.35 (m, 10H), 8.40 (d, 2H), 8.47 (t, 1H)]; 17 % of Ag_3L_3 [$\delta = 4.28$ (t, 2H), 5.45 (t, 2H), 5.56 (t, 2H), 6.81 (t, 2H), 6.92 (t, 4H), 7.05 (d, 4H), 7.63 (d, 2H), 7.91 (t, 1H)]; and 48 % of Ag_2L_2 [$\delta = 4.39$ (t, 2H), 5.01 (t, 2H), 5.11 (t, 2H), 7.05–7.35 (m, 10H), 8.22 (d, 2H), 8.31 (t, 1H)]; ^1H NMR (300 MHz, [D$_3$]nitromethane, 0.1M, 21 °C, TMS): two species: 16 % of Ag_3L_3 [$\delta = 4.52$ (t, 2H), 5.56 (t, 2H), 5.67 (t, 2H), 6.93 (t, 2H), 7.04 (t, 4H), 7.12 (d, 4H), 7.93 (d, 2H), 8.12 (t, 1H)]; and 84 % of Ag_2L_2 [$\delta = 4.79$ (t, 2H), 5.32 (t, 2H), 5.52 (t, 2H), 7.10–7.22 (m, 8H), 7.24–7.31 (m, 2H), 8.37 (d, 2H), 8.44 (t, 1H)]; ^{109}Ag NMR (27.93 MHz, [D$_3$]acetonitrile, 0.1M, −40 °C, $AgNO_3$): $\delta = 494.2$ (int. = 1), 501.0 (int. = 0.5), 534.3 (int. = 0.2).

$[Ag_2(R,R\text{-}\mathbf{L_3})_3]^{2+}$ generated in situ: ^1H NMR (300 MHz, [D$_3$]acetonitrile, 0.1M, −40 °C, TMS): approx. 70 % of Ag_2L_3 [$\delta = 3.54$ (t, 2H), 3.84 (t, 2H), 4.70 (t, 2H), 5.95 (d, 4H), 6.95–7.35 (m, 10H), 8.40 (d, 2H), 8.50 (t, 1H)]; ^{109}Ag NMR (27.93 MHz, [D$_3$]acetonitrile, −40 °C, $AgNO_3$): $\delta = 503.6$.

$[Ag_3(R,R\text{-}L_4)_3](BF_4)_3$: M.p. 200–210 °C (decomp); ^1H NMR (300 MHz, [D$_3$]acetonitrile, −40 °C, TMS): more than 95 % of Ag_3L_3 [$\delta = 1.34$ (t, 6H), 3.65 (t, 2H), 3.77 (t, 2H), 4.25 (t, 2H), 5.39 (t, 2H), 5.49 (t, 2H), 6.38 (d, 4H), 6.94 (d, 4H), 7.66 (d, 2H), 7.93 (t, 1H)]; ^{109}Ag NMR (27.93 MHz, [D$_3$]acetonitrile, −40 °C, $AgNO_3$): $\delta = 532.5$; $Ag_3C_{81}H_{81}N_9O_{12}B_3F_{12}$: calcd C 49.72, H 4.17, N 6.44; found: C 49.38, H 4. 18, N 6.36.

^1H NMR titrations: These were all carried out by the same procedure, the only difference being the temperature (20 or −40 °C). All spectra were recorded on a Varian Gemini-300 NMR spectrometer at 300 MHz. The first spectrum was that of the free ligand in CD_3CN (0.7 mL), except for $\mathbf{L_4}$ where 10 % of CD_3Cl was added. The starting solution was between 5×10^{-2} and 10^{-1}M. Small amounts (0.1– 0.5 equiv) of a concentrated solution of silver(I) tetrafluoroborate in CD_3CN were added, and a spectrum was recorded after each addition. The concentration range of the silver solution was between 5×10^{-1} and 1M. The populations of the complexes were estimated from the integrals.

^{109}Ag NMR measurements: ^{109}Ag NMR spectra were recorded at 27.93 MHz on a Bruker AMX 2-600 in a BBO probehead (reference: $AgNO_3$ in D_2O, $\delta = 0$) using 10 mm tubes and relatively high concentrations ($[Ag^+] \approx 0.1$M). In view of the very long T_1 relaxation times of this nucleus, no attempt was made to calibrate the pulse, and it was found by trial and error that an acquisition time of 2.9 s and a delay of 2 s gave an acceptable signal-to-noise ratio. Between 350 and 3000 pulses were needed, depending on the sample: the complexes generally gave shorter T_1 values than free Ag^+.

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