JOC Article
pubs.acs.org/joc

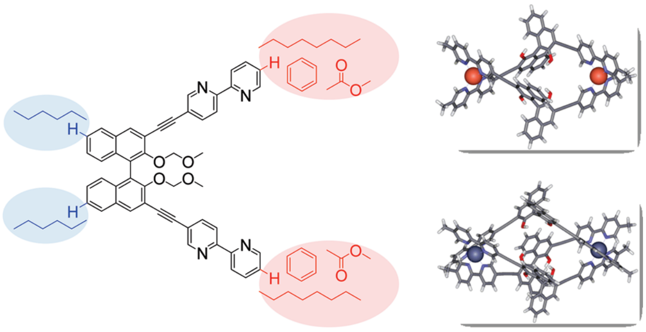
# Surprising Substituent Effects on the Self-Assembly of Helicates from Bis(bipyridyl) BINOL Ligands

Jens Bunzen, Rainer Hovorka, and Arne Lützen*

*Kekulé Institute of Organic Chemistry und Biochemistry, University of Bonn, Gerhard-Domagk-Str. 1, 53121 Bonn, Germany*

*arne.luetzen@uni-bonn.de*

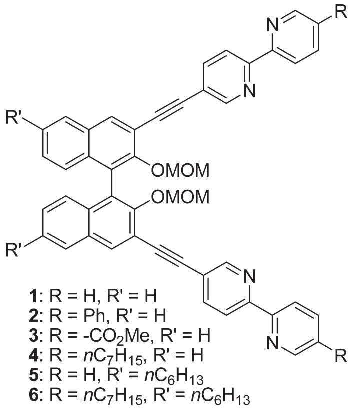
*Received February 6, 2009*



A number of different bis(bipyridyl) BINOL ligands were prepared using a convergent building block approach. These were studied with regard to their ability to undergo self-assembly to dinuclear helicates upon coordination to suitable late-transition-metal ions. Surprisingly, the substituents at the periphery of the ligand structure were found to have a marked influence on the outcome of the self-assembly processes with regard to the helicates composition, the stereoselectivity of the helicate formation, their redox reactivity, and their electronical properties as scrutinized by NMR- and CD-spectroscopic methods as well as ESI-mass spectrometric methods.

## Introduction

Since the beginning of supramolecular chemistry, chemists have tried to build up complex structures via self-assembly, thereby mimicking nature.[1] One of the most challenging aspects of these efforts is the implementation of information into the different moieties supposed to form the supramolecular structures. Chirality is one of the most prominent features in this context, and there have been quite a number of beautiful examples where (dia-)stereoselective self-assembly could be achieved.[2] However, the field is far from being mature because it is still almost impossible to predict the degree of selectivity of these processes provided by a given ligand structure and even more difficult to predict the configuration of newly formed stereochemical elements in the self-assembled supramolecular aggregates.



**1**: R = H, R' = H
**2**: R = Ph, R' = H
**3**: R = $-CO_2Me$, R' = H
**4**: R = $nC_7H_{15}$, R' = H
**5**: R = H, R' = $nC_6H_{13}$
**6**: R = $nC_7H_{15}$, R' = $nC_6H_{13}$

In 2002, we reported on the synthesis and self-assembly behavior of chiral ligand **1**.[3] This ligand is able to form

---

(1) Some general reviews: (a) Lindsey, J. S. *New J. Chem.* **1991**, *15*, 153–180. (b) Lawrence, D. S.; Jiang, T.; Levett, M. *Chem. Rev.* **1995**, *95*, 2229–2260. (c) Fyfe, M. C. T.; Stoddart, J. F. *Acc. Chem. Res.* **1997**, *30*, 393–401. (d) Greig, L. M.; Philp, D. *Chem. Soc. Rev.* **2001**, *30*, 287–302.

(2) Some recent reviews about stereoselective self-assembly: (a) Spector, M. S.; Selinger, J. V.; Schnur, J. M. *Top. Stereochem.* **2003**, *24*, 281–372. (b) Hamilton, T. D.; MacGillivray, L. R. *Cryst. Growth Design* **2004**, *4*, 419–430. (c) Mateos-Timoneda, M. A.; Crego-Calama, M.; Reinhoudt, D. N. *Chem. Soc. Rev.* **2004**, *33*, 363–372. (d) Crego-Calama, M., Reinhoudt, D. N., Eds. Supramolecular Chirality. *Top. Curr. Chem.* 2006, 265. (e) He, C.; Zhao, Y.; Guo, D.; Lin, Z.; Duan, C. *Eur. J. Inorg. Chem.* **2007**, 3451–3463. (f) Lee, S. L.; Lin, W. *Acc. Chem. Res.* **2008**, *41*, 521–537. For a more comprehensive list of references on the diastereoselective self-assembly of helicates see references listed in ref 19.

(3) Lützen, A.; Hapke, M.; Griep-Raming, J.; Haase, D.; Saak, W. *Angew. Chem., Int. Ed.* **2002**, *41*, 2086–2089.

Published on Web 06/11/2009
DOI: 10.1021/jo900254r

enantiomerically pure double- and triple-stranded helicates with transition-metal ions in a completely diastereoselective self-assembly process. This encouraging result was only dimmed by the low solubility of the helicate obtained with the OH-free ligand, which precipitated from organic solutions within minutes to hours after formation depending on the concentration of the initial mixture. We therefore decided to introduce substituents into the ligand structure in order to enhance the solubility and to further elaborate our concept. The positioning of each substituent was a crucial part of the design of the modified ligands. We chose the 5′-position on the 2,2′-bipyridine moiety and the 6-position on the 1,1′-binaphthyl (BINOL) part because interactions with the self-assembly process should be at a minimum using these positions.

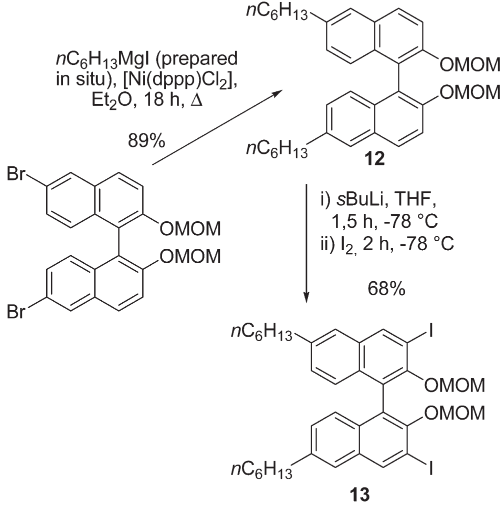
## Results and Discussion

**Synthesis.** The main and last step in the synthesis of ligands (*P*)- and (*M*)-**2**−**6** is a 2-fold Sonogashira cross-coupling of the BINOL and the bipyridine moieties, thereby connecting the two main building blocks, which have to be prepared prior to these reactions. By using this convergent strategy, we were able to build up the ligand structures in a concise manner with a minimum amount of time and resources, thereby minimizing the number of steps which would otherwise lie between 10 and 14 steps per ligand.

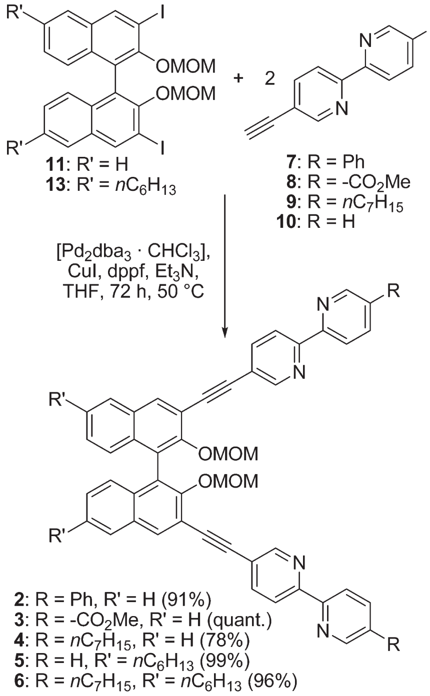
The 2,2′-bipyridine building blocks **7**−**10** were synthesized according to known procedures starting from (functionalized) 2-chloro- or 2-bromopyridines,[4−10] which were coupled via our modified Negishi cross-coupling procedure[10,11] (see the Supporting Information for details).

Two different BINOL moieties were prepared. Starting from enantiomerically pure BINOL, 3,3′-diiodo-2,2′-di(methoxymethoxy)-1,1′-binaphthyl (**11**) could be generated by introducing the acetal protecting group,[12] followed by *ortho*-lithiation and subsequent quenching with an iodine solution.[13] In the case of BINOL **13**, the first step of the reaction sequence was a bromination followed by the introduction of the MOM protecting group to give **12** (Scheme 1).[12,14] Then, a Kumada protocol was applied in order to introduce the *n*-hexyl chains in **12**,[15] which was followed by *ortho*-lithiation and subsequent iodination to afford the desired product **13** (Scheme 1).[13b] Following these sequences, we obtained **11** and **13** in both enantiomeric forms each. These compounds proved to be configurationally very stable because boiling in toluene for 1 week did not result in racemization.

**SCHEME 1. Synthesis of BINOL Building Block 13**



**SCHEME 2. Synthesis of Ligands 2−6 via 2-Fold Sonogashira Cross-Coupling**



As mentioned before, the 2,2′-bipyridine and BINOL building blocks were finally connected in usually very good yields by a 2-fold Sonogashira coupling procedure. Scheme 2 depicts these last reactions in the transformation sequences of the ligands **2**−**6**, which were prepared in both enantiomeric forms each.

**Metal Coordination Studies.** After having finished the syntheses, we started to investigate the complexation behavior of each ligand. For our studies, we chose silver(I),

---

(4) (a) Hama, Y.; Nobuhara, Y.; Aso, Y.; Otsubo, T.; Ogura, F. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1683–1686. (b) Dolci, L.; Dolle, F.; Valette, H.; Vaufrey, F.; Fuseau, C.; Bottlaender, M.; Crouzel, C. *Bioorg. Med. Chem.* **1999**, *7*, 467–479.

(5) Daab, J. C.; Bracher, F. *Monatsh. Chem.* **2003**, *134*, 573–583.

(6) Bouillon, A.; Lancelot, J.-C.; Collot, V.; Bovy, P. R.; Rault, S. *Tetrahedron* **2002**, *58*, 2885–2890.

(7) Magidson, O.; Menchikov, G. *Chem. Ber.* **1925**, *58B*, 113–118.

(8) Baxter, P. N. W. *J. Org. Chem.* **2000**, *65*, 1257–1272.

(9) Grave, C.; Lentz, D.; Schaefer, A.; Samori, P.; Rabe, J. P.; Franke, P.; Schlüter, A. D. *J. Am. Chem. Soc.* **2003**, *125*, 6907–6918.

(10) Kiehne, U.; Bunzen, J.; Staats, H.; Lützen, A. *Synthesis* **2007**, 1061–1069.

(11) (a) Lützen, A.; Hapke, M. *Eur. J. Org. Chem.* **2002**, 2292–2297. (b) Lützen, A.; Hapke, M.; Staats, H.; Bunzen, J. *Eur. J. Org. Chem.* **2003**, 3948–3957. (c) Hapke, M.; Staats, H.; Wallmann, I.; Lützen, A. *Synthesis* **2007**, 2711–2719. (d) Hapke, M.; Brandt, L.; Lützen, A. *Chem. Soc. Rev.* **2008**, *37*, 2782–2797.

(12) (a) Ishitani, H.; Ueno, M.; Kobayashi, S. *J. Am. Chem. Soc.* **2000**, *122*, 8180–8186. (b) Yang, X.-W.; Sheng, J.-H.; Da, C.-S.; Wang, H.-S.; Su, W.; Wang, R.; Chan, A. S. C. *J. Org. Chem.* **2000**, *65*, 295–296.

(13) (a) Bähr, A.; Droz, A. S.; Püntener, M.; Neidlein, U.; Anderson, S.; Seiler, P.; Diederich, F. *Helv. Chim. Acta* **1998**, *81*, 1931–1963. (b) Yamashita, Y.; Ishitani, H.; Shimizu, H.; Kobayashi, S. *J. Am. Chem. Soc.* **2002**, *124*, 3292–3302.

(14) Cui, Y.; Evans, O. R.; Ngo, H. L.; White, P. S.; Lin, W. *Angew. Chem., Int. Ed.* **2002**, *41*, 1159–1162.

(15) Xiao, D.; Zhang, Z.; Zhang, X. *Org. Lett.* **1999**, *1*, 1679–1681.

copper(I), zinc(II), and iron(II) ions because these showed remarkable results with our initial ligand **1**: silver and copper ions were demonstrated to lead to double-stranded helicates whereas zinc and iron ions lead to triple-stranded helicates in a completely diastereoselective manner. As in our previous study, tetrafluoroborate salts of silver(I), copper(I), iron(II), and zinc(II) were chosen because this counterion has a weak coordination ability, thus making sure that they do not compete with the bipyridine ligands in the complex formation.[16] When acetonitrile solutions of the salts were mixed with dichloromethane solutions of the ligands, silver(I) always gave pale yellow to clear solutions, copper(I) was yellow to red brown but became green in a period of 24 h in the case of ligands **2** and **4** to **6**, and zinc(II) was pale to strong yellow. Iron(II) gave different tinges of red, depending on the ligand used and the concentration of the complex in solution, thus indicating the expected formation of iron(II) low-spin complexes.

This first encouraging hint at a successful complex formation was examined by ESI MS in order to check the correct stoichiometry of the coordination compounds. Therefore, mixtures of the ligands and the individual metal salts were prepared that would correspond to $5\times10^{-5}$ mol/L solutions of the expected dinuclear double- or triple-stranded helicates. These were inserted directly into the mass spectrometer. We discuss the mass spectra obtained for the iron(II), zinc(II), and silver(I) complexes of ligand **6** here first, which are also indicative for the behavior of ligands **2**, **4**, and **5** and which are very similar to the ones we obtained earlier for ligand **1**. The mass spectra show strong signals for the expected dinuclear triple-stranded aggregates in the case of the iron(II) and zinc(II) complexes: the spectrum of the iron complex shows the expected signal at $m/z$ = 849 which compares to the correct stoichiometry of a triple-stranded complex $[\mathrm{Fe}_2(\mathbf{6})_3]^{4+}$ without any counterions. The sole other signal at $m/z$ = 1170 is an adduct of two formate anions and one sodium ion $\{\mathrm{Na}[\mathrm{Fe}_2(\mathbf{6})_3](\mathrm{HCO}_2)_2\}^{3+}$, which derives from the internal standard used in our mass spectrometric analyses. A very similar spectrum was obtained for the zinc complex: Besides a signal at $m/z$ = 854 for the quadruply charged triple-stranded dinuclear complex $[\mathrm{Zn}_2(\mathbf{6})_3]^{4+}$, two smaller signals at $m/z$ = 1168 and $m/z$ = 1177 can be observed. The former stands for the complex with one tetrafluoroborate counterion $\{[\mathrm{Zn}_2(\mathbf{6})_3]\mathrm{BF}_4\}^{3+}$ and the latter gives the mass for the above-mentioned sodium formate adduct $\{\mathrm{Na}[\mathrm{Zn}_2(\mathbf{6})_3](\mathrm{HCO}_2)_2\}^{3+}$.

The spectrum of the silver(I) complex of **6**, however, does contain some more signals. Besides the expected one at $m/z$ = 1204 that results from the doubly charged double-stranded dinuclear helicate, we also observed some signals that can be assigned to a monomeric species $[\mathrm{Ag}(\mathbf{6})]^+$ and the protonated ligand. This behavior, which is most pronounced in this series in the case of the complexes of **6**, is rather typical for silver(I) helicates in our hands,[3,17,18] and these ions are rather fragments of the helicate that are formed during the ESI process than species that are present in solution since we cannot observe these with any other spectroscopic tool (see, e.g., NMR characterization below). Tandem MS experiments of the metal complexes of ligand **6** corroborate this: they revealed that the most stable dinuclear complexes are formed with iron(II) ions. In fact, the binding of the metal ions is so strong that the ion of the intact dinuclear complex ($m/z$ = 850) loses the acetal groups and the alkyl chains by breaking C−O and C−C bonds upon collision-induced dissociation (CID) first instead of falling apart by losing bipyridine ligands or mononuclear iron complexes (or fragments thereof). The zinc complex ($m/z$ = 854) also loses acetal groups upon CID; however, it also fragments into a doubly charged species containing one zinc atom and either one or two ligands at $m/z$ = 579 and $m/z$ = 1128 by losing a ligand and a zinc ion, respectively. It is important to note, however, that we never observed a fragment containing two zinc ions and two ligand strands which would result from the loss of a single ligand. This also means that the observation of an $[\mathrm{Zn}_2\mathrm{L}_2]^{4+}$ ion indicates that this dinuclear double-stranded species is actually present in solution and not a fragment of a triple-stranded one. Very similarly, the doubly charged double-stranded silver(I) complex at $m/z$ = 1204 fragments into a singly charged species containing one silver ion and one ligand as can be observed from the isotopic pattern.

In the case of copper(I), the ESI mass spectra reveal another interesting feature of ligands **2**, **4**, **5**, and **6** that we did not observe in the earlier studies with ligand **1**: in the case of ligand **6**, e.g., there is a signal at $m/z$ = 1159 that results from the expected double-stranded helicate $[\mathrm{Cu}_2(\mathbf{6})_2]^{2+}$; however, an even stronger signal is found at $m/z$ = 854. This unexpected new species can be assigned to a triple-stranded complex of copper(II) $[\mathrm{Cu}_2(\mathbf{6})_3]^{4+}$. Obviously, making the bipyridine more electron-rich by substitution with an aryl or an alkyl group leads to an easier oxidation of the copper(I), and the same seems to be true for introducing steric bulk in the BINOL core which might cause a larger dihedral angle between the two naphthyl groups of the BINOL that induces some steric strain and hence destabilizes the double-stranded aggregate but favors the triple-stranded arrangement and thus facilitates the oxidation.

Interestingly, ligand **3** as the most electron-deficient ligand of this series behaves quite differently: similar to the behavior of ligand **1**, the copper(I) complexes of **3** proved to be much less prone to oxidation and thus only signals arising from the expected dinuclear double-stranded complex $[\mathrm{Cu}_2(\mathbf{3})_2](\mathrm{BF}_4)_2$ but no signals of a triple-stranded dinuclear copper (II) could be detected even after several days. A second remarkable and unique feature of this ligand compared to its derivatives is the complexation behavior toward zinc(II) ions. Besides a signal that can be assigned to the expected triple-stranded coordination compound $[\mathrm{Zn}_2(\mathbf{3})_3]^{4+}$ at $m/z$ = 668, another signal of very small intensity can be found that arises from a dinuclear species that carries only two ligand strands $[\mathrm{Zn}_2(\mathbf{3})_2]^{4+}$ at $m/z$ = 455. Also, two other signals were observed that could be assigned to the 1- and 2-fold protonated ligand **3** at $m/z$ = 847 and 424, respectively. This is surprising because zinc(II) complexes of this class of complexes are usually very stable under the ESI MS conditions in our hands and, hence, give very clean spectra that only contain signals that arise from one dinuclear species. This can have two reasons: either this dinuclear zinc(II)

---

(16) Please note that our equipment does not allow us to measure elemental analyses of fluorine-containing samples. Thus, we could not measure these for our metal complexes.

(17) (a) Kiehne, U.; Weilandt, T.; Lützen, A. *Org. Lett.* **2007**, *9*, 1283–1286. (b) Kiehne, U.; Lützen, A. *Org. Lett.* **2007**, *9*, 5333–5336. (c) Kiehne, U.; Weilandt, T.; Lützen, A. *Eur. J. Org. Chem.* **2008**, 2056–2064.

(18) Bunzen, J.; Bruhn, T.; Bringmann, G.; Lützen, A. *J. Am. Chem. Soc.* **2009**, *131*, 3621–3630.

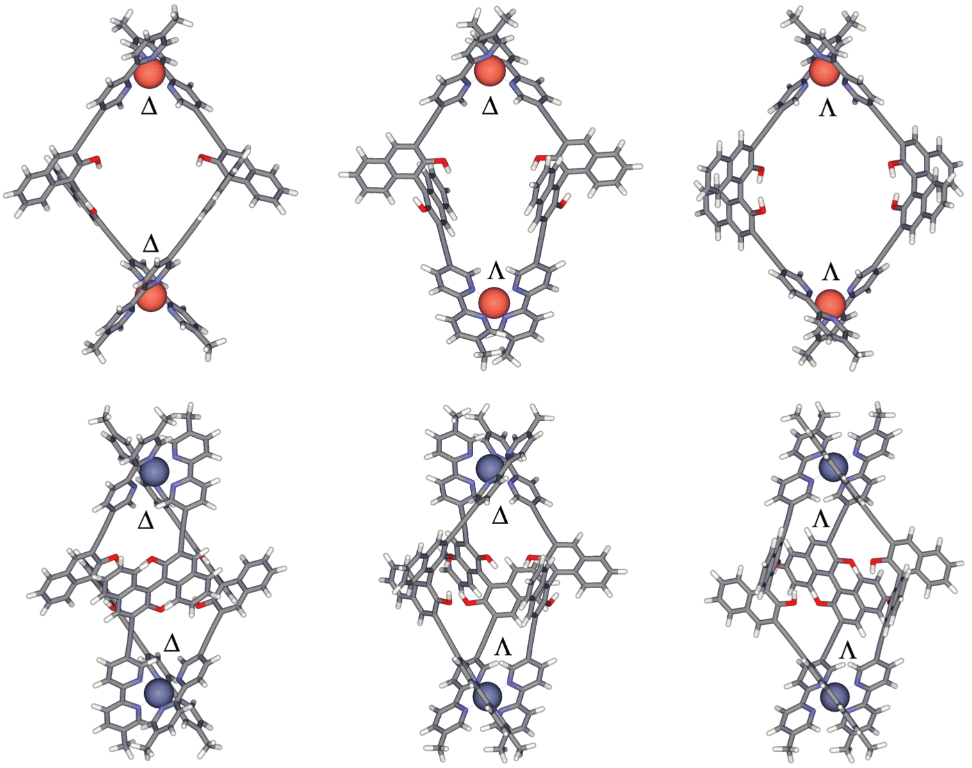


**FIGURE 1.** PM3-TM (Spartan)-minimized structures of the three possible diastereomers of (*P*)-ligand **4** with copper(I) (top row) and zinc(II) (bottom row) (methoxymethoxy groups omitted and heptyl chains reduced to methyl groups for viewing clarity, chirality descriptors for the metal complexes follow the *oriented skew line* system).

coordination compound is not as stable as the others due to the electron-withdrawing substituents on the bipyridines, which make it more prone to fragmentation, or the self-assembly process of the coordination compound formed with zinc(II) ions and ligand **3** is not selective with regard to the stoichiometry. This could be caused by the steric effects since the steric crowding is definitely more pronounced in a tris (bipyridyl) complex where the ester groups are in very close proximity than in a bis(bipyridyl) complex. Thus, the double-stranded helicate might become similarly favored.[17a,19] To distinguish between these two possibilities, we performed a tandem MS study. Since we again did not find the $[Zn_2(\mathbf{3})_2]^{4+}$ ion as a fragment of $[Zn_2(\mathbf{3})_3]^{4+}$ in an MS/MS experiment, we believe that the latter explanation is true and the self-assembly is not selective with regard to the stoichiometry of the assembly. Only the spectra of the silver(I) and iron(II) complexes, however, do show similar ions like the ones obtained with ligands **2**, **4**, **5**, and **6** with the expected stoichiometry corresponding to the double- and triple-stranded species $[Ag_2(\mathbf{3})_2]^{2+}$ and $[Fe_2(\mathbf{3})_3]^{4+}$, respectively. Again, tandem ms experiments with the silver(I) and the iron(II) complex showed the same fragmentation as the complexes of ligand **6**.

The observation of specific and (in most cases) expected stoichiometry of the complexes is a good proof for the successful self-assembly behavior of our ligands. But mass spectrometry is of course very limited when it comes to specifying the stereochemical arrangement of the complexes (Figure 1).

Therefore, we turned to NMR studies next. Despite the fact that the kinetic lability of copper(I) helicates could be proven by ligand-exchange experiments with isotopically labeled ligands in the case of **1**,[3] we could still measure NMR spectra of the copper(I) complexes of **1** and **3**. However, only these could be studied in detail by NMR since the oxidation to paramagnetic copper(II) in all other systems severely hampered long-term experiments. The spectra show sharp signals directly after mixing of the copper(I) salt and the ligands and prove instant formation of the dinuclear complexes. However, only a few hours later they undergo oxidation, finally resulting in a total breakdown of the signals due to the presence of the paramagnetic metal centers and thus preventing experiments that require longer times.

Hence, we rather discuss the results of our NMR studies with the silver(I) and zinc(II) complex solutions here first. Both silver(I) and zinc(II) complex solutions usually give rise to sharp signals.

Figure 2 depicts the spectra obtained from the complexes of ligand **4**. The shifts of the signals, especially the ones of the bipyridine moiety, are easy to recognize and exceptionally strong. This is another indication for the successful formation of defined metal coordination compounds with the particular metal ion, thus corroborating the results obtained by mass spectrometry. In principle, three different diastereomers of a dinuclear helicate can be formed from an enantiomerically pure dissymmetric bis(bipyridine) ligand as shown in Figure 1. In almost all cases, we observed only a single set of signals indicating that the self-assembly process is completely diastereoselective.[20]

---

(19) Sigel, H.; Martin, R. B. *Chem. Soc. Rev.* **1994**, *23*, 83–91.

(20) We also performed variable-temperature NMR studies and found that the spectra did not change when we lowered the temperature (until the complexes precipitated from solution). Due to the use of dichloromethane, however, we could not perform any high-temperature experiments to observe thermal dissociation of our helicates.

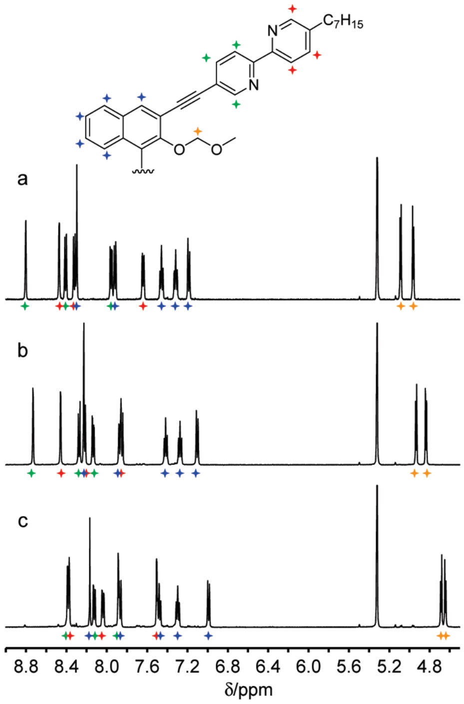


**FIGURE 2.** $^1$H NMR spectra of ligand **4** (500.1 MHz, 4.5 mM; $CD_2Cl_2/CD_3CN$ 4:1 at 300 K): (a) free ligand **4**, (b) 1:1 mixture of **4** and $[Ag(CH_3CN)_4]BF_4$, (c) 3:2 mixture of **4** and $Zn(BF_4)_2$ (note that there are traces of free ligand visible in the spectrum).

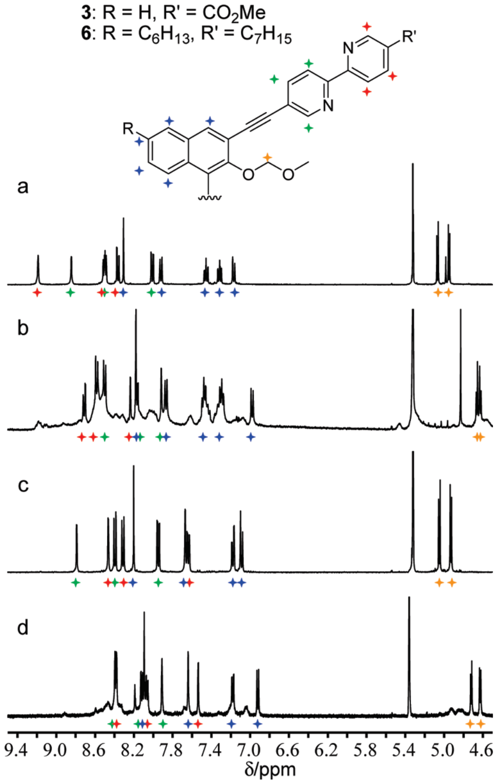


**FIGURE 3.** $^1$H NMR spectra of ligands **3** and **6** (500.1 MHz, 1.4 mM; $CD_2Cl_2/CD_3CN$ 3:1 at 298 K): (a) ligand **3**, (b) 3:2 mixture of ligand **3** and $Zn(BF_4)_2$, (c) ligand **6**, (d) 3:2 mixture of ligand **6** and $Zn(BF_4)_2$.

However, there are three exceptions to this rule: the first one is the zinc(II) complex of ligand **3**, which already gave unexpected mass spectra that indicated the formation of more than one type of aggregate upon coordination to zinc(II) ions.

However, the spectra of the zinc complexes of **5** and **6** also reveal the presence of at least one more species besides the expected *D*-symmetric main component (Figure 3). In the cases of **5** and **6**, however, we could only observe dinuclear triple-stranded zinc coordination compounds by mass spectrometry. To rule out the formation of polymeric species, we made dilution experiments in order to make sure that we are below the concentration that would favor the formation of polymeric rather than discrete species, but the ratio of the main species relative to the secondary one remained unchanged. Thus, we conclude that these ligands do undergo selective self-assembly in terms of the stoichiometric ratio of metal ions and ligands, but they are not selective with regard to the stereochemical outcome of the assembly.

Nevertheless, simple $^1$H NMR experiments do already allow us to make a first assignment of the stereochemical arrangement of our helicates: the dominant (and in most cases the exclusively formed) dinuclear coordination compounds in solution cannot be (Δ,Λ)-configured because this would result in much more complex spectra due to the lower symmetry ($C_n$ vs $D_n$) compared to the dissymmetric diastereomers whose metal centers have the same configuration ((Δ,Δ) or (Λ,Λ)) and hence consist of two homomorphous portions as the ligand does.

Unfortunately, the spectra of the iron solutions in mixtures of deuterated dichloromethane and acetonitrile could not be interpreted because of an exceptional strong broadening of the peaks, despite ruling out that this is a result of paramagnetic contamination by iron(III) ions. Again, we performed dilution studies down to concentrations close to the ones used for the ESI MS experiments where we only found signals arising from the discrete dinuclear complexes but the spectra did not change, thus also ruling out the formation of coordination polymers. As observed in previous cases, this is rather due to the dynamic nature of these aggregates because of intramolecular rearrangements (ligand exchange can also not be ruled out). Since the iron complexes tend to precipitate from these solutions at temperatures around 0 °C, we were not able to slow these processes enough to obtain sharp signals by temperature-dependent experiments. However, as demonstrated for a similar ligand,[18] these dynamic processes could be slowed considerably by changing the solvent to a mixture of deuterated dichloromethane and DMSO. Therefore, we also examined the iron complexes in this solvent. After proving the formation of dinuclear triple-stranded coordination compounds by ESI MS, we recorded NMR spectra of these helicates. Actually, the ligand exchange in these solutions was found to be so slow that we could observe the initial formation of a number of coordination compounds directly after mixing as they slowly equilibrate to finally give the most stable *D*-symmetric diastereomer (almost) exclusively (Figure 4).

Interestingly, ligand **3** behaves different again: whereas all iron complexes of the other ligands gave red solutions as expected for iron(II) low-spin tris(bipyridine) complexes, the dinuclear complexes of **3** were found to give green solutions (in $CD_2Cl_2/CD_3CN$ 3:1 the complex solution is red). This indicates that the iron should not be a low-spin iron(II) but

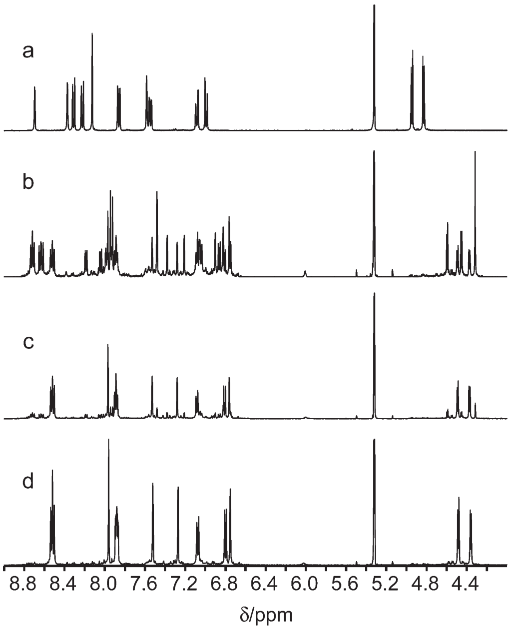


**FIGURE 4.** $^1$H NMR spectra of iron(II) complexes of ligand **6** (500.1 MHz, 1.4 mM; $CD_2Cl_2$/DMSO-$d_6$ 3:1 at 298 K): (a) ligand **6** (400 MHz), (b) 3:2 mixture of **6** and $Fe(BF_4)_2 \cdot 6\,H_2O$ 1 h after mixing, (c) the same mixture after 24 h, (d) the same mixture after 3 d.

has a different electron configuration resulting in a paramagnetic species. This assumption is also corroborated by the NMR spectra of this complex because the signals do show significant broadening compared to the iron complexes of the other ligands. Also, an ESI MS of this green iron(II) complex showed only one signal at $m/z$ = 663 resulting from the expected dinuclear triple-stranded species $[Fe_2(\mathbf{3})_3]^{4+}$, that readily fragments at 20 eV, which reveals a lower stability of the complex in comparison to the red iron(II) complexes of, e.g., ligand **6** as was expected for changing the electron configuration from diamagnetic low-spin to some paramagnetic species.

Finally, we also performed DOSY NMR experiments to study the aggregates' size and composition. For the silver(I), zinc(II), and iron(II) complexes of ligands **3** and **6**, DOSY experiments showed just one species in solution (the minor species of the zinc(II) complexes were undetectable) with the diffusion constants growing from the triple-stranded zinc complexes (**3**: $D = 7.34 \times 10^{-10}$ m$^2$/s; **6**: $D = 4.55 \times 10^{-10}$ m$^2$/s) to the double-stranded silver complexes (**3**: $D = 7.65 \times 10^{-10}$ m$^2$/s; **6**: $D = 5.33 \times 10^{-10}$ m$^2$/s) and the free ligand (**6**: $D = 7.03 \times 10^{-10}$ m$^2$/s). Although the lack of any reliable data for the viscosity of the solvent mixture used for these experiments did not allow the calculation of any hydrodynamic radii of the aggregates, the relative differences already corroborate the conclusions drawn from the ESI MS and NMR experiments, since triple-stranded complexes contain the longest axis and should therefore have the smallest diffusion constant. Also, the constants are larger for the corresponding complexes of ligands **3** compared to the ones of **6**, which was expected, taking into account that the complexes of **3** with the ester groups are considerably smaller than those of **6** carrying the long alkyl chains. Unfortunately, the iron(II) complexes were measured in another solvent mixture and could therefore not really be compared with the other complexes (**3**: $D = 4.04 \times 10^{-10}$ m$^2$/s; **6**: $D = 2.29 \times 10^{-10}$ m$^2$/s) except for the fact that these experiments again confirm that the triple-stranded helicates of ligand **6** are larger than the ones of ligand **3** with almost the same ratio of the $D$ values of $D(\mathbf{6})/D(\mathbf{3}) \approx 0.6$.

To finally discern between the two $D_n$-symmetric possibilities, we measured ROESY-NMR spectra, but the distances between the BINOL and the bipyridine moieties are too large to get ROE-contacts strong enough to allow an unambiguous assignment of one or the other diastereomer. Therefore, we applied chiral dichroism spectroscopy (CD spectroscopy). This powerful chirooptical method is the best known approach to investigate chiral metal complexes in solution.[21] In particular, chiral 2,2′-bipyridine complexes were examined thoroughly in recent years.[22]

Since our ligands proved to be configurationally stable when we heated them for longer periods in toluene, the CD spectra prove that the optical antipodes of ligands **2**−**6** give rise to enantiomeric dinuclear helicates. We discuss the results obtained with ligand **4** exemplarily here. Free ligand **4** and its silver and copper helicate solutions give very similar spectra. This behavior can be understood if one takes into account the exiton theory: opposite cotton effects cancel each other to zero, when the angle between the dipoles of the ligands is 90° as it is (nearly) found in a tetrahedral coordination of a metal ion by two 2,2′-bipyridine ligands that adopt an (almost) perpendicular orientation in a double-stranded helicate. Thus, CD-spectroscopy cannot be used alone to discriminate between the two possible isomers of our silver and copper complexes. However, as we found out earlier with ligand **1** and other dissymmetric bis(bipyridine) BINOL-based ligands,[3,18] the stereochemical information of the ligands usually induces the same configuration of the metal centers regardless if they are double- or triple-stranded. Thus, the stereochemical assignment of the triple-stranded helicates can usually be transferred to the double-stranded analogues (as long as the self-assembly process is highly stereoselective, of course). Hence, we turned to the CD spectroscopic analysis of the triple-stranded aggregates. As expected, the spectra of the iron and zinc helicates show great differences compared to the one of free ligand **4**, thus corroborating the before mentioned theoretical considerations.[21] Compared with CD data from the literature there is clear evidence that the iron complexes with ($M$)-configured ligands give (Λ,Λ)-configured helicates and a ($P$)-configuration of the ligands results in a (Δ,Δ)-configuration of the metal centers, respectively. Of course, the spectroscopic behavior of all of these complexes is in accordance with the exiton theory: the negative exiton couplet in the region from 300 to 425 nm of the ($P$)-ligands gives an unambiguous proof for a (Δ,Δ)-configuration at the stereogenic metal centers.[23] Therefore, we can assign a (Δ,Δ)-configuration for iron(II) complexes

---

(21) (a) von Zelewsky, A. *Stereochemistry of Coordination Compounds*; John Wiley & Sons: Chichester, 1996. (b) Ziegler, M.; von Zelewsky, A. *Coord. Chem. Rev.* **1998**, *177*, 257–300.

(22) (a) Quinodoz, B.; Labat, G.; Stoeckli-Evans, H.; von Zelewsky, A. *Inorg. Chem.* **2004**, *43*, 7994–8004. (b) Murner, H.; von Zelewsky, A.; Hopfgartner, G. *Inorg. Chim. Acta* **1998**, *271*, 36–39. (c) Prabaharan, R.; Fletcher, N. C.; Nieuwenhuyzen, M. *J. Chem. Soc., Dalton Trans.* **2002**, 602–608. (d) Prabaharan, R.; Fletcher, N. C. *Inorg. Chim. Acta* **2003**, *355*, 449–453.

(23) Berova, N., Nakanishi, K., Woody, R. W., Eds. *Circular Dichroism: Principles and Applications*, 2nd ed.; Wiley-VCH: Weinheim, 2000.

based on ($P$)-configured ligands and a ($\Lambda$,$\Lambda$)-configuration based on ($M$)-configured ligands. The sole exception to this rule is observed for the green iron(II) complex in $CD_2Cl_2$/DMSO of ligand **3**. The CD spectrum of this complex shows no complex specific cotton effects revealing just the spectrum of the free ligand. In the case of octahedral coordination of metal centers this behavior would be possible in three scenarios where two opposite complex specific cotton effects would compensate each other: either a $\Delta$,$\Lambda$-species is formed selectively, which would be quite unexpected given the results of all other ligands, or a 1:1 mixture of the $\Delta$,$\Delta$- and $\Lambda$,$\Lambda$-species would be formed by accident, or probably the most likely scenario a (statistical) mixture of all three possible diastereomeric complexes is generated. Unfortunately, the broadening of the NMR signals of this complex make these spectra uninterpretable and therefore no further information about the selectivity of the self-assembly process could be obtained in this case.

The spectra of the zinc complexes are very similar to the ones of the red low-spin iron(II) helicates. Every ligand exerts strong cotton effects-even the solutions of ligands **3**, **5**, and **6** that do not self-assemble in a completely selective manner although they each form one clearly dominant species that should rule the spectrum compared to the minor (in most cases diastereomeric) byproducts. Even though there is not as much comparable circular dichroism data for zinc complexes to be found in the literature than for the respective iron complexes,[22b,22c] the cotton effects nevertheless clearly hint at a ($\Lambda$,$\Lambda$) configuration of the stereogenic metal centers in the helicates based on ligands with an ($M$)-configured ligand and vice versa. This is of course again in accordance with the exiton theory.

Furthermore, the bands point into the same direction as in the case of the respective iron helicates, indicating the same absolute configuration at the metal centers. This result is also corroborated by our previous work where we assigned a ($\Delta$,$\Delta$) configuration to helicates derived from ($P$)-ligand **1** based on ROESY NMR experiments and an X-ray diffraction analysis of the molecular structure of the ($\Delta$,$\Delta$)-$\{Zn_2[(P)\text{-}\mathbf{1}]_3\}(BF_4)_4$ helicate.[3]

## Conclusion

We prepared a series of bis(bipyridine)BINOL ligands in a concise manner using a convergent building block approach. These ligands are "programmed" to form dinuclear helicates upon coordination to suitable late-transition-metal ions and were designed to enhance the solubility of the ligands and the metallosupramolecular aggregates compared to the one of previously reported lead structure **1**. This objective was fully achieved; the solubility of the ligands and the resulting helicates could be enhanced by the introduction of substituents having a maximum with ligand **6**. However, the different solubilizing substituents used for these purposes turned out to have some surprising effects on the self-assembly of these metallosupramolecular entities which was investigated in solution using NMR and CD spectroscopy as well as ESI mass spectrometry.[24]

In most cases, these processes happen in a completely or at least highly diastereoselective manner: the triple-stranded helicates formed by iron(II) and zinc(II) ions and ($P$)-ligands were found to have a ($\Delta$,$\Delta$)-configuration of the metal centers, and the ($M$)-ligands were found to induce a ($\Lambda$,$\Lambda$)-configuration. Unexpectedly, however, the introduction of $n$-hexyl chains at the remote 6- and 6′-positions on the BINOL core reduces the diastereoselectivity of the self-assembly processes leading to triple-stranded zinc(II) helicates. Other astonishing effects were observed when electron-withdrawing groups like acyl groups were introduced in the 5′-position of the 2,2′-bipyridine units like in ligand **3**: in this case, the self-assembly process of dinuclear zinc(II) complexes was found to be unselective with regard to the stoichiometry of the resulting helicate since both double- and triple-stranded species were found. Furthermore, **3** as the most electron-deficient ligand of this series obviously induces a different electron configuration of iron(II) centers in the helicates in a mixture of dichloromethane/DMSO because we observed the formation of a paramagnetic, green triple-stranded dinuclear complex (most probably as a mixture of all possible diastereomers) instead of the expected diamagnetic, red low-spin iron(II) complexes which are formed with all other ligands. In contrast, electron-donating alkyl or phenyl groups in the 5′-position of the 2,2′-bipyridine groups, however, do not influence the stereoselectivity of these processes but were found to have a remarkable effect on the redox chemistry of the dinuclear coordination compounds since dinuclear double-stranded copper(I) helicates were found to undergo rapid oxidation (and rearrangement) to dinuclear triple-stranded paramagnetic copper(II) helicates. Interestingly, this behavior was not observed for lead structure **1** or the acylated ligand **3**. These results clearly demonstrate how sensitive these processes are to subtle changes in the ligand structure. Even the introduction of substituents in remote positions of the ligand structures was proven to have a marked and not always obvious influence on the selectivity of the self-assembly of triple-stranded helicates. This is by far less pronounced in case of the formation of double-stranded helicates. Another interesting feature is the surprisingly strong effect of substituents at the bipyridines on the redox behavior of copper helicates and the electron configuration of iron helicates which will be explored in future studies.

## Experimental Section

**($M$)- or ($P$)-6,6′-Di($n$-hexyl)-2,2′-di(methoxymethoxy)-1,1′-binaphthyl (12).** An 82 mg (3.38 mmol; 7.2 equiv) portion of magnesium powder (activated with 1,2-dibromoethane) was suspended in 20 mL of dry diethyl ether. To this mixture was added 416 $\mu$L (598 mg, 2.82 mmol; 6 equiv) of $n$-hexyl iodide dropwise at rt. The solution was refluxed for 2 h. After cooling, the solution was added to a solution of 250 mg (0.47 mmol; 1 equiv) of ($M$)- or ($P$)-6,6′-dibromo-2,2′-di(methoxymethoxy)-1,1′-binaphthyl and 25 mg ($4.7 \times 10^{-5}$ mol; 10 mol %) of (dppp)-$NiCl_2$ in 30 mL of dry diethyl ether at 0 °C. The reaction mixture was refluxed for 18 h. After that time, the reaction was stopped by quenching with diluted hydrochloric acid, followed by extraction with dichloromethane. The organic layer was dried with sodium sulfate. After removal of the solvent, the crude product was purified by flash column chromatography on silica gel (hexane/ethyl acetate + triethyl amine 10:1 + 5%): $R_f$ 0.47; yield 226 mg (89%); pale yellow oil; $^1H$ NMR (400 MHz,

---

[24] Please note that other techniques like vapor pressure osmometry (vpo) or dynamic light scattering (dls) are not really applicable to establish the composition of this kind of ionic aggregates.

CDCl$_3$) $\delta$ 0.92 (t, 6H, C$H_3$CH$_2$−, $^3J$ = 7.0 Hz), 1.29−1.44 (m, 12H, alkyl chain), 1.65−1.75 (m, 4H, alkyl chain), 2.74 (t, 4H, −C$H_2$-BINOL, $^3J$ = 7.8 Hz), 3.17 (s, 6H, C$H_3$O−), 4.98, (d, 2H, −OC$H_2$O−, $^2J$ = 6.7 Hz), 5.08 (d, 2H, −OC$H_2$O−, $^2J$ = 6.7 Hz), 7.09−7.15 (m, 4H, BINOL), 7.56 (d, 2H, BINOL, $^3J$ = 9.1 Hz), 7.67 (s, 2H, BINOL), 7.89 (d, 2H, BINOL, $^3J$ = 9.1 Hz) ppm; $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ 14.2 ($C$H$_3$CH$_2$−), 22.7 (alkyl chain), 29.2 (alkyl chain), 31.4 (alkyl chain), 31.9 (alkyl chain), 36.0 (−$C$H$_2$-BINOL), 55.9 ($C$H$_3$O−), 95.6 (−O$C$H$_2$O−), 117.6 (BINOL), 121.7 (BINOL), 125.7 (BINOL), 126.3 (BINOL), 128.0 (BINOL), 128.9 (BINOL), 130.2 (BINOL), 132.6 (BINOL), 138.7 (BINOL), 152.2 (BINOL) ppm; MS (EI) *m/z* 542.4 (100) [C$_{36}$H$_{46}$O$_4$]$^+$; HRMS (EI) calcd for [C$_{36}$H$_{46}$O$_4$]$^+$ 542.3396, found 542.3390; RP (*M*) $[\alpha]_D^{20}$ = +25.4 ($c$ = 0.5075, CH$_2$Cl$_2$), (*P*) $[\alpha]_D^{23.5}$ = −24.9 ($c$ = 0.495, CH$_2$Cl$_2$). Anal. Calcd for C$_{36}$H$_{46}$O$_4$·$^1/_5$H$_2$O: C, 79.14; H, 8.56. Found: C, 79.16; H, 8.30.

**(*M*)- and (*P*)-6,6′-Di(*n*-hexyl)-3,3′-diiodo-2,2′-di(methoxymethoxy)-1,1′-binaphthyl (13).** A 233 mg (0.43 mmol, 1 equiv) portion of (*M*)- or (*P*)-**12** was dissolved in 30 mL of dry THF, and 1.465 mL (1.76 mmol; 1.2 M in cyclohexane, 4.1 equiv) of *s*-butyllithium solution was added dropwise at −78 °C. After the mixture was stirred for 1.5 h at this temperature, 652 mg (2.57 mmol, 6 equiv) of iodine in 5 mL of dry THF was added. The resulting mixture was stirred for 2 h at −78 °C. After that time, the reaction mixture was quenched with methanol and water and the solution was allowed to warm to rt. After extraction with dichloromethane, the organic layer was dried with sodium sulfate and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/ethyl acetate + triethylamine 10:1 + 5%): $R_f$ 0.7; yield 229 mg (67%); yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.90 (t, 6H, C$H_3$CH$_2$−, $^3J$ = 7.1 Hz), 1.25−1.39 (m, 12H, alkyl chain), 1.61−1.71 (m, 4H, alkyl chain), 2.61 (s, 6H, C$H_3$O−), 2.72 (t, 4H, −C$H_2$-BINOL, $^3J$ = 7.9 Hz), 4.67 (d, 2H, −OC$H_2$O−, $^2J$ = 5.7 Hz), 4.79 (d, 2H, −OC$H_2$O−, $^2J$ = 5.7 Hz), 7.09 (d, 2H, BINOL, $^3J$ = 8.7 Hz), 7.15 (dd, 2H, BINOL, $^3J$ = 8.7 Hz, $^4J$ = 1.9 Hz), 7.52 (d, 2H, BINOL, $^4J$ = 1.9 Hz), 8.46 (s, 2H, BINOL) ppm; $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ 14.2 ($C$H$_3$CH$_2$−), 22.7 (alkyl chain), 29.1 (alkyl chain), 31.2 (alkyl chain), 31.8 (alkyl chain), 35.9 (alkyl chain), 56.6 ($C$H$_3$O−), 92.4 (BINOL), 99.5 (−O$C$H$_2$O−), 125.1 (BINOL), 126.3 (BINOL), 126.5 (BINOL), 128.9 (BINOL), 132.4 (BINOL), 132.6 (BINOL), 139.5 (BINOL), 140.7 (BINOL), 151.5 (BINOL) ppm; MS (EI) *m/z* 794.2 (30) [C$_{36}$H$_{44}$I$_2$O$_4$]$^+$, 718.1 (100) [C$_{36}$H$_{44}$I$_2$O$_4$ − C$_3$H$_8$O$_2$]$^+$, 591.2 (90) [C$_{36}$H$_{44}$I$_2$O$_4$ − C$_3$H$_8$IO$_2$]$^+$, 465.3 (20) [C$_{36}$H$_{44}$I$_2$O$_4$ − C$_3$H$_8$I$_2$O$_2$]$^+$; HRMS (EI) calcd for [C$_{36}$H$_{44}$I$_2$O$_4$]$^+$ 794.1329, found 794.1319; RP (*M*) $[\alpha]_D^{22.7}$ = −12.1 ($c$ = 1.4725, CH$_2$Cl$_2$), (*P*): $[\alpha]_D^{25.1}$ = +12.2 ($c$ = 0.625, CH$_2$Cl$_2$). Anal. Calcd for C$_{36}$H$_{44}$I$_2$O$_4$·$^1/_2$C$_6$H$_{14}$: C, 55.92; H, 6.14. Found: C, 56.25; H, 5.88.

**General Procedure 1 for the Synthesis of Ligands 2−6 Exemplified for the Synthesis of (*M*)- or (*P*)-2,2′-Di(methoxymethoxy)-3,3′-di(5-ethynediyl-5′-phenyl-2,2′-bipyridyl)-1,1′-binaphthyl (2).** A 116 mg (0.19 mmol, 1 equiv) portion of (*M*)- or (*P*)-2,2′-di(methoxymethoxy)-3,3′-diiodo-1,1′-binaphthyl (**11**), 100 mg (0.39 mmol, 2.1 equiv) of 5-ethynyl-5′-phenyl-2,2′-bipyridine (**7**), 8 mg (7.6 $\mu$mol, 4 mol %) of [Pd$_2$dba$_3$·CHCl$_3$], 8.5 mg (15.2 $\mu$mol, 8 mol %) of 1,1′-diphenylphosphinoferrocene (dppf), and 6 mg (30.4 $\mu$mol, 16 mol %) of CuI was thoroughly evacuated and flushed with argon. Eight milliliters of dry triethylamine and 3 mL of dry THF were added, and the reaction mixture was heated to 45 °C and stirred at this temperature for 70 h. After the mixture was cooled to room temperature, saturated ethylene diaminetetraacetic acid (EDTA) and satd sodium carbonate solutions were added, and the mixture was stirred for 15 min. Then the aqueous solution was extracted with dichloromethane. The organic layer was dried with sodium sulfate and concentrated in vacuo to afford the crude product. This was purified by flash column chromatography on silica gel (eluent: hexane/ethyl acetate/triethyl amine 3:1:1): $R_f$ 0.38; yield 153 mg (91%); white solid; mp = 184−188 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 2.60 (s, 6H, −OC$H_3$), 4.98 (d, 2H, −OC$H_2$O−, $^2J$ = 6.2 Hz), 5.19 (d, 2H, −OC$H_2$O−, $^2J$ = 6.2 Hz), 7.27 (d, 2H, BINOL, $^3J$ = 8.4 Hz), 7.34 (ddd, 2H, BINOL, $^3J$ = 8.4 Hz, $^3J$ = 7.0 Hz, $^4J$ = 0.9 Hz), 7.40−7.52 (m, 8H, BINOL, phenyl), 7.66 (m, 4H, phenyl), 7.89 (d, 2H, H-6, $^3J$ = 8.2 Hz), 7.98 (dd, 2H, bipy, $^3J$ = 8.2 Hz, $^4J$ = 2.0 Hz), 8.03 (dd, 2H, bipy, $^3J$ = 8.3 Hz, $^4J$ = 2.1 Hz), 8.29 (s, 2H, BINOL), 8.50 (m, 4H, bipy), 8.87 (s, 2H, bipy), 8.93 (s, 2H, bipy) ppm; $^{13}$C NMR (125.8 MHz, CDCl$_3$) $\delta$ 56.2 (−O$C$H$_3$), 90.7 (−$CC$−), 90.8 (−$CC$−), 99.1 (−O$C$H$_2$O−), 116.8 (BINOL), 120.2 (bipy), 120.5 (bipy), 121.4 (bipy), 125.7 (BINOL), 125.9 (BINOL), 126.6 (BINOL), 127.1 (phenyl), 127.6 (BINOL), 127.7 (BINOL), 128.3 (phenyl), 129.1 (phenyl), 130.3 (BINOL), 134.0 (BINOL), 134.6 (BINOL), 135.3 (bipy), 136.8 (bipy), 137.4 (phenyl), 139.3 (pipy), 147.6 (bipy), 151.6 (bipy), 153.1 (BINOL), 154.1 (bipy), 154.6 (bipy) ppm; MS (ESI, pos. mode) *m/z* 883.3 (100) [C$_{60}$H$_{42}$N$_4$O$_4$ + H]$^+$; RP (*M*) $[\alpha]_D^{20}$ = −345.6 ($c$ = 0.725, CH$_3$Cl), (*P*) $[\alpha]_D^{20}$ = +352.3 ($c$ = 0.66, CH$_3$Cl); CD ($\lambda$ ($\Delta\varepsilon$)) (*M*) = 235 (−5.8), 271 (5.0), 322 (3.6), 362 (−10.3); (*P*) = 236 (6.4), 271 (−5.2), 323 (−3.4), 363 (12.0). Anal. Calcd for C$_{60}$H$_{42}$N$_4$O$_4$·CH$_3$COOC$_2$H$_5$: C, 79.16; H, 5.19; N, 5.77. Found: C, 79.56; H, 5.34; N, 5.92.

**Procedure for the Generation of Helicates Exemplified for the Synthesis of {Ag$_2$[(*P*)-2]$_2$}(BF$_4$)$_2$.** A 6.25 mg (7.09 $\mu$mol) portion of (*P*)-**2** was dissolved in 0.6 mL of CD$_2$Cl$_2$, and 2.594 mg (7.09 $\mu$mol) of [Ag(CH$_3$CN)$_4$]BF$_4$ was dissolved in 0.2 mL of CD$_3$CN. The metal salt solution was added to the solution of the ligand resulting in a pale yellow solution of the helicate. This solution was studied by NMR. Likewise, a solution was generated with a concentration of $5 \times 10^{-5}$ mol/L in nondeuterated dichloromethane/acetonitrile 1:1. This solution was directly used for the MS analysis. The same solution was also used to measure the CD spectra.

**{Ag$_2$[(*M*)-2]$_2$}(BF$_4$)$_2$/{Ag$_2$[(*P*)-2]$_2$}(BF$_4$)$_2$:** $^1$H NMR (500 MHz, CD$_2$Cl$_2$/CD$_3$CN; 4:1) $\delta$ 2.45 (s, 12H, −OC$H_3$), 4.86 (d, 4H, −OC$H_2$O−, $^2J$ = 5.8 Hz), 4.95 (d, 4H, −OC$H_2$O−, $^2J$ = 5.8 Hz), 7.11 (d, 4H, BINOL, $^3J$ = 8.5 Hz), 7.28 (ddd, 4H, BINOL, $^3J$ = 8.5 Hz, $^3J$ = 7.4 Hz, $^4J$ = 0.7 Hz), 7.40−7.49 (m, 16H, BINOL, phenyl), 7.64 (m, 8H, phenyl), 7.86 (d, 4H, BINOL, $^3J$ = 8.2 Hz), 8.18 (dd, 4H, bipy, $^3J$ = 8.4 Hz, $^4J$ = 1.8 Hz), 8.24 (s, 4H, BINOL), 8.27 (dd, 4H, bipy, $^3J$ = 8.4 Hz, $^4J$ = 2.1 Hz), 8.35 (d, 4H, bipy, $^3J$ = 8.4 Hz), 8.38 (d, 4H, bipy, $^3J$ = 8.4 Hz), 8.81 (d, 4H, bipy, $^4J$ = 1.8 Hz), 8.91 (d, 4H, bipy, $^4J$ = 2.1 Hz) ppm; $^{13}$C NMR (125.8 MHz, CD$_2$Cl$_2$/CD$_3$CN; 4:1) $\delta$ 55.8 (−O$C$H$_3$), 89.1 (ethynyl), 92.4 (ethynyl), 98.9 (−O$C$H$_2$O−), 116.0 (BINOL), 121.9 (bipy), 122.1 (bipy), 122.8 (bipy), 125.7 (bipy), 125.9 (bipy), 126.1 (BINOL), 127.0 (phenyl), 127.8 (BINOL), 127.9 (BINOL), 129.1 (phenyl), 129.3 (phenyl), 130.2 (BINOL), 134.1 (BINOL), 134.9 (BINOL), 135.8 (phenyl), 137.0 (bipy), 138.4 (bipy), 140.9 (bipy), 149.2 (bipy), 150.1 (bipy), 150.8 (bipy), 152.6 (bipy), 152.7 (BINOL) ppm; MS (ESI, pos. mode) *m/z* 991.3 ([Ag$_2$(**2**)$_2$]$^{2+}$, [**2** + Ag]$^+$, 100), 883.4 ([**2** + H]$^+$, 15); CD ($\lambda$ ($\Delta\varepsilon$)) (*M*) = 235 (−11.2), 270 (8.9), 324 (6.8), 364 (−20.0); (*P*) = 235 (12.8), 271 (−10.0), 326 (−6.7), 362 (23.5).

**{Zn$_2$[(*M*)-2]$_3$}(BF$_4$)$_4$/{Zn$_2$[(*P*)-2]$_3$}(BF$_4$)$_4$:** $^1$H NMR (500 MHz, CD$_2$Cl$_2$/CD$_3$CN; 4:1) $\delta$ 2.26 (s, 18H, −OC$H_3$), 4.71 (m, 12H, −OC$H_2$O−), 7.01 (d, 6H, BINOL, $^3J$ = 8.4 Hz), 7.31 (ddd, 6H, BINOL, $^3J$ = 7.7 Hz, $^3J$ = 8.4 Hz, $^4J$ = 0.9 Hz), 7.34−7.40 (m, 30H, phenyl), 7.49 (ddd, 6H, BINOL, $^3J$ = 8.2 Hz, $^3J$ = 7.7 Hz, $^4J$ = 0.7 Hz), 7.88 (d, 6H, BINOL, $^3J$ = 8.2 Hz), 7.98 (d, 6H, bipy, $^4J$ = 1.7 Hz), 8.07 (d, 6H, bipy, $^4J$ = 2.1 Hz), 8.18 (m, 12H, BINOL, bipy), 8.46 (dd, 6H, bipy, $^3J$ = 8.6 Hz, $^4J$ = 2.1 Hz), 8.49 (d, 6H, bipy, $^3J$ = 8.4 Hz), 8.57 (d, 6H, bipy, $^3J$ = 8.6 Hz) ppm; $^{13}$C NMR (125.8 MHz, CD$_2$Cl$_2$/CD$_3$CN; 4:1) $\delta$ 55.5 (−O$C$H$_3$), 88.4 (ethynyl), 94.8 (ethynyl), 98.8 (−O$C$H$_2$O−), 115.3 (BINOL), 123.6 (bipy), 123.9 (bipy), 124.6 (bipy), 126.1 (BINOL), 126.4 (BINOL), 127.2 (phenyl), 128.2 (BINOL), 128.5 (BINOL), 129.7 (phenyl), 130.1

(phenyl), 130.4 (BINOL), 134.6 (phenyl), 134.7 (BINOL), 136.2 (BINOL), 140.2 (bipy), 140.6 (bipy), 143.6 (bipy), 146.0 (bipy), 147.2 (bipy), 147.6 (bipy), 150.0 (bipy), 152.4 (BINOL) ppm; MS (ESI, pos. mode) *m*/*z* 694.8 ($[Zn_2(\mathbf{2})_3]^{4+}$, 100); CD ($\lambda$ ($\Delta\varepsilon$)) (*M*) = 233 (−23.9), 260 (8.3), 293 (−7.8), 354 (−12.3), 390 (38.4); (*P*) = 233 (26.8), 260 (−9.4), 294 (8.4), 351 (13.0), 391 (−39.7).

**$\{Cu_2[(M)\text{-}\mathbf{2}]_2\}(BF_4)_2/\{Cu_2[(P)\text{-}\mathbf{2}]_2\}(BF_4)_2//\{Cu_2[(M)\text{-}\mathbf{2}]_3\}(BF_4)_4/\{Cu_2[(P)\text{-}\mathbf{2}]_3\}(BF_4)_4$:** MS (ESI, pos. mode) *m*/*z* 946.2 ($[Cu_2(\mathbf{2})_2]^{2+}$, $[\mathbf{2} + Cu)]^{+}$ (minimal amount), 100), 694.0 ($[Cu_2(\mathbf{2})_3]^{4+}$, 90).

**$\{Fe_2[(M)\text{-}\mathbf{2}]_3\}(BF_4)_4/\{Fe_2[(P)\text{-}\mathbf{2}]_3\}(BF_4)_4$:** MS (ESI, pos. mode) *m*/*z* 690.0 ($[Fe_2(\mathbf{2})_3]^{4+}$, 100); CD ($\lambda$($\Delta\varepsilon$)) (*M*) = 239 (−27.2), 265 (9.1), 314 (−21.5), 399 (38.9), 497 (3.3), 567 (−5.1); (*P*) = 38 (30.1), 265 (−10.9), 312 (23.5), 398 (−41.2), 500 (−2.9), 573 (6.4).

**Acknowledgment.** Financial support from the Deutsche Forschungsgemeinschaft (SFB 624) is gratefully acknowledged. We thank Mrs. K. Peters-Pflaumbaum for measuring a number of ESI mass spectra.

**Supporting Information Available:** Experimental details for ligands **3**−**6** and their metal complexes, schematic representations of the synthesis of the pyridines and 2,2′-bipyridines, as well as spectroscopic data (NMR, CD, and ESI-MS) of ligands **2-6** and their metal complexes not depicted in Figures 2−4. Coordinates for the metal complex structures shown in Figure 1 that were obtained from molecular modeling studies. This material is available free of charge via the Internet at http://pubs.acs.org.