Self-Recognition Based on Atropoisomerism with New Chiral Bidentate Ligands and Copper(I)

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Abstract: A new family of atropoisomeric bidentate ligands that have a dissymmetric benzimidazole-pyridine binding site has been synthesized. Aromatic rings, that is, naphthyl, tolyl, and cumyl, were introduced in order to fine tune the complexation properties of the ligands. The tetrahedral copper(I) complexes L_2Cu were prepared and the structure of the complex with the naphthyl-substituted ligand was established by X-ray diffraction. The behavior of the L_2Cu complexes in solution was studied by ^1H NMR spectroscopy. With the most crowded cumyl-derived ligand, ligand self-recognition based on chirality occured: 95% of the complex was present in solution as a racemate *RR*Δ/*SS*Λ, the heterochiral *RS*Δ/*SR*Λ isomers represented only 5% of the mixture, and the *RR*Λ/*SS*Δ isomers were not detected. Owing to lower steric repulsions within the other L_2Cu complexes (i.e., with the naphthyl- and tolyl-based ligands) the homorecognition is less pronounced, as diastereomeric excesses of 6 and 26% were measured, respectively.

Keywords: atropoisomerism · chirality · copper · N ligands · self-assembly

Introduction

In 1993, Lehn and co-workers[1] introduced the ligand self-recognition process as a new paradigm for the selective synthesis of supramolecular architectures.[2] The synthesis of a well-defined superstructure can be programmed by using a mixture of "instructed" components that contain steric and electronic information. By treating copper(I) ions with a mixture of oligo-2,2′-bipyridine strands, which differ in the number of binding sites, self-assembly of the double helicates with two di-, tri-, tetra-, or penta-topic [oligo(2,2′)-bipyridine] occured spontaneously. Other examples of ligand homorecognition in helicates have been reported based on 1) the preferred coordination geometry of the metal ions in the presence of an appropriate structure of the ligand,[1] 2) the differences in distances between the metal-chelating groups of ligands,[3] or 3) the nature of the countercation that binds to the tetra-anionic complexes formed.[4]

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Ligand recognition based on chirality was shown to play an important role in the non-linear effects in asymmetric reactions.[5] However, in such cases the heterorecognition is favored; this leads to the formation of heterochiral, oligomeric metal species. Recently, Stack and co-workers reported the first example of ligand homorecognition based solely on chirality.[6] Starting from a racemic mixture of a tetradentate amino ligand that contained a *trans*-1,2-diaminocyclohexane backbone, a racemic mixture of stereospecific, homochiral, binuclear complexes Λ,Λ-$[\{Cu(^{RR}L)\}_2]^{2+}$ and Δ,Δ-$[\{Cu(^{SS}L)\}_2]^{2+}$ was formed selectively. The homochiral complexes produced a more compact and stable cubic structure than the heterochiral ones. A more intricate example of self-recognition based on chirality was described in the self-assembly of [2 × 2] grids from ditopic ligands that possess terpyridine-like binding sites.[7]

We were interested in studying the self-recognition process for a structure encountered widely in coordination chemistry: two bidentate ligands arranged in a tetrahedral complex. Here, we report that a racemate of an atropoisomeric bidentate ligand can self-assemble stereoselectively in the presence of copper(I) ions in such a way as to favor the formation of homochiral complexes.

Results and Discussion

Preparation of the ligands: The ligands **4**, **5**, and **6**, which contain a dissymmetric binding site with a pyridine and a benzimidazole ring, were prepared as racemic mixtures (Scheme 1). The pyridine-benzimidazole moiety has proved

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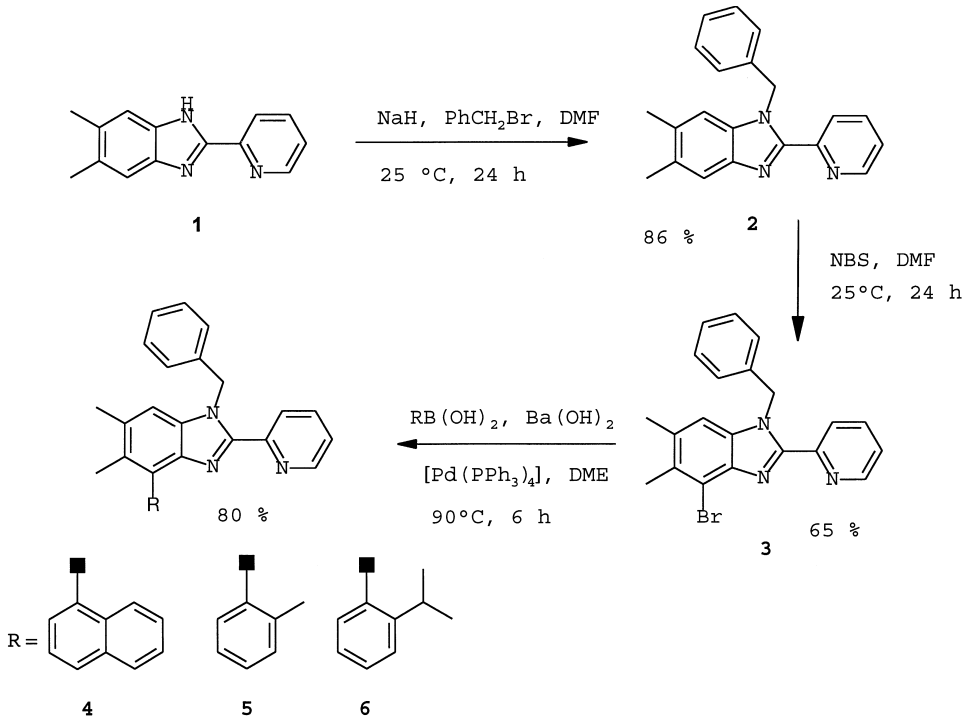

Scheme 1. Reaction pathway for the synthesis of **4**, **5**, and **6**.

to be a very efficient complexation unit for transition metals.[8] The methyl groups at the 5- and 6-positions play a triple role: 1) they are very useful ^{1}H NMR probes, 2) they protect the most reactive positions of the benzimidazole ring, thereby forcing the bromination reaction to occur at the less reactive 4-position of the benzyl derivative **2**, and 3) they prevent complete rotation around the chirality axis. In short, the functionnalization at the 4-position of the benzimidazole moiety is the key feature of this new class of atropoisomeric ligands. They possess a rigid structure and a chirality axis, perpendicular to the axis that contains the ligating atoms, that favors steric interactions between the ligands within the same complex, thus allowing the isomers to be discriminated. Moreover, an aryl ring introduced at the 4-position will experience a coplanar relationship with the π system of the second partner involved in a tetrahedral complex. Depending on the atropoisomer, π overlap will occur between the aryl substituent and either the pyridyl or the benzimidazole part of the complementary ligand, which leads to a fine tuning of the energy of the system.

The ligands **4**, **5**, and **6** were obtained through a three-step procedure (Scheme 1) from the previously synthesized ligand **1**,[9] which was prepared according to the method described by Reed and co-workers.[10] The benzylated compound **2**, obtained by a standard procedure with NaH and benzylbromide, was selectively monobrominated with N-bromosuccinimide (NBS) in DMF. A Suzuki coupling reaction was used to introduce the *o*-tolyl, *α*-naphthyl, or the *o*-cumyl groups. Enantiomerization energies of 20.7, 23.4, and 29.1 kcal mol^{-1} for **4**, **5**, and **6** respectively, were found with AM1 semi-empirical calculations (CAChe 3.1). These values are in between those found for 1,1′-binaphthyl (19 kcal mol^{-1}) and 2,2′-binaphthol (33.8 kcal mol^{-1}) groups.

Abstract in French: *Une nouvelle famille de ligands bidentates atropoisomères possédant un site de complexation dissymétrique (benzimidazole-pyridine) a été synthétisée. Des substituants aromatiques de tailles variées, naphtyle, tolyle ou cumyle, ont été introduits afin de modifier les propriétés complexantes des ligands. Les complexes tétrahèdriques de cuivre(*i*) L_2Cu ont été synthétisés et la structure du complexe avec le ligand substitué par un noyau naphtyle a été résolue par diffraction des rayons X. Une étude par RMN ^1H de ces complexes en solution a permis de mettre en évidence un processus d'auto-reconnaissance de ligand basé sur la chiralité. En solution dans le dichlorométhane, l'espèce L_2Cu obtenue avec le ligand substitué par le groupe cumyle se présente sous forme d'un complexe homochiral racémique RRΔ/SSΛ. Les isomères hétérochiraux RSΔ/SRΛ ne représentent que 5 % du mélange alors que les isomères RRΛ/SSΔ ne sont pas détectés. Les répulsions stériques étant moins fortes dans les complexes L_2Cu dont les ligands sont substitués par les groupes naphtyle ou tolyle, le phénomène d'auto-reconnaissance est moins important, conduisant à des excès diastéréoisomériques mesurés de 6 et 26 % respectivement.*

Preparation of the complexes 4a, 5a, and 6a: The copper(i) complexes $[Cu(\mathbf{4})_2]PF_6$ (**4a**), $[Cu(\mathbf{5})_2]PF_6$ (**5a**), and $[Cu(\mathbf{6})_2]PF_6$ (**6a**), were prepared by treating two equivalents of the corresponding ligand with $[Cu(CH_3CN)_4]PF_6$. Crystals of **4a** suitable for single-crystal X-ray diffraction studies were obtained by slow diffusion of petroleum ether into a solution of the complex in 1,2-dichloroethane. The asymmetric cell shows the presence of a racemic mixture of stereospecific homochiral complexes Δ-$[Cu(^R\mathbf{4})_2]^+$, *RR*Δ, and Λ-$[Cu(^S\mathbf{4})_2]^+$, *SS*Λ(Figure 1).

The Cu ions are located in a strongly distorded tetrahedral environment. As expected, in the primary structure, strong intramolecular stacking interactions were observed and plane to plane distances were measured at around 3.5 Å. It should be noted that in the *RR*Δ/*SS*Λ enantiomers these π-π interactions arise from the preferential overlaping of the naphthalene ring of one ligand with the pyridine ring of the other. Intermolecular π-stacking interactions (3.8 Å) were also observed in the secondary structure (Figure 1).

Ligand self-recognition process: The schematic representation of the possible isomers formed upon self-assembly of the racemic ligands with copper(i) (Figure 2) clearly shows that

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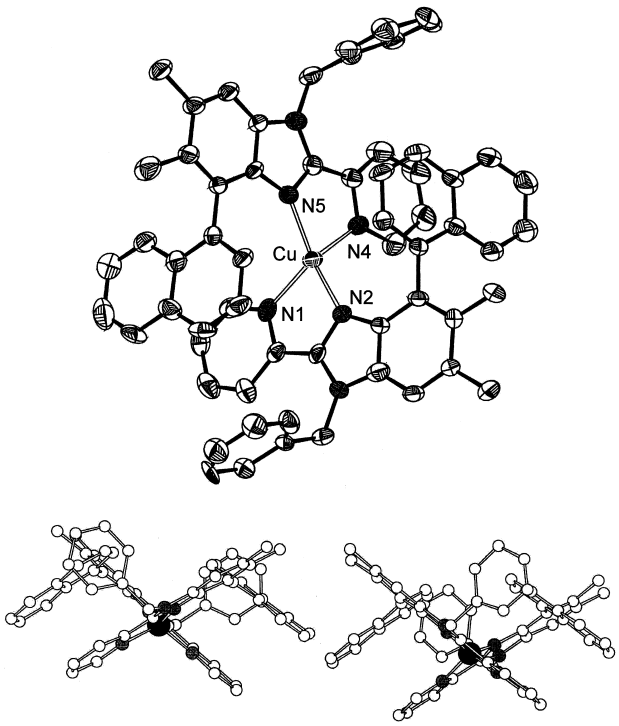

Figure 1. Top: Ortep representation of Δ-[Cu(*R*-**4**)$_2$]$^+$ (**4a**). Bottom: Ball and stick representation of the racemate (*RR*Δ/*SS*Λ) present in the cell which reveals the intra- and intermolecular π-stacking interactions. Selected bond lengths [Å] and angles [°]: Cu–N1 2.037(12), Cu–N2 2.027(11), Cu–N4 2.059(11), Cu–N5 2.013(10); N5-Cu-N2 143.6(4), N1-Cu-N4 123.3(5), N4-Cu-N2 114.3(4), N5-Cu-N1 119.4(4), N1-Cu-N2 81.5(5), N5-Cu-N4 80.4(4).

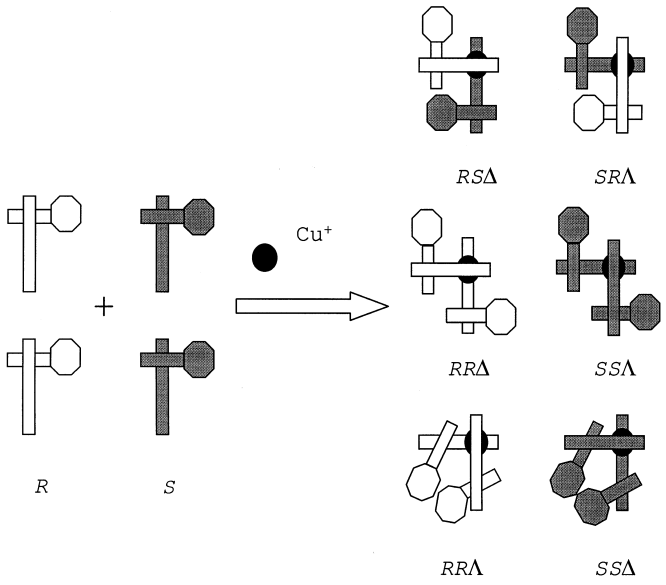

Figure 2. Schematic representation of the possible isomers formed upon complexation of **6** with Cu$^+$.

the methyl groups of the three pairs of enantiomers lie in very different chemical environments; this allows the characterization of each couple of isomers by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra were recorded at $-20\,^\circ$C or $-40\,^\circ$C in order to decrease the resonance broadening due to ligand exchange (Figure 3).

When two equivalents of **6** are treated with [Cu^I(MeCN)$_4$]$^+$ (one equivalent) in [D$_2$] dichloromethane, the ^{1}H NMR spectrum of the complex generated in situ displays the formation of a single metal species with C_2 symmetry (Figure 2) which was attributed to the homochiral enantiomers *RR*Δ/*SS*Λ (95%). The same spectrum was obtained by dissolving crystals of **6a** in [D$_2$] dichloromethane (Figure 3). The heterochiral isomers *RS*Δ/*SR*Λ were also present in small amount (5%), whereas the other set of homochiral isomers (*RR*Λ/*SS*Δ) was not observed.

The diastereomeric excess (*de*) is thus equal to 90% (Table 1). With the less crowded ligands **4** and **5**, the self-recognition process is less pronounced with *de* values of 6% and 26% for **4a** and **5a**, respectively.

The ^{1}H NMR assignments for **6a** were done by comparison with the spectra obtained for the complexes **4a** and **5a** (Figure 3). The ^{1}H NMR spectrum of **4a** displays eight well-resolved CH_3-benzimidazole resonances in agreement with a mixture of the possible isomers, for example *RR*Δ/*SS*Λ, *RR*Λ/*SS*Δ, and *RS*Δ/*SR*Λ.

The C_2 symmetric homochiral *RR*Δ/*SS*Λ and *RR*Λ/*SS*Δ complexes have only two distinct CH_3-benzimidazole resonances for each pair of enantiomers thus leading to four resonances. In the heterochiral *RS*Δ/*SR*Λ isomers, four CH_3-benzimidazole were differenciated owing to a lower symmetry; this led to another set of four resonances. With the tolyl derivative **5a**, a similar pattern is obtained, except that four additional CH_3-tolyl resonances were observed: one for each pair of the homochiral isomers and two for the heterochiral one.

The schematic representation of the isomers formed upon complexation with copper(I) allows the key structural features that promote such a discrimination to be easily visualized (Figure 2). In the *RR*Λ/*SS*Δ isomers, the steric repulsions between the isopropyl groups preclude their formation. In the heterochiral complexes, only the use of bulky isopropyl groups can prevent their formation, since, in that case, the steric hindrance is due to interaction between an isopropyl group and a hydrogen atom from the *o*-cumyl ring of the other ligand. Accordingly, extended MM2 calculations (Cache 3.1) have clearly shown that the homochiral *RR*Δ/*SS*Λ isomers are much favored over *RR*Λ/*SS*Δ ones, with a difference in minimization energy of 6 kcal mol^{-1} found in the case of **6a**.

Interestingly, for all the ligands studied herein, the complexation is diastereoselective, since the homochiral *RR* complexes mainly display the Δ configuration, whereas the *SS* isomers are Λ. Examples of stereoselective complexation with two chiral bidentate ligands are scarce.[11] The selective complexation of platinum(IV) or copper(I) has been achieved by using thienylpyridine[12] and phenanthroline[13] ligands, respectively, substituted with chiral terpene moieties.

As expected for copper(I) complexes associated with bidentate ligands, the isomers are in equilibrium in solution. Upon crystallization (slow diffusion of petroleum ether into a solution of **4a** or **5a** in 1,2-dichloroethane) these equilibria were displaced toward the selective precipitation of the *RR*Δ/*SS*Λ racemate. Ground crystals of pure, recrystallized **4a** or **5a** were dissolved at $-60\,^\circ$C in [D$_2$] dichloromethane and their ^{1}H NMR spectra immediately recorded at $-40\,^\circ$C. In both cases, the major species found in solution were the *RR*Δ/*SS*Λ complexes (85%), that is, those found in the crystal of **4a**, whereas the *RR*Λ/*SS*Δ and *RS*Δ/*SR*Λ isomers were present

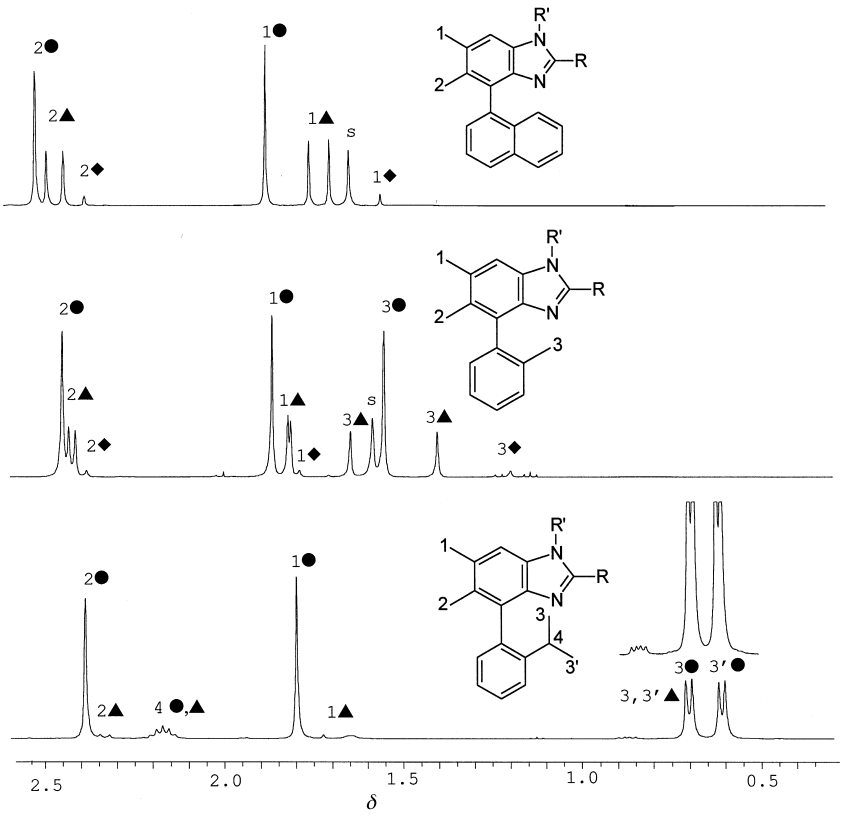

Figure 3. ^{1}H NMR at 400 MHz in CD_2Cl_2 (methyl region) of **4a** ($-40\,^\circ$C, top), **5a** ($-20\,^\circ$C, middle), and **6a** ($-40\,^\circ$C, bottom). ● *CH*$_3$-resonances for *RR*Δ/*SS*Λ, ◆ for *RR*Λ/*SS*Δ, ▲ for *RS*Δ/*SR*Λ, S = residual water.

Table 1. Isomeric ratios for complexes **4a**, **5a**, and **6a**.

Complex	*RR*Δ/*SS*Λ	*RR*Λ/*SS*Δ	*RS*Δ/*SR*Λ	*de*[a]
statistical ratio	25%	25%	50%	0%
4a	49%	4%	47%	6%
5a	60%	3%	37%	26%
6a	95%	< 1%	5%	90%

[a] Diastereomeric excess.

only in small amounts (4% and 11%, respectively). The time course behavior of the ratio of complexes clearly shows that *RR*Δ/*SS*Λ concentration decreases as *RS*Δ/*SR*Λ concentration increases and *RR*Λ/*SS*Δ remains constant, equilibrium being reached after five hours at $-40\,^\circ$C.

Conclusion

The judicious design of the new, chiral, bidentate ligand **6** allowed the stereoselective self-assembly of the mononuclear, homochiral copper(I) complex **6a** *RR*Δ/*SS*Λ starting from the racemic ligand. We are currently working on the resolution of the ligands to further study their stereoselective complexation properties and their ability to catalyze enantioselective reactions in the presence of transition metals.

Experimental Section

General procedures: The chemicals were obtained commercially and were used without further purification. The previously synthesized ligand **1**[9] was prepared according to the procedure described by Reed and co-workers.[10] The *o*-tolylboronic acid was purchassed commercially (Lancaster). The α-naphthylboronic-acid was obtained by using the classical procedure from 1-bromonaphtalene, $B(OMe)_3$, and *n*Bu-Li. The *o*-cumylboronic acid was prepared according to Yamamoto and co-workers.[14] The solvents were of commercial analytical grade. Thin-layer chromatography (TLC) was performed on polyester sheets coated with silica gel 60 F_{254} (SDS 321334), or coated with neutral alumina 60 F_{254} (Polygram 802023). After elution, the plates were scrutinized under a UV lamp. Column chromatography was carried out on neutral alumina (Aldrich 19, 997-4, 150 mesh). Liquid secondary-ion-mass spectrometry (LSIMS) was carried out in the positive-ion mode with a cesium atom beam on a CG AutoSpec-Q spectrometer. The ^{1}H NMR spectra were recorded on either a Bruker AM200 (200 MHz) or a DPX400 (400 MHz) spectrometer. ^{1}H NMR spectra for the complexes were performed at 400 MHz on aliquots of each complex (10 mg) dissolved in CD_2Cl_2 (0.5 mL). Cyclic voltammetry (CV) was carried out with a Pt working electrode, a Pt control electrode, and a saturated calomel electrode as reference. $(nBu)_4NPF_6$ was used as support electrolyte.

Preparation of 2: Ligand **1** (3.2 g, 14.2 mmol) was added in small portions to a NaH suspension (60%, 0.64 g, 16.0 mmol) in dry DMF (70 mL) at 0 °C, under an inert atmosphere. After one hour at ambient temperature, $PhCH_2Br$ (1.98 mL, 16.7 mmol) was added dropwise and the solution was stirred for 24 h. The mixture was poured into water (800 mL) that was vigourously stirred. The precipitate was collected by filtration and washed with water and diethyl ether. The resultant powder was dissolved in CH_2Cl_2 and dried over $Mg(SO_4)_2$. After evaporation, **2** was obtained as a yellowish powder in 86% yield. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 8.59$ (d, 1H), 8.42 (d, 1H), 7.80 (t, 1H), 7.64 (s, 1H), 7.22 (m, 7H), 6.16 (s, 2H), 2.39 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): $\delta = 151.77$, 150.12, 149.44, 142.37, 138.74, 137.62, 136.46, 133.88, 132.73, 129.46, 128.12, 127.64, 125.40, 124.42, 121.05, 111.70, 49.77, 21.63, 21.24; LSIMS-MS: *m*/*z* (%): 314 (100) $[M+1]^+$.

Preparation of 3: A solution of NBS (1.25 g, 7.00 mmol) dissolved in dry DMF (20 mL) was added dropwise to a solution of **2** (2 g, 6.37 mmol) in dry DMF (80 mL). After being stirred for 48 h at ambient temperature, the solution was poured into water (1 L); this led to the precipitation of a pale yellow powder. The powder was dissolved in CH_2Cl_2, dried over $Mg(SO_4)_2$, and, after evaporation, the solid was washed with hot ethanol which gave **3** in 65% yield. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 8.58$ (d, 1H), 8.52 (d, 1H), 7.80 (t, 1H), 7.21 (m, 7H), 6.13 (s, 2H), 2.50 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): $\delta = 150.35$, 149.51, 148.39, 140.52, 137.32, 136.67, 134.97, 133.75, 130.81, 128.50, 127.25, 126.59, 125.09, 123.71, 115.73, 110.13, 49.00, 22.09, 18.99; MS (EI): *m*/*z* (%): 391 (100) $[M-H]^+$.

Preparation of 4 and 5: Bromo derivative **3** (2 g, 5.1 mmol), $Ba(OH)_2$ (2.4 g, 7.65 mmol), $[Pd(PPH_3)_4]$ (0.3 g, 25.5×10^{-5} mol), and the corresponding boronic acid (5.60 mmol) were heated under reflux in DME (90 mL) and H_2O (15 mL) under an inert atmosphere for six hours, dichloromethane and water were added. The organic phase was then separated and dried over $Mg(SO_4)_2$. After column chromatography with neutral alumina (dichloromethane/petroleum ether, 50:50), ligands **4** and **5** were isolated as white powders in 80% yield.

Ligand **4**: ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): $\delta = 8.48$ (d, 1H), 8.00 (d, 1H), 7.91 (d, 2H), 7.59 (t, 2H), 7.46-7.12 (m, 10H), 6.20 (d, 1H), 6.05 (d, 1H), 2.40 (s, 3H) 1.92 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): $\delta =$

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151.3, 149.7, 148.9, 141.9, 138.7, 137.5, 137.2, 135.5, 134.2, 133.8, 131.4, 130.7, 129.1, 128.7, 128.5, 127.9, 127.8, 127.4, 126.9, 126.4, 126.2, 126.1, 125.1, 124.0, 110.9, 49.3, 21.9, 17.1; LSIMS-MS: *m/z* (%): 440 (100) $[M+1]^+$; elemental analysis calcd (%) for $C_{31}H_{25}N_3$ (439.3): C 84.74, H 5.69, N 9.56; found C 84.26, H 5.74, N 9.49.

Ligand **5**: ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): $\delta = 8.5$ (d, 1H), 8.22 (d, 1H), 7.7 (t, 1H), 7.3 (m, 11H), 6.23 (d, 1H), 6.08 (d, 1H), 2.42 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): $\delta = 152.1$, 150.8, 149.7, 140.4, 141.9, 139.6, 138.7, 137.9, 136.0, 134.6, 134.0, 131.6, 131.1, 130.5, 129.7, 128.5, 128.4, 128.0, 126.6, 125.8, 124.7, 111.2, 49.9, 22.6, 21.0, 17.4; LSIMS-MS: *m/z* (%): 404 (100) $[M+1]^+$; elemental analysis calcd (%) for $C_{28}H_{25}N_3$ (403.3): C 83.38, H 6.20, N 10.42; found C 82.90, H 6.30, N 10.36.

Preparation of 6: Bromo derivative **3** (1.4 g, 3.6 mmol), $Cs(CO_3)_2$ (3.47 g, 10.6 mmol), $[Pd(PPH_3)_2Cl_2]$ (0.5 g, 7.1×10^{-4} mol), and cumylboronic acid (1.2 g, 7.3 mmol) were stirred in DMF (60 mL) at 95 °C for five hours under an inert atmosphere. Dichloromethane was added, and the organic phase was washed four times with water and then dried over $Mg(SO_4)_2$. After column chromatography with neutral alumina (dichloromethane/petroleum ether, 50:50) an amorphous solid was precipitated in ethanol; compound **6** was isolated as a white powder in 65% yield. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): $\delta = 8.41$ (d, 1H), 8.18 (d, 1H), 7.61 (t, 1H), 7.30, (m, 10H), 6.22 (d, 1H), 5.98 (d, 1H), 2.60 (sept, 1H), 2.38 (s, 3H), 2.04 (s, 3H), 1.1, (d, 3H), 1.05 (d, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): $\delta =$ 149.79, 147.70, 145.30, 137.94, 137.30, 136.50, 136.07, 135.52, 135.47, 132.50, 132.29, 130.11, 129.77, 129.02, 126.99, 126.42, 126.04, 124.88, 123.92, 122.26, 110.29, 49.95, 30.56, 24.33, 23.83, 22.10, 17.13; LSIMS-MS: *m/z* (%): 432.2 (100) $[M+1]^+$.

Preparation of complexes $[Cu(4)_2]PF_6$, (4a), $[Cu(5)_2]PF_6$, (5a), and $[Cu(6)_2]PF_6$, (6a): Ligand **4**, **5**, or **6** (two equivalents) in deoxygenated CH_2Cl_2 was added to $[Cu(CH_3CN)_4]PF_6$ (one equivalent) and the solution taken to dryness. Recrystallization of **4a** and **5a** (1,2-dichloroethane/petroleum ether) afforded black-brown crystals in 85% yield. Compound **6a** was recrystallized by slow evaporation of a solution of the complex in EtOH/CH_2Cl_2, 2:1.

Compound **4a**: ^{1}H NMR (400 MHz, CD_2Cl_2, −40 °C, TMS): homochiral species *RR*Δ/*SS*Λ: $\delta = 1.87$ (s, 6H), 2.51 (s, 6H), 5.84 (dd, 4H), 6.2–8.2 (c, 34H); *RR*Λ/*SS*Δ: $\delta = 1.55$ (s, 6H), 2.37 (s, 6H); heterochiral species *RS*Δ/*SR*Λ: $\delta = 1.69$ (s, 3H), 1.74 (s, 3H), 2.43 (s, 3H), 2.48 (s, 3H); LSIMS-MS: *m/z* (%): 941 (100) $[M-PF_6]^+$; elemental analysis calcd (%) for $C_{62}H_{50}N_6PF_6Cu \cdot CH_3CN$ (1128.2): C 68.14, H 4.70, N 8.70, P 2.74, F 10.10, Cu 5.62; found C 67.56, H 4.65, N 8.72, P 2.66, F 10.09, Cu 5.74; $E_{1/2}$ vs. SCE = 400 mV.

Compound **5a**: ^{1}H NMR (400 MHz, CD_2Cl_2, −20 °C, TMS): homochiral species *RR*Δ/*SS*Λ: $\delta = 1.55$ (s, 6H), 1.85 (s, 6H), 2.43 (s, 6H), 5.85 (brs, 4H), 6.48 (t, 2H), 6.74 (d, 2H), 7.25-7.85 (c, 18H), 8.17 (d, 2H); *RR*Λ/*SS*Δ: $\delta =$ 1.13 (s, 6H), 1.77 (s, 6H), 2.37 (s, 6H); heterochiral species *RS*Δ/*SR*Λ: $\delta =$ 1.33 (s, 3H), 1.65 (s, 3H), 1.80 (s, 3H), 1.81 (s, 3H), 2.40 (s, 3H), 2.42 (s, 3H); LSIMS-MS: *m/z* (%): 869 (100) $[M-PF_6]^+$; elemental analysis calcd (%) for $C_{56}H_{50}N_6PF_6Cu \cdot H_2O$ (1033.1): C 65.10, H 5.03, N 8.13, P 3.00, F 11.01, Cu 6.15; found C 64.50, H 5.00, N 7.71, P 3.10, F 10.45, Cu 6.47; $E_{1/2}$ vs. SCE = 440 mV.

Compound **6a**: ^{1}H NMR (400 MHz, CD_2Cl_2, −40 °C, TMS): homochiral species *RR*Δ/*SS*Λ: $\delta = 0.61$ (d, 6H), 0.70 (d, 6H), 1.80 (s, 6H), 2.18 (m, 2H), 2.40 (s, 6H), 5.88 (c, 6H), 6.35 (d, 2H), 6.63 (d, 2H), 6.82 (t, 2H), 7.2-7.6 (c, 16H), 7.76 (t, 2H), 8.00 (d, 2H); LSIMS-MS: *m/z* (%): 926 (100) $[M-PF_6]^+$; elemental analysis calcd (%) for $C_{60}H_{58}N_6PF_6Cu$ (1071.1): C 67.27, H 5.41, N 7.84, P 2.89, F 10.64, Cu 5.93; found C 67.18, H 5.38, N 7.91, P 2.88, F 10.25, Cu 6.12.

X-ray crystal structure analysis: Crystal data for $[Cu(C_{31}H_{25}N_3)_2]_2 \cdot (PF_6)_2 \cdot (C_5H_{12})_{0.99} \cdot (C_6H_{14})_{0.79}$ from a single red crystal of $0.51 \times 0.1 \times 0.12$ mm. Data were collected on a Enraf Nonius CAD4 four-circle diffractometer at 293 K with graphite monochromated CuKα radiation ($\lambda = 1.541\,80$ Å). Monoclinic space group $P2(1)/n$, $Z = 4$, $a = 23.656(5)$, $b = 15.0676(10)$, $c =$ 31.163(4) Å, $\alpha = 90°$, $\beta = 91.280(9)°$, $\gamma = 90°$, $V = 11\,105.1(28)$ Å^3, $\rho_{calcd} =$ 1.385 g cm^{-3}, $F(000) = 4823$, $\mu = 1.400$. θ range: 2.32–67.89, index ranges: $-28 \le h \le 28$, $0 \le k \le 18$, $0 \le l \le 37$, 18973 collected reflexions, 18973 unique, R(int) = 0.0000, 6070 observed $[I > 2\sigma(I)]$, 18965 were used to fit 79 restraints and 1486 parameters. The structure was refined by full-matrix least-square calculation (SHELLX93), R values: $R = 0.1259$ for 6070 observed reflexions, $wR2 = 0.5254$ for 18973 unique reflexions, goodness of fit on $F^2 = 1.003$. Residual electron density between −0.719 and 0.721 e Å^{-3}. The whole cationic structure was refined anisotropically. The solvent and anions show severe disorder, and the solvent molecules were treated isotropically. The best refinement was obtained with population factors of 0.99 for pentane and 0.79 for hexane. The anions were refined on split positions; the major position was refined anisotropically and for the minor position isotropically. All hydrogen positions were calculated. The complex crystallizes together with PF_6 ions and solvent molecules (two *n*-hexane and one *n*-pentane). The asymmetric cell shows two complex molecules that are enantiomers. These two molecules are effectively related by the following mirror plane: $x_2 = x_1 + 0.50750$, $y_2 = y_1 + 0.01602$, $z_2 = z_1 + 0.00322$. This plane is not a plane of symmetry for the cell because the solvent molecules and the PF_6 ions do not respect this symmetry and show severe disorder. As a result of this loss of symmetry, one of the parameters of the cell is doubled, and, therefore, the required number of data is also doubled and their intensities are weakened. Taken together this explains the rough R factors observed for this structure. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Center as supplementary publication no.CCDC-134368. Copies of the data can be obtained free of charges on application to CCDC, 12, Union Road, Cambridge, CB2 1EZ (UK) (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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