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Design and Synthesis of Molecules with Switchable Chirality via Formation and Cleavage of Metal−Ligand Coordination Bonds

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The dazzling potential envisaged by application of molecular memory elements for data storage and information processing has gained an unprecedented interest in the past decade.[1] Among the known to date general approaches to the design of molecular switches, such as redox switches,[2] switchable rotaxanes and catenanes,[3] and switchable allosteric receptors,[4] the organic chiroptical molecular switches[5] are currently the most promising systems in the bottom-up approach to nanoscale information technology of the future. One of the major advantages of chiroptical switches is the feasibility of nondestructive read out of optical information via, for instance, simple recording of optical rotation.

In general, a molecular switch is based on a molecule that can reversibly change distinct states (on and off) upon an external stimulus (light, heat, pressure, etc.). In the case of chiroptical molecular switches, the most commonly used design is based on reversible and stereochemically controlled transformation of one optically pure diastereomer to another. One of the major issues in the design of molecular switches is a fatigue resistance or durability of a potential molecular device. In this regard, the currently known models have one inherent problem: that is the switch between diastereomers involves the cleavage and formation of a covalent chemical bond. Since a chemical reaction cannot proceed with 100% yield, the lifetime of such molecular switches might be relatively short.

Here we describe a design and synthesis of organic molecules with switchable central chirality via simple cleavage and formation of metal−ligand coordination bonds, as a potentially useful and conceptually new approach to the design of a new generation of organic chiroptical molecular switches. As a proof of principle, we demonstrate that a simple achiral organic molecule upon coordination with Ni(II) or Pd(II) gives rise to the corresponding complexes possessing central and axial elements of chirality and therefore a ground for diastereomeric relationships. The switch between the diastereomers takes place upon recoordination of stereochemically equivalent ligand moieties leading to regeneration of the axial and inversion of the central chirality.

The general idea of our design is presented in Figure 1. We assume that achiral, C_2-symmetric pentadentate ligand **1** upon coordination with d^8 metal (Ni, Pd) will produce tetracoordinated complexes **2** of usual square planar geometry. Our next assumption is that coordination of **Z** or **Z′** to the metal will make the arms **Y**−**Z** and **Y′**−**Z′** stereochemically nonequivalent[6] and therefore will generate a central chirality on the previously prochiral element **X**. Next, the position of the noncoordinated group **Z** or **Z′**, relatively up or down the coordination plane, will create an axial chirality, which in combination with the central chirality on **X** will give rise to diastereomeric relationships. Finally, assuming that the noncoordinated arm **Z** is up, as for instance in (*R*,*R*)-**2**, we expect that its move to the metal coordination sphere will discoordinate and push down the arm **Z′**. This concurrent motion of arms **Z** and **Z′** is expected to have some quite dramatic stereochemical consequences.

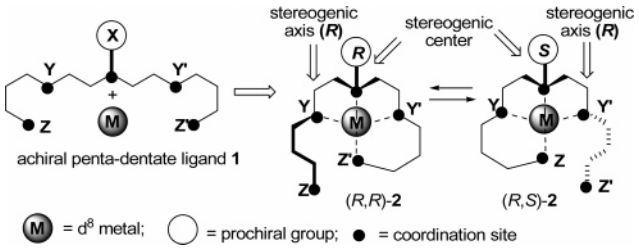

Figure 1. General design.

First, the axial chirality on the arm **Y**−**Z** will disappear with simultaneous generation of a new chiral axis of the same stereochemical sense (handedness) on the arm **Y′**−**Z′**. Second, the coordination of arm **Y**−**Z** to the metal and discoordination of the arm **Y′**−**Z′** will change their stereochemical priority and therefore reverse the absolute configuration of the central chirality. Overall, this unidirectional motion will provide for reversible transformation between, for instance, the diastereomers (*R*,*R*)-**2** and (*R*,*S*)-**2**. The geometric difference between the diastereomers is that the noncoordinated arm **Y**−**Z** and the substituent on the stereogenic center in (*R*,*R*)-**2** are on the same side of the metal coordination plane, while in (*R*,*S*)-**2**, the arm **Y′**−**Z′** and the corresponding substituent are on opposite sides of the coordination plane. This stereochemical difference between the diastereomers (*R*,*R*)-**2** and (*R*,*S*)-**2** can be used as a molecular binary logic element and potentially influenced by an external stimulus.

Drawing inspiration from the works reported by Hamilton,[7] Borovik,[8] and Parquette,[9] we design the C_2-symmetric pentadentate ligand **3** using three structural modules, as shown in Scheme 1. The "Phenone" module **4** was acetylated with "Acid" module **5** to give rise to the intermediate amide **6** in quantitative chemical yield. Bisalkylation of "Amine" module **7** with 2 equiv of compound **6** proceeded relatively slow but cleanly producing the desired ligand **3** in high chemical yield (>95%). Heating the achiral ligand **3** in methanol solution and in the presence of Ni(II) or Pd(II) resulted in formation of the corresponding complexes **8a**,**b** and **9a**,**b**. The complexes **8a** and **9a**, containing Ni(II), are neutral, very well soluble in polar organic solvents, and have typical orange-red color. In the ^{1}H NMR spectrum of compounds **8a** and **9a**, taken at ambient temperature, one can observe relatively sharp peaks of aromatic protons and extremely broadened resonances of aliphatic protons. These spectral features can be explained by the expected interconversion of the diastereomers **8a** and **9a**. Variable temperature ^{1}H NMR experiments revealed that this motion can be slowed at low temperatures as indicated by noticeable sharpening of the resonances of the aliphatic protons. However, the unambiguous characterization of the diastereomers **8a** and **9a** by NMR was not possible. On the other hand, X-ray analysis revealed that Ni-containing complexes crystallized in a single (*S*,*S*)-**8a** diastereomeric form, existing in the unit cell with its (*R*,*R*) enantiomer. The chiral stereogenic center in **8a** is located on the benzylamine nitrogen, while the stereogenic

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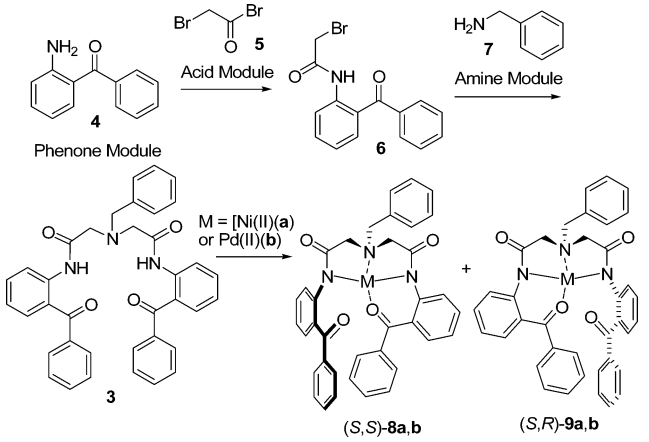
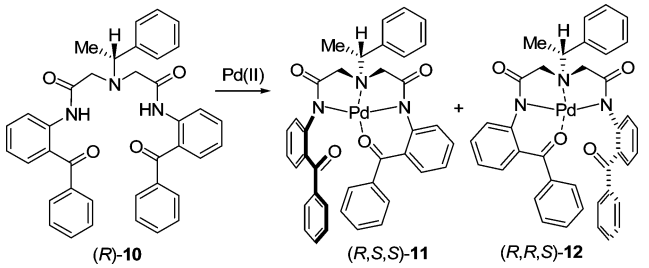
Scheme 1



Scheme 2



axis is directed along with the noncoordinated C−N bond of the *o*-(amino)benzophenone residue.

The complexes **8b** and **9b**, containing Pd(II), are also neutral and very well soluble in polar organic solvents and have characteristic yellow-orange color. The ^{1}H NMR spectroscopic properties of compounds **8b** and **9b** are very similar to those described for diastereomers **8a** and **9a**. Fortunately, X-ray analysis revealed that Pd-containing complexes crystallized in a single (*S*,*R*)-**9b** diastereomeric form, existing in the unit cell with its (*R*,*S*) enantiomer. The nature of the stereogenic center and axis in **9b** is the same as discussed for diastereomer (*S*,*S*)-**8a**, except that the absolute configuration of the stereogenic nitrogen is opposite, due to the coordination of different oxygen of the *o*-(amino)benzophenone residue to the metal. Thus, the crystallographic analysis of Ni(II)- and Pd(II)-containing complexes (*S*,*S*)-**8a** and (*S*,*R*)-**9b** undoubtedly confirmed that coordination of the achiral C_2-symmetric pentadentate ligand **3** with d^8 metal (Ni, Pd) produced the corresponding tetracoordinated complexes possessing elements of central and axial chirality.

Finally, to explore a possibility of preparation of this type of complexes in enantiomerically pure form, we prepared chiral ligand (*R*)-**10** (Scheme 2). Synthesis of the ligand (*R*)-**10** was conducted according to Scheme 1, except that (*R*)-α-(phenyl)ethylamine was used in place of benzylamine, as an "Amine" module. Heating an acetonitrile solution of (*R*)-**10** in the presence of Pd(II) resulted in formation of yellow-orange colored diastereomeric products (*R*,*S*,*S*)-**11** and (*R*,*R*,*S*)-**12**. These products were carefully purified by column chromatography on silica gel. Only one colored spot was observed during the purification step as well as on TLC using various eluents, suggesting that the stereochemical information of the stereogenic center in starting ligand **10** was quantitatively transferred to the newly created stereogenic nitrogen as well as the axis of chirality. Unfortunately, investigation of the diastereomers (*R*,*S*,*S*)-**11** and (*R*,*R*,*S*)-**12** by NMR was not possible due to fast interconversion between them. On the other hand, as it follows from the X-ray studies, only enantiomerically pure diastereomer (*R*,*S*,*S*)-**11** was observed in the solid state. Assignments of the absolute configuration in **11** were made as follows: stereogenic carbon (*R*), stereogenic nitrogen (*S*), and stereogenic axis (*S*).

In summary, we proposed here a new approach to the design of organic molecules with switchable central chirality based on the cleavage and formation of metal coordination bonds. Feasibility of this approach was demonstrated by preparation of achiral pentadentate ligand **3** and its coordination with d^8 metal (Ni, Pd) to produce the corresponding tetracoordinated complexes possessing elements of central and axial chirality. The formation of the corresponding diastereomers by coordination of the different arms of the ligand was confirmed by crystallographic analyses of complexes (*S*,*S*)-**8a** and (*S*,*R*)-**9b**. Moreover, we demonstrated virtually faultless chiral communication between the central chirality of ligand (*R*)-**10** and the central and axial chirality of complexes of this type, allowing preparation of enantiomerically pure (*R*,*S*,*S*)-**11** in the solid state.

Taking into account synthetically simple and straightforward preparation of pentadentate ligands **3** and (*R*)-**10**, as well as virtually unlimited structural flexibility provided by the modular nature of our design, various ligands of this type can be prepared and fine-tuned to control stability and rate of interconversion of the corresponding diastereomeric complexes and make them more selective to an external stimulus, leading to the development of a new generation of organic chiroptical molecular switches.

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Supporting Information Available: Experimental procedures, characterizations of new compounds, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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