

Synthesis and Properties of Ruthenocene Derivatives with [7]Helicene as Ligands

Three types of ruthenocenes coordinated by dinaphtho[2,1-*c*:1',2'-*g*]fluorenyl (**Dnf**) anion(s), a [7]helicene with a cyclopentadienyl moiety at the center of its skeleton, were synthesized: mono-helicene ruthenocene **1** with one **Dnf** bound to one ruthenium atom, bis-helicene ruthenocene **2** with two **Dnf** moieties, and bimetallic ruthenocene **3** in which two ruthenium atoms are bound to a **Dnf** in η^5 and η^6 manners. Since **Dnf** has a high racemization barrier, each of their enantiomers could be isolated in its pure form, which showed large optical rotation and intense circular dichroism (CD) response.

The isomerization behavior of a metal-bound helicene was investigated using bis-helicene ruthenocene **2**. It was found that there was an equilibrium between a mixture of (*P,P*)-**2** and (*M,M*)-**2** (*rac*-**2**), and (*P,M*)-**2** (*meso*-**2**). The isomerization barrier ΔG^\ddagger from *rac*-**2** to *meso*-**2** and the energy difference between the isomers ΔG were estimated to be 36.1 kcal mol⁻¹, and 2.3 kcal mol⁻¹, respectively. Further experiments suggested that the diastereomerization occurred not through the ligand exchange between (*P,P*)-**2** and (*M,M*)-**2**, but through helical inversion of the ligand.

Furthermore, we found that bimetallic complex **3** exhibited phosphorescence in both solution (31%, 77 K in BuCN) and solid state (18%, 77 K), although monometallic complexes **1** and **2** did not show any emission at all even at 77 K. The phosphorescence quantum yield is much higher than that of ruthenocene derivatives which have been reported so far. We conducted DFT calculations to clarify the mechanism of the emission. It is implied that the emission was the transition from inter-ligand and metal-to-ligand charge transfer excitation state of the central η^5 ruthenium atom.

