

# Synthesis of a Novel Tridentate Ligand System Bearing a Benzene Ring Condensed with Two Seven Membered Rings and Its Application

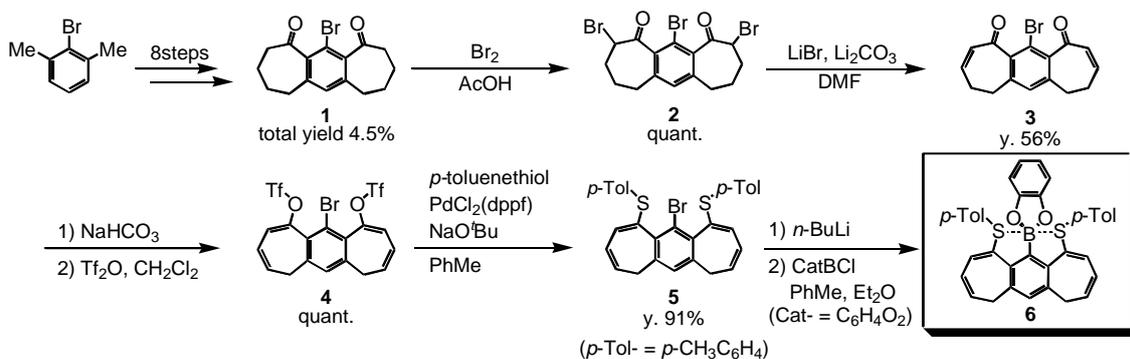
○Tatsuya Inoue<sup>1</sup>, Yohsuke Yamamoto<sup>1</sup>

<sup>1</sup>Graduate School of Science, Hiroshima University

Recently, we reported on the synthesis and isolation of hypervalent pentacoordinate carbon and boron compounds bearing either a rigid anthracene skeleton<sup>1a</sup> or a relatively flexible van Koten skeleton.<sup>1b</sup> X-ray analyses and density functional calculations of these compounds clearly showed the presence of interaction between the central carbon (or boron) and the two coordinating oxygen atoms. Unfortunately, these interactions were weak. In order to accomplish stronger interaction between the central atom and the coordinating atoms, we designed a novel tridentate ligand bearing a benzene ring condensed with two seven membered rings having  $\alpha,\beta$ -double bonds and sulfur atoms as the coordinating sites. By using the new ligand system, we could obtain some novel pentacoordinate carbon compounds.<sup>2</sup> However, tetracoordinate compounds where only one of the sulfur atoms was coordinated to the central carbon, were also obtained depending upon the substituents on the central carbon atom. To induce stronger interaction by adding more rigidity to the tridentate, we have designed and examined a novel ligand with  $\gamma,\delta$ -double bonds additionally introduced to the 7-membered rings.

The synthesis of precursor **5** was carried out according to Scheme 1. Diketone **1** was prepared by a known procedure from 1-bromo-2,6-xylene in 8 steps. This diketone (**1**) was treated with bromine, followed by dehydrobromination to give  $\alpha,\beta$ -unsaturated ketone **3**. Conversion to a bistriflate and subsequent coupling with a palladium catalyst gave **5**, a novel rigid ligand precursor. The boron atom was introduced by the reaction of B-chlorocatechol borane with a lithiated derivative of **5** to give boron compound **6**. X-ray analysis of this compound showed it to be a hypervalent pentacoordinate species. In this presentation, its structure and properties will be discussed in detail.

Scheme 1



[1] (a). Akiba, K.-y.; Yamashita, M.; Yamamoto, Y.; Nagase, S. *J. Am. Chem. Soc.* **1999**, *121*, 10644-10645. (b). Akiba, K.-y.; Moriyama, Y.; Mizozoe, M.; Inohara, H.; Nishii, T.; Yamamoto, Y.; Minoura, M.; Hashizume, D.; Iwasaki, F.; Takagi, N.; Ishimura, K.; Nagase, S. *J. Am. Chem. Soc.* **2005**, *127*, 5893-5901. [2] Masui, T. *Master's thesis*. **2004**.