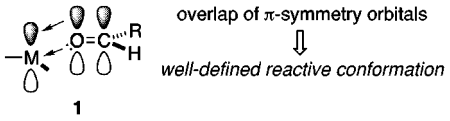
First Synthesis and Structural Characterization of an Enantiomerically Pure Planar−Chiral Lewis Acid Complex

Jennifer Tweddell, Diego A. Hoic, and Gregory C. Fu*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

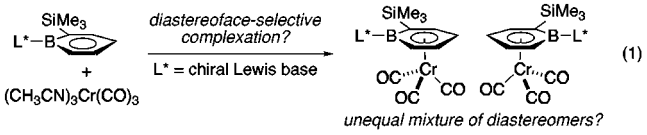
Received September 19, 1997

While important advances have been made in the development of chiral Lewis acid catalysts, the ultimate goal of discovering a single catalyst that can effect a wide range of processes with high levels of enantioselectivity has not yet been achieved.[1,2] We recently proposed a new approach to chiral Lewis acid design in which a carbonyl group is activated through simultaneous σ-symmetry (oxygen lone pair) and π-symmetry (carbonyl π system) interactions with a divalent Lewis acid; the activating nature of the π-symmetry interaction defines the reactive conformation of the substrate−Lewis acid complex (**1**).[3] In our initial work in this area, we reported crystallographic and spectroscopic studies that suggest that the boron atom of (η^6-borabenzene)$Cr(CO)_3$ can function as the required σ- and π-Lewis−acidic divalent metal.[3] In this paper, we describe the synthesis and the structural characterization of a *chiral* (η^6-borabenzene)$Cr(CO)_3$ adduct; to the best of our knowledge, this is the first planar−chiral Lewis acid complex (Figure 1) that has been prepared in enantiomerically pure form.



1

Our approach to the synthesis of an enantiomerically pure (η^6-borabenzene)$Cr(CO)_3$-derived Lewis acid relies on stereoselective complexation to $Cr(CO)_3$ of one diastereotopic face of a chiral borabenzene−ligand adduct (eq 1).[4] We prepared an enantiopure borabenzene adduct



(1)

according to the pathway outlined in Figure 2.[5] Thus, treatment of stannacyclohexadiene **2**[6] with LDA followed by Me_3SiCl affords stannacycle **3** in excellent yield.[7] Transmetalation through treatment of **3** with BCl_3 then provides boracyclohexadienes **4** and **5**.[8] Finally, reaction

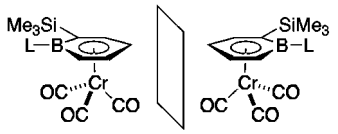


Figure 1. Planar−chiral Lewis acid complexes.

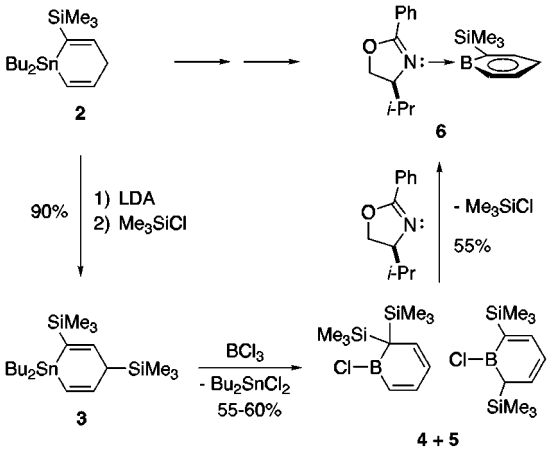
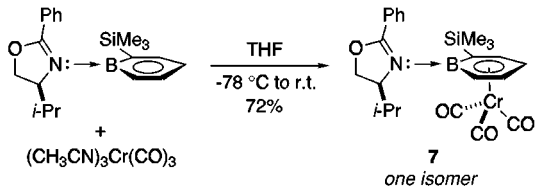


Figure 2. Synthesis of an enantiopure borabenzene−ligand adduct.

of this mixture of boracycles with an (*S*)-valinol-derived oxazoline generates enantiopure borabenzene-ligand adduct **6**.

Adduct **6** appears by ^1H NMR spectroscopy to be a single atropisomer.[9] The stereochemistry illustrated in Figure 2 has been assigned by X-ray crystallography[10] and is supported by NOE studies. Ab initio calculations, as well as simple model building, suggest that isomer **6** is the more stable of the two possible atropisomers (by 3.38 kcal/mol [6-31G**]).[11]

We were pleased to discover that treatment of adduct **6** with $(CH_3CN)_3Cr(CO)_3$ in THF at −78 °C cleanly affords the $Cr(CO)_3$-bound η^6-borabenzene complex *as a single stereoisomer* (eq 2; 9:1 selectivity at rt).[12] We



(2)

established the structure of this complex by X-ray

(1) For early work, see: (a) Hashimoto, S.; Komeshima, N.; Koga, K. *J. Chem. Soc., Chem. Commun.* **1979**, 437−438. (b) Bednarski, M.; Danishefsky, S. *J. Am. Chem. Soc.* **1983**, *105*, 3716−3717.

(2) For recent reviews, see: (a) Ishihara, K.; Yamamoto, H. In *Advances in Catalytic Processes*; Doyle, M. P., Ed.; JAI: Greenwich, CT, 1995; Vol. 1, pp 29−59. (b) Deloux, L.; Srebnik, M. *Chem. Rev.* **1993**, *93*, 763−784. (c) Narasaka, K. *Synthesis* **1991**, 1−11.

(3) Amendola, M. C.; Stockman, K. E.; Hoic, D. A.; Davis, W. M.; Fu, G. C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 267−269.

(4) For stereoselective complexation of enantiopure benzene derivatives to $Cr(CO)_3$, see: Alexakis, A.; Mangeney, P.; Marek, I.; Rose-Munch, F.; Rose, E.; Semra, A.; Robert, F. *J. Am. Chem. Soc.* **1992**, *114*, 8288−8290.

(5) For previous reports of the synthesis of neutral borabenzene−ligand adducts, see: (a) Boese, R.; Finke, N.; Henkelmann, J.; Maier, G.; Paetzold, P.; Reisenauer, H. P.; Schmid, G. *Chem. Ber.* **1985**, *118*, 1644−1654. (b) Boese, R.; Finke, N.; Keil, T.; Paetzold, P.; Schmid, G. *Z. Naturforsch., B* **1985**, *40*, 1327−1332. (c) Hoic, D. A.; Wolf, J. R.; Davis, W. M.; Fu, G. C. *Organometallics* **1996**, *15*, 1315−1318. (d) Reference 3.

(6) (a) Ashe, A. J., III; Chan, W.-T.; Smith, T. W.; Taba, K. M. *J. Org. Chem.* **1981**, *46*, 881−885. (b) Reference 5c.

(7) For related work, see: Jutzi, P.; Baumgartner, J. *J. Organomet. Chem.* **1978**, *148*, 247−255.

(8) Amendola, M. C. M. S. Thesis, Massachusetts Institute of Technology, 1995. We thank Dr. Kenneth E. Stockman for optimizing the synthesis of **4** and **5**.

(9) 300 MHz ^1H NMR spectra were obtained at room temperature and at −78 °C.

(10) For details regarding the X-ray crystal structure of adduct **6**, see the Supporting Information.

(11) We thank Prof. Bruce Tidor and Justin A. Caravella (MIT) for performing these calculations.

(12) We observed lower levels of diastereoselectivity when complexing $Cr(CO)_3$ to other (2-(trimethylsilyl)borabenzene)−L* adducts (L* = tertiary amines, other oxazolines).

S0022-3263(97)01757-X CCC: $14.00

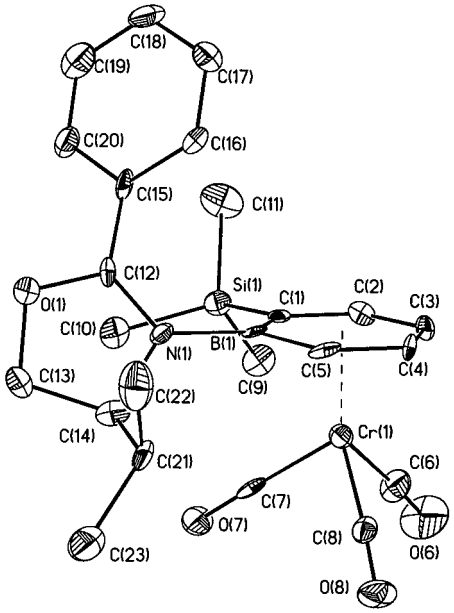


Figure 3. ORTEP illustration, with thermal ellipsoids drawn at the 35% probability level, of complex **7**.

crystallography (Figure 3), which reveals that the Cr(CO)$_3$ group is bound to the less hindered face of the borabenzene ring. The dihedral angle between the borabenzene and oxazoline rings is 66°, a conformation that minimizes steric interactions between the Ph, SiMe$_3$, Cr(CO)$_3$, and *i*-Pr substituents (Figure 4). Steric interactions may also be responsible for the observed bending of the SiMe$_3$ group away from boron (Figure 3: ∠B1−C1−Si1 = 129.9(7)°). The B−N bond length in complex **7** is 1.529(12) Å. No other boron-bound oxazoline has been structurally characterized,[13] but this B−N bond distance may be compared to distances reported for boron-bound imino esters, which range from 1.52 to 1.63 Å.[14] The relatively short B−N bond length in **7** is probably attributable to the high Lewis acidity of the sp^2-hybridized boron orbital.[15]

In summary, we have prepared and structurally characterized the first example of an enantiopure planar−chiral Lewis acid complex; the key step in the synthesis is a highly diastereoselective complexation of a chiral

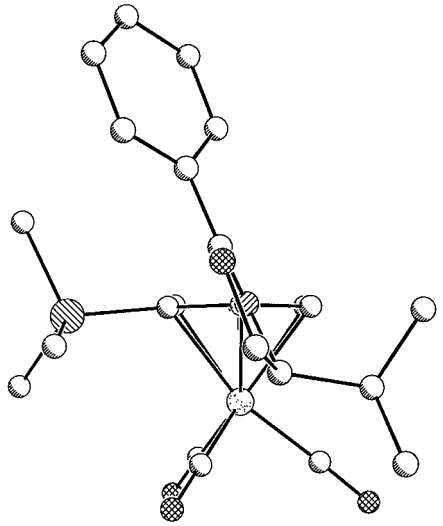


Figure 4. View of complex **7** along the N−B axis.

borabenzene−oxazoline adduct to Cr(CO)$_3$. In future work, we will explore the application of this family of complexes in asymmetric catalysis.

Acknowledgment. Support has been provided by the Alfred P. Sloan Foundation, the American Cancer Society, the Camille and Henry Dreyfus Foundation, Eli Lilly, Firmenich, Glaxo Wellcome, the National Science Foundation (Young Investigator Award to G.C.F., with funding from Procter & Gamble, Merck, Bristol-Myers Squibb, DuPont, Pfizer, Rohm & Haas, Pharmacia & Upjohn, and Bayer), the Natural Sciences and Engineering Research Council of Canada (predoctoral fellowship to J.T.), and the Research Corporation. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the ACS, for partial support of this research.

Supporting Information Available: Experimental procedures, compound characterization data, and crystal structure data (32 pages).

JO971757K

(13) Based on a search of the Cambridge Crystallographic Database.

(14) Based on a search of the Cambridge Crystallographic Database. (a) 1.52 Å: Siriwardane, U.; Chu, S. S. C.; Hosmane, N. S.; Zhang, G.; Zhu, W.; Zhu, H. *Acta Crystallogr., Sect. C* **1989**, *45*, 294−297. (b) 1.63 Å: Koster, R.; Kucznierz, R.; Schussler, W.; Blaser, D.; Boese, R. *Liebigs Ann. Chem.* **1993**, 189−200.

(15) We suspect that "free" (no 1-substituent) borabenzene derivatives will be extremely challenging to isolate. See: (a) Schulman, J. M.; Disch, R. L.; Sabio, M. I. *J. Am. Chem. Soc.* **1982**, *104*, 3785−3788. (b) Raabe, G.; Heyne, E.; Schleker, W.; Fleischhauer, J. *Z. Naturforsch., A* **1984**, *39*, 678−681. (c) Maier, G. *Pure Appl. Chem.* **1986**, *58*, 95−104. (d) Raabe, G.; Schleker, W.; Heyne, E.; Fleischhauer, J. *Z. Naturforsch., A* **1987**, *42*, 352−360. (e) Maier, G.; Reisenauer, H. P.; Henkelmann, J.; Kliche, C. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 295−296. (f) Schulman, J. M.; Disch, R. L. *Organometallics* **1989**, *8*, 733−737. (g) Cioslowski, J.; Hay, P. J. *J. Am. Chem. Soc.* **1990**, *112*, 1707−1710. (h) Maier, G.; Wolf, H.-J.; Boese, R. *Chem. Ber.* **1990**, *123*, 505−511.