Pergamon

Tetrahedron Letters, Vol. 36, No. 2, pp. 221-224, 1995
Elsevier Science Ltd
Printed in Great Britain
0040-4039/95 $9.50+0.00

0040-4039(94)02227-5

Chiral Lewis Acids Derived from 1,8-Naphthalenediylbis-(dichloroborane): Mechanistic Aspects

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Abstract: Chiral Lewis acids derived from 1,8-Naphthalenediylbis(dichloroborane), a novel bidentate Lewis acid, have been found to be active catalysts for the asymmetric Diels-Alder reaction. Utilizing chiral ligands derived from amino acids, a range of enantioselectivities have been achieved with cyclopentadiene and various α,β-unsaturated aldehydes. Some mechanistic aspects of this novel asymmetric bidentate catalyst have been addressed.

Lewis acid complexation to carbonyl compounds is known to have a dramatic effect on reactivity and selectivity in a variety of reactions.[1] One recent development has been in the area of asymmetric catalysis by chiral Lewis acids.[2] There are two major variables that influence highly selective Lewis acid catalyzed reactions such as the Diels-Alder reaction. The first is the strength of the Lewis acid, which must match the specific functional group of the reaction at hand, and the second is the highly ordered transition state assembly. While the strength of the Lewis acid can be controlled through the proper choice of chiral ligand, the conformation and the transition state assembly often can not be controlled predictably with current monodentate Lewis acids. The application of chiral bimetallic Lewis acids to the asymmetric Diels-Alder reaction promises to offer excellent control over both of these aspects.

Our investigation into this area focuses on the perceived ability of a bimetallic chiral Lewis acid to simultaneously coordinate to a carbonyl group[3] (Structure **1**) or play an organizational role in coordinating a chiral ligand and a carbonyl group[4] (Structure **2**) with each Lewis acidic metal center. This behavior should lessen the degree of conformational ambiguity found in the Diels-Alder transition state and may eventually lead to the development of highly efficient asymmetric catalysts for this important transformation. We have shown that chirally modified **5** will catalyze asymmetric Diels-Alder reactions with moderate enantioselectivities.[5] We have also shown with 2,5-dimethylpyranone that complex **3** is feasible.[6] However, with excess carbonyl compound complex **4** is favored. The question we address at the present is on the mechanistic aspects of this system and show that this system catalyzes the reaction through an intermediate of type **2** and not **1**.

Our initial efforts were to compare the activity of compound **5** and phenylboron dichloride. The results in Table 1 indicate that the two are of comparable activity. Comparison with dienophile **7** gave 14% and 17% yield after one hour (entries 1 and 3). Using twice the amount of phenylboron dichloride to the bidentate catalyst gave approximately twice the yield of product (entries 2 and 4).

We compared the enantioselectivity of the catalyst modified with ligands derived from a variety of amino acids.[7] The results are summarized in Table 2. Excellent to moderate ee's were obtained with the tryptophan derived ligand for the *endo*-adducts and only 8% ee's was obtained with the phenyl alanine derived ligand. Ligands derived from amino acids without aromatic groups gave no enantioselectivity, indicating π-interaction in the transition state. Addition of a sterically hindered amine base, pentamethylpipyridine, showed that traces of HCl were not inhibiting the enantioselectivity(entry 4). We have already shown that 4Å molecular

Figure

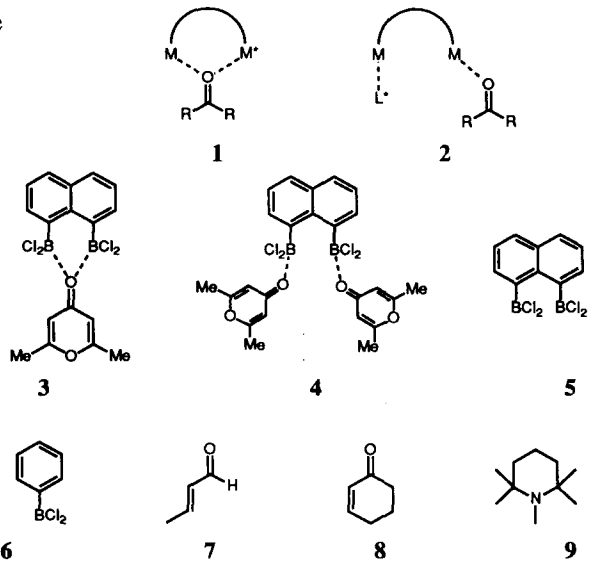


Table 1. Diels-Alder reactions of **7** and **8** with cyclopentadiene[a]

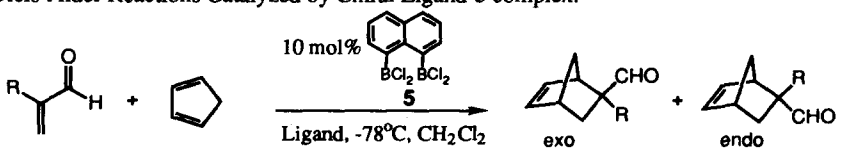
Entry	Catalyst	Amount	dienophile	Yield(%)
1	**5**	10 mol%	**7**	14
2	**5**	10 mol%	**8**	12
3	**6**	10 mol%	**7**	17
4	**6**	20 mol%	**8**	35

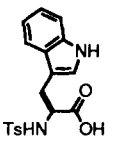
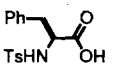
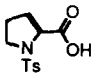
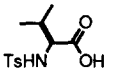
a) reaction conditions: CH_2Cl_2, -78°C, 1 h for **7** and 36 h for **8**.

sieves did not enhance enantioselectivity.[6]

Mechanistic investigation on chiral boronic Lewis acids derived from tryptophan show that π-interactions of the indole group with the dienophile play an important role.[8] Sulphonamide groups also play an important role and toluenesulphonamide in particular, seems to give the best enantioselectivities. In light of the good enantioselectivities achieved with the N-toluenesulfonamide tryptophan derived catalytic system, we wish to present a model based on the following. It is known that boron Lewis acids coordinate *syn* to the aldehyde hydrogen.[9] In the case of Lewis acids derived from **5**, there are two Lewis acidic sites which can play a coordinative role. The role that each Lewis acidic site assumes depends upon the steric environment around each center and the peri-effect which has been well documented in 1,8-disubstituted naphthalene systems.[10] The rate studies discussed above and the fact that structure **4** is favored under catalytic amounts of **5** based on previous NMR studies rule out a transition state of type **1**.[6] With these parameters in mind, we postulate a transition state assembly model of the type **10**. Molecular modeling indicates π-interaction between the toluenesulfonamide and the naphthalene system as well as between the indole moiety and the dienophile.[11] Transition state assembly **10** also takes into account the anti-orientation of the indole moiety and the toluenesulfonamide group. Peri-interaction dictates the two boron atoms be skewed out of the plane of the

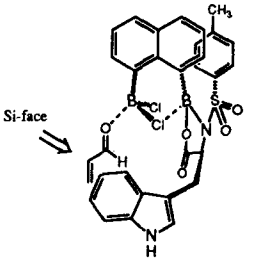
Table 2. Diels-Alder Reactions Catalyzed by Chiral Ligand-5 complex.



Entry	R	Ligand	exo:endo[b]	%ee exo:endo[c,d]	yield(%)[e]
1	Br		92:8	44: -	84[f]
2	CH_3		63:37	20:100	46[f]
3	H		6:94	- : 62	53[f]
4	H	+ **9**	20:80	-:38	74
5	Br		89:11	8:-	83[f]
6	H		2:98	-:0	82
7	H		2:98	-:0	84

a) Equivalents of Ligand to **5**. b) The ratios were obtained by integration of the aldehyde ^1H NMR resonance. c) ee's were determined by (+)-Eu(hfc)$_3$ shift reagent. d) absolute configuration was assigned by comparing optical rotation with literature data, reference 8c. e) isolated yields of Diels-Alder adducts. f) taken from reference 5.

naphthalene system and away from each other. Because of the proximity of the two boron atoms, chloride bridging should have a stabilizing effect on the electron deficient boron atom.[12]



10

In summary, we have shown that 1,8-Naphthalenediylbis(dichloroborane) derived bidentate Lewis acids catalyze the Diels-Alder reaction through a complex of the type **2**. We also propose a working model transition state assembly **10**, which is in agreement with the previously proposed transition state assembly of oxazaborolidines derived from amino acids[8] and which adequately rationalizes the selectivities achieved to date. Transition state **10** also takes into account the additional factors of 1,8-peri-interactions of naphthalene as well as chloride bridging.

ACKNOWLEDGMENT: This research was supported in part by the Dr. Nuala McGann Drescher Award to T. Oh.

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(*Received in USA* 4 *October* 1994; *revised* 2 *November* 1994; *accepted* 10 *November* 1994)