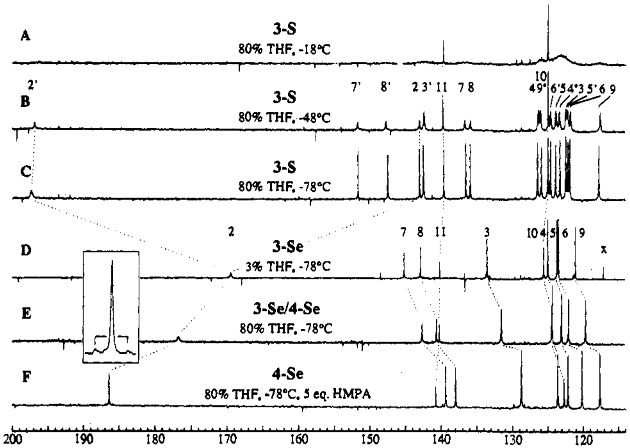

Figure 1. ^{13}C NMR spectra (90.56 MHz) of solutions of **3**-S and **3**-Se. The inset in spectrum F shows the ^{77}Se satellites of C-2 (J_{SeC} = 85 Hz).

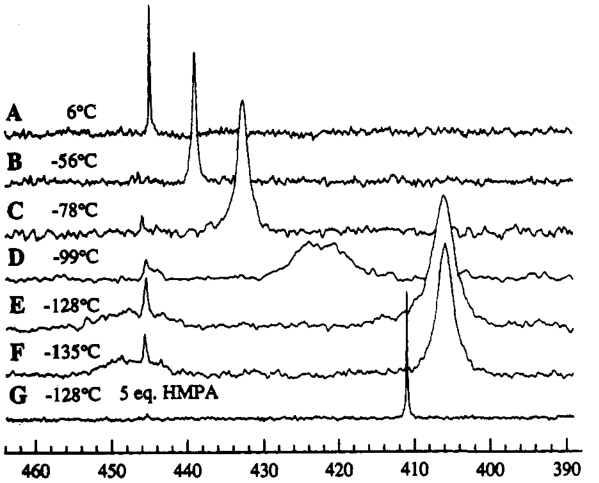

Figure 2. ^{77}Se NMR spectra (68.68 MHz) of solutions of **3**-Se and **4**-Se in 80% THF/ether (A–F) and THF/ether/HMPA (G). Chemical shifts are referenced to Me_2Se in $CDCl_3$ at 25 °C.

proportions of **4**-Se at lower temperatures. The ^{77}Se spectrum broadened and decoalesced at ≈−128 °C (Figure 2E) to a broad signal at 447 ppm for **3**-Se and one at 406 ppm for **4**-Se.[13] The sharp signal at 446 ppm is the protonation product of **3**-Se. The spectra in Figure 2A–F and corresponding ^{13}C spectra (not shown) can be used to determine the temperature dependence of the **3**-Se/**4**-Se equilibrium. A plot of $\Delta G°$ vs T gives $\Delta H° = -2.5 \pm 1$ kcal/mol, $\Delta S° = -14 \pm 5$ eu. Equilibria between solvent-separated and contact lithium ion pairs in ether solvents are temperature dependent, with lower temperatures favoring separated ions.[14] Equilibria between aryllithium reagents (contact ions) and the ate complexes Ph_2ILi and Ph_3TeLi (separated ions in THF) also follow this pattern.[1c] Figure 2G shows the spectrum of the ate complex **4**-Se in THF/HMPA.

Summary. The enormous rate acceleration of the intramolecular Li/S exchange **3**-S/**3'**-S and the unusual stability of the selenium ate complex **4**-Se suggest that the structure of **4** is close to the ideal geometry of such ate complexes, and provides support for the intermediacy of ate complexes in Li/S and Li/Se exchanges.

Acknowledgment. We thank the National Science Foundation for support of this work.

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(13) Upfield ^{125}Te and ^{77}Se shifts are found for the conversion of Ph_2Te (688 ppm) to Ph_3TeLi (327 ppm),[1c,d] and Ph_2Se (402 ppm) to Ph_4Se (373.7 ppm)[4b] as well as their dibenzoselenophene analogs.[4c] However, the conversion Ph_4Te (529 ppm) to Ph_5TeLi (622 ppm) results in a downfield shift.[1d]

(14) For the equilibration of lithium fluorenide contact and separated ion pairs in THF: $\Delta H° = -7.5$ kcal/mol and $\Delta S° = -22$ eu;[14a] for equilibration of PhLi/PhI with Ph_2ILi, $\Delta H° = -9.9$ kcal/mol and $\Delta S° = -44$ eu.[1c] Rate studies for the PhLi/ArBr exchange in ether ($\Delta H^* = 14$ kcal/mol, $\Delta S^* = -24$ eu)[14b] and THF (223 K, $\Delta H^* = 9.5$ kcal/mol, $\Delta S^* = -30$ eu)[1f] show negative entropies of activation. (a) Hogen-Esch, T. E. *Adv. Phys. Org. Chem.* **1977**, *15*, 153. O'Brien, D. H.; Russell, C. R.; Hart, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 633. (b) Winkler, H. J. S.; Winkler, H. *J. Am. Chem. Soc.* **1966**, *88*, 964, 969. Rogers, H. R.; Houk, J. *J. Am. Chem. Soc.* **1982**, *104*, 522.

X-ray Crystallographic and NMR Studies on the Origins of High Enantioselectivity in Diels–Alder Reactions Catalyzed by a Chiral Diazaaluminolidine

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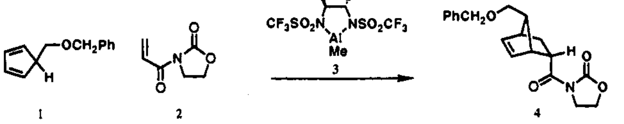
Received July 8, 1992

The use of chiral aluminum-containing catalysts for enantioselective Diels–Alder reactions has recently been reported.[1] For instance, the reaction of 5-(benzyloxymethyl)-1,3-cyclopentadiene (**1**) and 3-acryloyl-1,3-oxazolidin-2-one (**2**), when catalyzed by the (*S*,*S*)-diazaaluminolidine **3** (ca. 10 mol %) at −78 °C, produced after 18 h the adduct **4** in 93% yield and with ca. 97:3 enantioselectivity.[2] This useful and interesting process has now been examined for mechanistic detail on the control of enantioselectivity within the catalytic transition-state assembly. We present herein X-ray crystallographic and NMR evidence for the basis of enantioselectivity in this system.



The structure of the chiral Diels–Alder catalyst in the crystalline state was determined by an X-ray diffraction study. The catalyst was prepared with rigorous exclusion of oxygen and moisture by the method used earlier,[1,3] and crystals were grown from a methylene chloride–heptane bilayer at 23 °C. A crystal of size 0.21 × 0.31 × 0.35 mm was sealed in a glass capillary for X-ray analysis, which revealed that two units of the diazaaluminolidine system **3** are associated as shown in structure **5**.[4] In the dimer

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(1) (a) Corey, E. J.; Imwinkelried, R.; Pikul, S.; Xiang, X. B. *J. Am. Chem. Soc.* **1989**, *111*, 5493–5495. (b) Corey, E. J.; Imai, N.; Pikul, S. *Tetrahedron Lett.* **1991**, *32*, 7517–7520.

(2) For a review of this and other applications of chiral 1,2-diphenyl-1,2-diaminoethane-derived reagents, see: Corey, E. J. *Pure Appl. Chem.* **1990**, *62*, 1209–1216.

(3) For details of the preparation of the catalyst and its use in a Diels–Alder reaction, see: Pikul, S.; Corey, E. J. *Org. Synth.*, in press. A flame-dried, 250-mL, three-necked flask equipped with a magnetic stirring bar and a reflux condenser was charged with 1.31 g (2.75 mmol) of the bistriflamide of (*S*,*S*)-1,2-diphenyl-1,2-diaminoethane (dried at 80 °C and 1 mmHg) and placed under dry argon. 1,2-Dichloroethane (20 mL) was added, and the mixture was heated to 80 °C with stirring to effect solution, cooled to ambient temperature, and treated dropwise with 1.37 mL (2.74 mmol) of 2 M trimethylaluminum in toluene. After the evolution of gases ceased, the homogeneous mixture was heated to 80 °C (oil bath) for 3 h. The mixture was cooled to ambient temperature, and the solvent was removed under vacuum, which was maintained for an additional 30 min. The resulting solid was dissolved in 10 mL of dry methylene chloride and overlayered with 50 mL of dry heptane. Colorless, clear crystals of catalyst were deposited after 20 h. The supernatant was drawn off by syringe. Since trimethylaluminum can also catalyze Diels–Alder reactions of **2** with dienes, it is essential that this and other Lewis acids be removed from catalyst **3**.

(4) Detailed X-ray crystallographic data are available from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, U.K. Data for empirical formula $Al_2C_{34}H_{30}N_4O_8S_4F_{12}$ (1032.9): space group $P2_1$, a = 10.798 (5) Å, b = 16.264 (9) Å, c = 12.406 (7) Å, α = 90.00°, β = 92.87 (4)°, γ = 90.00°, V = 2176 (2) Å^3, 2 molecules per unit cell, d = 1.58 g/cm^3; Mo Kα radiation (23 °C); 2341 reflections obtained (1643 with $I > 3\sigma$), R index = 0.069; GOF = 1.04.

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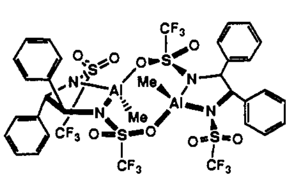
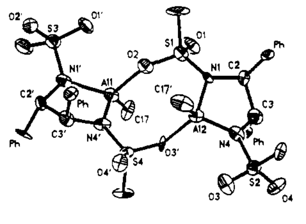


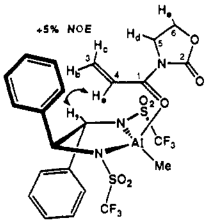
5



5 (TELP plot)

structure 5, the monomeric subunits are joined by Lewis acid-base association of a sulfonyl oxygen with aluminum to form an 8-membered ring consisting of two Al-N-S-O sequences joined head to tail. The S(1)-O(2) and S(4)-O(3′) bond lengths (ca. 1.46 Å) indicate extensive double-bond character for the S-O bonds in the 8-membered ring. The nitrogen atoms have sp^2 geometry. The ^{1}H NMR spectrum of a solution of the catalyst in CD_2Cl_2 at 23 °C is also consistent with the dimeric structure **5**; two $AlCH_3$ peaks appear at δ -0.32 and -0.54, and four benzylic C-H peaks appear at δ 4.82, 4.85, 4.88, and 5.24. The ^{13}C NMR spectrum in CD_2Cl_2 provides further support for the dimeric structure of **5** with benzylic carbon peaks at δ 72.2, 67.7, and 66.9 and four peaks for the attached aromatic (ipso) carbons at δ 138.5, 139.9, 140.4, and 140.8, as well as four different overlapping CF_3 quartets. As indicated below, the addition of 1 equiv of dienophile **2** to the catalyst results in the total conversion to a new species as shown by the appearance of new NMR peaks due to a 1:1 complex of dienophile **2** and monomeric catalyst **3**, the structure of which is indicated by the NMR data.

The dienophile **2** is monocoordinated to aluminum in the 1:1 complex at the *acryloyl oxygen*, as depicted in 6 and as revealed clearly by the ^{1}H and ^{13}C NMR data listed (for CD_2Cl_2 solution at 23 °C). Especially noteworthy are the downfield shifts on complexation for C_1 and C_3 and for H_b and H_c and the lack of the same for the oxazolidinone moiety.[5]

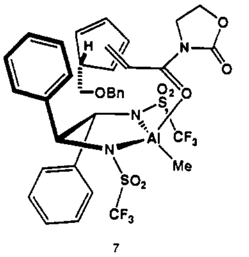


6

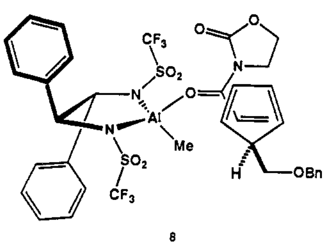
^{1}H NMR (δ; Hz)		^{13}C NMR (δ)	
2	6	2	6
H_a 7.45	H_a 7.74	C_1 165.1	C_1 172.8
H_b 5.87	H_b 6.60	C_2 153.8	C_2 150.7
H_c 6.49	H_c 7.15	C_3 131.4	C_3 144.3
J_{ab} =8.6	J_{ab} =13.6	C_4 127.5	C_4 127.4
J_{ac} = 15.2	J_{ac} = 21.3	C_5 42.9	C_5 44.3
J_{bc} = 1.8	J_{bc} < 1	C_6 62.7	C_6 63.7
H_d 4.03	H_d 4.25		
H_e 4.40	H_e 4.38		

In the ^{1}H NMR spectrum of the 1:1 complex (CD_2Cl_2, 23 °C) there is a single $AlCH_3$ peak at δ -0.19 and two benzylic CH peaks at δ 5.13 and 4.76. In addition, there is a 5% positive NOE enhancement between the benzylic H_f (δ = 4.76) and H_a of the acryloyl subunit. These data support the geometry shown in 6 for the 1:1 complex of **2** and **3**, which presumably is the reactive species in the catalyzed Diels-Alder process. The ^{13}C NMR data for the diazaaluminolidine moiety of the complex are consistent with this formulation; there are two benzylic carbon peaks (δ 68.7 and 67.6), two peaks due to the attached aromatic carbons (δ 141.6 and 140.9), and two overlapping quartets due to the CF_3 carbons (center at δ 120).

Expression 6 for the complex of catalyst and activated dienophile strongly suggests that the transition-state assembly for the formation of Diels-Alder adduct **4** is that shown in **7**, which is uniquely consistent with the X-ray and NMR results and also the absolute configuration of the reaction product. Although the three-dimensional assembly **8** which was suggested earlier[1] cannot be ruled out, it is out of harmony with the ^{1}H NOE data for 6. In structure **7** it is necessary that the two O_2S-CF_3 bonds project away from the same face of the diazaaluminolidine ring to make room for the approaching diene. One of the phenyl substituents then plays the crucial role of shielding one face of the *s-trans*-acryloyl subunit from attack by the diene. A structure analogous to **7** is capable of explaining the enantioselective Diels-Alder addition of cyclopentadiene to menthyl acrylate under catalysis by **3**.[1,6]



7



8

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[5] The carbonyl carbons in the 1:1 complex were assigned using coupled ^{1}H-^{13}C NMR measurements. The acryloyl carbonyl (C_1) was identified by long-range couplings to the vinylic protons.

[6] This research was assisted financially by grants from the National Science Foundation and the National Institutes of Health.

Boron Analogs of Cyclopropenium Cation: $B_3H_6^+$, the First Three-Membered Nonplanar 2π Aromatic

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Received March 26, 1992

The nonplanar structure of cyclobutadiene dication came as a revelation to chemists; 2π aromaticity no longer requires planarity.[1] The neutral boron analog, 1,3-diborocyclobutadiene, has been structurally characterized.[2] The isoelectronic boron analogs of the cyclopropenyl cation, the smallest 2π aromatic ring, **1**,[3] are C_2BH_3 (**2**, C_{2v}),[4] CB_2H_4 (**3**, C_{2v}),[5] B_3H_5 (**4**, C_{2v}),[6] and $B_3H_6^+$ (**5**, D_{3h}). We present here theoretical results to show that **2-4** are indeed planar and aromatic but **5** represents a transition state. A nonplanar aromatic structure (**6**, C_{3v}) is found to be a minimum. There are interesting implications to this observation in areas as different as polylithium compounds and metallaboranes. Isomers of **1-5** which lie close in energy are also studied here.

Ab initio MO theory at the 6-31G*,[7] MP2/6-31G*,[8] and QCISD(T)/6-31G*[9] levels is used in this study.[10] Unless oth-

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