conjugate base of **2b** ligated to Cu(I) was investigated as a catalyst in the cyclopropanation of diazoacetate esters with styrene in direct analogy with our parallel studies on the undeprotonated ligand **2b** summarized in Table I. In their study using ethyl diazoacetate, the authors have misassigned the absolute stereochemistry of their major *trans*-cyclopropane product. We have repeated the Masamune experiments using **2b** in both neutral and charged variants and have concluded that their major trans diastereomer **5** should be (1*R*,2*R*) rather than (1*S*,2*S*) as reported. Furthermore, we have shown that base-catalyzed epimerization of the minor cis diastereomer **6R** affords **6S**, the enantiomer of the major product diastereomer. This observation is also inconsistent with the Masamune stereochemical assignment.

Acknowledgment. Dr. Tarek Sammakia is gratefully acknowledged for helpful discussions. Support for this research was provided by the National Science Foundation and the National Institutes of Health. The NIH BRS Shared Instrumentation Grant Program 1 S10 RR01748-01A1 is acknowledged for providing NMR facilities.

Supplementary Material Available: Full details for the synthesis of catalyst **3b** and *ent*-**3b**, spectral and analytical data for ligands **1a**, **2a**,**b**, and **3a**, representative experimental procedures, and characterization of reaction products (8 pages). Ordering information is given on any current masthead page.

---

(17) Lowenthal, R. E.; Abiko, A.; Masamune, S. *Tetrahedron Lett.* **1990**, *31*, 6005–6008.

Designed Catalyst for Enantioselective Diels–Alder Addition from a C_2-Symmetric Chiral Bis(oxazoline)–Fe(III) Complex

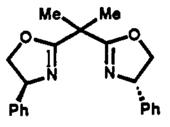
E. J. Corey,* Nobuyuki Imai, and Hong-Yue Zhang

Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

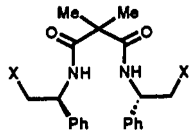
Received October 22, 1990

The Diels–Alder reaction is arguably the most powerful construction process in organic synthesis, and for this reason there has been much research on the development of enantioselective versions,[1] including most recently the use of chiral catalysts.[2] Recent experience with the use of a chiral 1,2-diamino-1,2-diphenylethane as a controller ligand for enantioselective catalytic reactions such as the Diels–Alder and olefin dioxyosmylation cycloadditions[2c,3] suggested the investigation of the rigid ligand 2,2-bis[2-[4(*S*)-phenyl-1,3-oxazolinyl]] propane (**1**) as a component of new catalytic systems.[4] The results of such a study for the Diels–Alder reaction are outlined herein.[5,6]

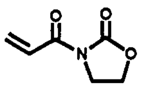
The chiral ligand **1** was readily prepared as follows. (*S*)-(+)-Phenylglycinol[7] (2 equiv) and Et_3N (2 equiv) in CH_2Cl_2 at 0 °C were treated with 1 equiv of dimethylmalonyl chloride[8] and allowed to react at 23 °C for 16 h to give **2** as a colorless solid (97%), further converted by reaction with excess $SOCl_2$ at reflux for 4 h to **3** [mp 164–166 °C, $[\alpha]^{23}_D$ +86.7° (c = 1.1, $CHCl_3$)]. Reaction of **3** with 5.5 equiv of 0.5 M NaOH in 1:1 methanol-water at reflux for 1 h followed by extractive isolation, filtration through silica gel, and distillation (193 °C at 0.03 Torr) afforded **1** as a viscous oil (78% overall from **2**): $[\alpha]^{23}_D$ −171.3° (c = 1.0, EtOH); MS, m/e 335.1761 (calcd 335.1759); ^1H NMR ($CDCl_3$, 500 MHz) δ 1.64 (s, 6 H), 4.12 (t, 2 H, J = 8.4, 7.7 Hz), 4.63 (dd, 2 H, J = 10.1, 8.4 Hz), 5.19 (dd, 2 H, J = 10.1, 7.7 Hz), 7.18–7.24 (m, 6 H), 7.27–7.30 (m, 4 H).



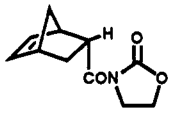
1



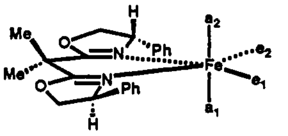
2 X= OH
3 X= Cl



4



5



6

For catalytic studies of the Diels–Alder reaction using **1** as a chiral controller ligand, Fe(III) halides were selected as the Lewis acidic metal component, 3-acryloyl-1,3-oxazolidin-2-one (**4**)[9] as a bidentate dienophile, and cyclopentadiene as the prototypical diene component. It was envisaged that a structure in which both **1** and **4** are chelated to FeX_2^+ (X = halogen) with octahedral geometry about iron could be highly activated toward reaction with a 1,3-diene at low temperature. This expectation was confirmed experimentally. An equimolar mixture of anhydrous $FeCl_2$ and ligand **1** was stirred at 40 °C in dry CH_3CN for 1 h, cooled to 23 °C, and treated with 0.5 equiv of I_2. Removal of solvent in vacuo and addition of dry CH_2Cl_2 gave a dark brown solution of the catalytic complex, presumed to be **1**·$FeCl_2I$. The reaction of dienophile **4** and cyclopentadiene (3 equiv) in CH_2Cl_2 at −50 °C for 15 h using 10 mol % of catalyst proceeded with 90:10 enantioselectivity to give the endo adduct **5** (endo:exo ratio 97:3) in 85% isolated yield. The major product was shown to be the 2*R* enantiomer by measurement of rotation, $[\alpha]^{23}_D$ +126.7° (c = 1, $CHCl_3$), and comparison with an authentic sample.[2c,9] The 2*R*:2*S* ratio for the endo product was determined either directly or after conversion via the acid to iodo lactone by HPLC analysis of the enantiomeric mixture with a Daicel OD column using 5% *i*-PrOH in hexane, which cleanly separates the enantiomers.[10] The reaction of **4** with cyclopentadiene with the same catalyst, **1**·$FeCl_2I$, in 3:1 CH_2Cl_2–2-nitropropane at −50 °C also afforded **5** as major product with 93:7 enantioselectivity and 99:1 endo/exo selectivity. Similar results were obtained by using as catalyst **1**·$FeBr_3$ or **1**·FeI_3.[11] It was also found that the formation of adduct **5** from cyclopentadiene, **4**, and catalyst **1**·FeI_3 was accelerated by the inclusion of 1 equiv of I_2 in the reaction mixture; only 2 h sufficed for complete reaction at −50 °C to form **5** with 91:9 enantioselectivity and 96:4 endo/exo selectivity. Catalysis of the Diels–

---

(1) See: (a) *Nachr. Chem., Tech. Lab.* **1987**, *35*, 836–840. (b) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 876–889. (c) Helmchen, G.; Karge, R.; Weetman, J. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Springer Verlag: Berlin, 1986; Vol. 4, pp 261–306.

(2) (a) Iwasawa, N.; Sugimori, J.; Kawase, Y.; Narasaka, K. *Chem. Lett.* **1989**, 1947–1950 and references cited. (b) Corey, E. J. *Pure Appl. Chem.* **1990**, *62*, 1209–1216. (c) Corey, E. J.; Imwinkelried, R.; Pikul, S.; Xiang, Y. B. *J. Am. Chem. Soc.* **1989**, *111*, 5493–5494. (d) Furuta, K.; Shimizu, S.; Miwa, Y.; Yamamoto, H. *J. Org. Chem.* **1989**, *54*, 1481–1483.

(3) Corey, E. J.; Jardine, P. D.-S.; Virgil, S.; Yuen, P.-W.; Connell, R. D. *J. Am. Chem. Soc.* **1989**, *111*, 9243–9244.

(4) A series of 2,6-bis[2-[4(*S*)-alkyl-1,3-oxazolinyl]]pyridines has been described recently along with application to the catalytic enantioselective reduction of ketones. See: Nishiyama, H.; Sakaguchi, S.; Nakamura, T.; Horihata, M.; Kondo, M.; Itoh, K. *Organometallics* **1989**, *8*, 846–848.

(5) Our colleague Prof. David Evans has kindly informed us of independent studies in his group on the application of Cu(I) complexes of *gem*-bis(oxazolines) to the catalytic enantioselective cyclopropanation of olefins; see: Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.*, preceding paper in this issue.

(6) Unfortunately, **1** was found neither to complex with OsO_4 nor to accelerate its reaction with olefins in solution.

(7) Prepared in 87% yield by reduction of (*S*)-phenylglycine (Aldrich Co.) with $LiAlH_4$ by the method of Dickman et al.: Dickman, D. A.; Meyers, A. I.; Smith, G. A.; Gawley, R. E. *Organic Syntheses*; Wiley: New York, 1990; Collect. Vol. VII, pp 530–533.

(8) Pierce, C. C.; Eliel, E. L.; Convery, R. J. *J. Org. Chem.* **1957**, *22*, 347–348.

(9) Narasaka, K.; Inoue, M.; Okada, N. *Chem. Lett.* **1986**, 1109–1112.

(10) The Daicel OD column was obtained from Daicel, Inc., Fort Lee, NJ 07024.

(11) Catalyst **1**·FeI_3 was prepared from **1**, the appropriate amount of I_2, and either Fe or FeI_2 in CH_3CN or CH_2Cl_2.

0002-7863/91/1513-728$02.50/0

Alder reaction by I_2 is consistent with our original hypothesis that $\mathbf{1}\cdot FeX_2^+$ should be the catalytic species since I_2 is expected to favor cation generation by the process $\mathbf{1}\cdot FeI_3 + I_2 \rightarrow \mathbf{1}\cdot FeI_2^+ + I_3^-$, because of the affinity of I_2 for I^-.[12]

The chiral ligand **1** is readily and efficiently recoverable from these catalytic Diels–Alder reactions for reuse. Because of this fact, the ready availability of ligand **1**, and the low cost of iron salts, the methodology described herein promises to be practical.

The structural rigidity of the $\mathbf{1}\cdot FeX_2^+$ system permits a rational analysis of the stereochemical results described above, assuming that the C=C/C=O s-cis form of dienophile **4** chelates to $\mathbf{1}\cdot FeX_2^+$ prior to reaction with cyclopentadiene. If dienophile **4** chelates to $\mathbf{1}\cdot FeX_2^+$ via the equatorial sites e_1 and e_2 in **6**, the product of the Diels–Alder reaction clearly should be the 2*S* adduct rather than the 2*R* adduct **5** which is observed. This must not be the major binding mode for the catalytic pathway, and therefore, chelation to $\mathbf{1}\cdot FeX_2^+$ via a and e sites in **6** is indicated. Since site a_2–e_1 (or the C_2 equivalent a_1–e_2) is sterically unfavorable relative to a_1–e_1 (or its C_2 equivalent), the a_1–e_1 site should be preferred. Although there are two possible chelates of dienophile **4** at the a_1–e_1 site, the favored pathway for each chelate is that leading to 2*R*-adduct **5**, as observed experimentally.

The conclusion that the chelation of dienophile **4** with $\mathbf{1}\cdot FeX_2^+$ occurs at an a–e site rather than at the e–e site raises the question of why coordination of **4** at the e–e site is kinetically less favorable. One interesting possibility emerges from the likelihood that complex $\mathbf{1}\cdot FeX_2^+$ possesses square-planar geometry and that chelation of dienophile **4** takes place by the sequence (1) coordination of one of the carbonyl oxygens of **4** to an axial site and (2) chelate ring closure with e → a transposition of X. This pathway clearly would lead to predominant formation of the a–e chelate of **4**, as required for the above described mechanistic model.

Further study is planned to optimize this new enantioselective Diels–Alder addition, to determine its scope, and to gain deeper insights as to mechanism.[13,14]

---

(12) For examples of cationic complexes of aluminum with 3-acryloyl-1,3-oxazolidines as reactive species in Diels–Alder reactions, see: Evans, D. A.; Chapman, K. T.; Bisaha, J. *J. Am. Chem. Soc.* **1988**, *110*, 1238–1256.

(13) The following procedure illustrates the catalytic Diels–Alder reaction with $\mathbf{1}\cdot FeI_3$ and I_2 to form adduct **5**. To a mixture of 15.2 mg (0.272 mmol, 0.10 equiv) of powdered iron and 104 mg (0.408 mmol, 0.15 equiv) of iodine was added 2 mL of anhydrous CH_3CN. After stirring for 1 h at 40 °C, a solution of 109 mg (0.326 mmol, 0.12 equiv) of the bis(oxazoline) **1** in 2 mL of anhydrous CH_3CN was added dropwise at 23 °C to the black solution. The solution was stirred for 1 h at 40 °C and evaporated to afford a dark viscous oil, which was dissolved in 7 mL of anhydrous CH_2Cl_2 and treated at −78 °C with 69.1 mg (0.272 mmol, 0.10 equiv) of iodine, 385 mg (2.73 mmol, 1 equiv) of 3-acryloyl-1,3-oxazolin-2-one (**4**),[9] and 0.68 mL (8.19 mmol, 3 equiv) of precooled cyclopentadiene. After stirring for 2 h at −50 °C, the dark brown solution was quenched with 0.1 mL of Et_3N, diluted with ether–pentane, and washed first with aqueous sodium sulfite and then with aqueous cupric acetate. The organic layer was dried and concentrated in vacuo, and the crude product was chromatographed on silica gel with a 1:1 mixture of ethyl acetate and hexane to afford 539 mg (95% yield, endo:exo = 96:4, 82.2% ee) of 1*R*,2*R*,4*R*-adduct **5**.[2c,9] The ee was determined by HPLC analysis using a Daicel OD column with 10% *i*-PrOH in hexane for elution (1 mL/min; retention times 23.5 min for **5** and 21.4 min for the enantiomer of **5**). Treatment of the aqueous $Cu(OAc)_2$ extract described above with NH_4OH and extraction with 4:1 ether–CH_2Cl_2 afforded ligand **1** (>85%) for reuse.

(14) This work was assisted financially by grants from the National Science Foundation and the National Institutes of Health.

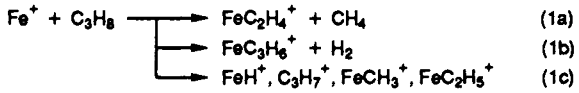
Threshold Collisional Activation of $Fe^+\cdot C_3H_8$: Probing the Potential Energy Surface

Richard H. Schultz and P. B. Armentrout*,†

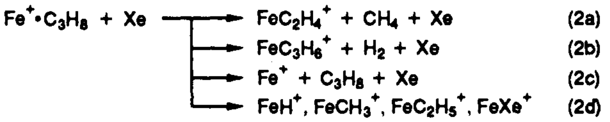
Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

Received August 10, 1990
Revised Manuscript Received October 17, 1990

The bimolecular reaction of Fe^+ with propane has been the subject of considerable research during the past decade, spanning a wide variety of gas-phase experimental techniques.[1,2] Two exothermic processes are observed, reactions 1a and 1b, and several endothermic processes, reactions 1c. Since reactions 1a and 1b



are barrierless, elucidating details of the potential energy surface (PES) of reaction 1 is difficult. Here, we describe a novel experiment that allows us to probe such details by entering the PES at a different place, namely, the bottom of the well associated with the assumed initial intermediate for reaction 1, the ion induced dipole bound complex, $Fe^+\cdot C_3H_8$.[2] We then collisionally activate this species to induce reactions 2a–d.



The guided-ion beam mass spectrometer on which these experiments were performed has been described previously.[3–5] Parent ions are formed in a meter-long flow tube[5] by termolecular collisions between Fe^+ (created in a DC discharge[6]), propane, and the He carrier gas. The complexes then undergo ~10^5 thermalizing collisions. The ions are mass and energy selected and then interact with Xe under single-collision conditions inside an octopole ion trap.[3,4] Reactant and product ions are mass analyzed and detected and their intensities converted to cross sections.[3]

Results of this threshold collisional activation (TCA) experiment are shown in Figure 1. The lowest energy processes are reactions 2a and 2b, while the major process is reaction 2c. The products of reaction 2d are also observed, which except for $C_3H_7^+$ and $FeXe^+$ are the same as those of reaction 1c. This correspondence indicates that reaction 2 is occurring on the same global PES as the bimolecular system. The dominance of reaction 2c suggests a $Fe^+\cdot C_3H_8$ structure for the parent ion since simple cleavage processes should be the main dissociation pathways at high collision energies. This conclusion is supported by recent work on TCA of $Fe^+\cdot C_2H_6$[7] that indicates that insertive structures have very different fragmentation patterns than simple adducts.

Quantitative information regarding reaction 2 can be obtained by measuring the product thresholds.[8] This analysis yields a threshold for process 2c of 0.82 ± 0.07 eV (19 ± 2 kcal/mol). Given the $Fe^+\cdot C_3H_8$ structure for the parent ion, this energy corresponds to the depth of the ion induced dipole well. This value can be verified by measuring the threshold for $FeCH_3^+$ formation, 2.17 ± 0.09 eV (50 ± 2 kcal/mol). Combined with $D^\circ[Fe^+(^6D){-}CH_3] = 58 \pm 2$ kcal/mol[2] and $D^\circ(CH_3{-}C_2H_5) = 88$ kcal/mol,[10] this threshold implies $D^\circ[Fe^+(^6D){-}C_3H_8] = 20 \pm 3$ kcal/mol, consistent with the directly measured value. Ad-

---

† Camille and Henry Dreyfus Teacher-Scholar, 1987–1992.

(1) (a) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6501. (b) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963. (c) Byrd, G. D.; Burnier, R. C.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 3365. (d) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 5197. (e) Houriet, R.; Halle, L. F.; Beauchamp, J. L. *Organometallics* **1983**, *2*, 1818. (f) Larsen, B. S.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 1912. (g) Tonkyn, R.; Ronan, M.; Weisshaar, J. C. *J. Phys. Chem.* **1988**, *92*, 92. (h) Hanton, S. D.; Noll, R. J.; Weisshaar, J. C. *J. Phys. Chem.* **1990**, *94*, 5655.

(2) Schultz, R. H.; Armentrout, P. B. *J. Phys. Chem.* **1987**, *91*, 4433. Schultz, R. H.; Elkind, J. L.; Armentrout, P. B. *J. Am. Chem. Soc.* **1988**, *110*, 411.

(3) Ervin, K. M.; Armentrout, P. B. *J. Chem. Phys.* **1985**, *83*, 166.

(4) Sunderlin, L. S.; Armentrout, P. B. *Chem. Phys. Lett.* **1990**, *167*, 188.

(5) Schultz, R. H.; Armentrout, P. B. *Int. J. Mass Spectrom. Ion Processes*, accepted for publication.

(6) Schultz, R. H.; Lian, L.; Elkind, J. L.; Armentrout, P. B., manuscript in preparation.

(7) Schultz, R. H.; Armentrout, P. B., work in progress.

(8) Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.* **1986**, *108*, 1806; *J. Phys. Chem.* **1987**, *91*, 6178.

(9) Schultz, R. H.; Haynes, C.; Fisher, E. R.; Armentrout, P. B., work in progress.