# Diels−Alder Reactions of Oxazolidinone Dienophiles Catalyzed by Zirconocene Bis(triflate) Catalysts: Mechanism for Asymmetric Induction

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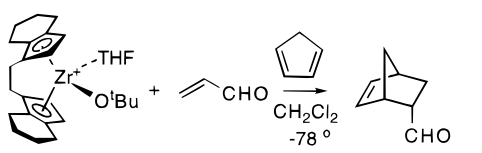
The Diels−Alder cycloaddition reaction between enoyl−oxazolidinones **3** and dienes is efficiently catalyzed by zirconocene bis(triflate) catalysts (**4** and **8**) in $CH_2Cl_2$ or nitroalkane solvents. The use of chiral catalyst [*S*]-**8** led to significant asymmetric induction in the adducts derived from dienophiles **3** and cyclopentadiene, but only in nitroalkane solution at low temperatures and at lower catalyst loadings. The binding of acryloyloxazolidinone **3a** to **8** was studied in detail by $^1$H, $^{13}$C, and $^{19}$F NMR spectroscopy in both $CD_2Cl_2$ and nitroalkane solvent. These studies reveal that two isomeric, five-coordinate, monotriflate complexes (**9a** and **9b**) are formed from **3a** and **8** in both solvents. The minor isomer (**9a**) has the carbamate C=O coordinated to the metal at a central site, while in the major isomer (**9b**) it is coordinated to a lateral site. In nitromethane solvent, the ratio of **9a**:**9b** ≈ 1:2.6 at −30 °C, while in $CD_2Cl_2$ the ratio is ∼1:6.7. These studies, along with the sense of asymmetric induction observed, suggest that it is the minor isomer **9a** that reacts most rapidly and selectively with dienes under catalytic conditions. The binding of **3a** to **8** is strongly favored in nitromethane solvent with $K_{eq} = 33.3 \pm 1.5$ at −30 °C. Thermodynamic parameters for substrate binding were derived from VT $^1$H NMR spectroscopic studies ($\Delta H_o = -9.8 \pm 1.0$ kcal mol$^{-1}$; $\Delta S_o = -33 \pm 3$ cal mol$^{-1}$ K$^{-1}$). Complexes **9a** and **9b** interconvert predominantly by an intramolecular process (as revealed by VT NMR studies at different concentrations of **3a** and **8** as well as 2D-EXSY spectra), while free triflate ion (formed via complexation of **3a** to **8**) undergoes rapid, associative exchange with bound triflate in residual complex **8** (as independently revealed by VT $^{19}$F NMR studies involving **8** and [$^n$Bu$_4$N][OTf]). The rates of both of these processes were studied by VT $^{19}$F NMR spectroscopy. The activation parameters for triflate exchange involving **8** are $\Delta H^{\ddagger} = 2.9 \pm 0.3$ kcal mol$^{-1}$ and $\Delta S^{\ddagger} = -26 \pm 3$ cal mol$^{-1}$ K$^{-1}$ while the barrier to interconversion between **9a** and **9b** is 13.8 ± 0.7 kcal mol$^{-1}$ at −30 °C with $\Delta H^{\ddagger} = 17.2 \pm 0.9$ kcal mol$^{-1}$ and $\Delta S^{\ddagger} = 13.9 \pm 0.7$ cal mol$^{-1}$ K$^{-1}$. Diels−Alder reactions of **3a** with, e.g., cyclopentadiene in nitroalkane or dichloromethane solvent are very rapid, even at low catalyst loadings and low temperatures, and rates of reaction cannot be conveniently monitored by $^1$H NMR spectroscopy. However, the enantioselectivity was shown to vary with conversion, indicating that non-Curtin−Hammett conditions apply.

## Introduction

Asymmetric catalysis of the Diels−Alder reaction using chiral Lewis acids is an area of intensive research.[1] Numerous examples of effective catalysts, both structurally well-defined and of uncertain structure, have been developed. Several years ago, we elected to study asymmetric catalysis using structurally well-defined metallocene complexes.[2] Our earlier work focused on the synthesis and utility of cationic alkoxide complexes of zirconium; despite the efficacy of these complexes as catalysts for a variety of C−C bond-forming reactions, the extent of asymmetric induction using chiral analogues (e.g. **1**, eq 1) was disappointingly low.[2b]




**1**

93 % yield
endo:exo 4.8:1
2S;2R-endo ~ 3:1

(1)

In the case of the Diels−Alder reaction catalyzed by zirconocene **1**, the modest enantioselectivities observed in the case of simple dienophiles might be attributed to both ineffective shielding of the C=C bond of the coordinated dienophile (in its most stable s-trans con-

(1) For a review, see: Pindur, U.; Lutz, G.; Otto, C. *Chem. Rev. (Washington, D.C.)* **1993**, *93*, 741.

(2) (a) Hong, Y.; Norris, D. J.; Collins, S. *J. Org. Chem.* **1993**, *58*, 3591. (b) Hong, Y.; Kuntz, B. A.; Taylor, N. J.; Collins, S. *Organometallics* **1993**, *12*, 964. (c) Collins, S.; Koene, B. E.; Ramamchandran, R.; Taylor, N. J. *Organometallics* **1991**, *10*, 2092.

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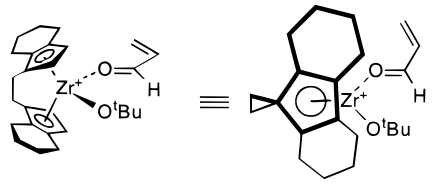
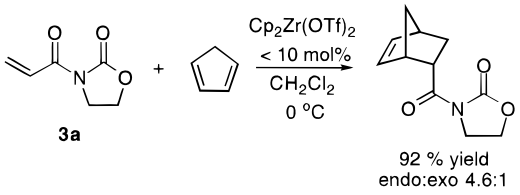
formation) coupled with the conformational mobility of this ligand about the Zr−O bond. It had occurred to us, based on this analysis, that if one could reduce the internal degrees of freedom available to the coordinated dienophile while at the same time enforcing s-cis geometry, the level of selectivity should increase; the conformer shown in eq 2, in particular, should react with cyclopentadiene to provide the 2R enantiomer more selectively.




(2)

The use of dienophiles which might chelate to the metal center, adopting an s-cis conformation, should address this issue, and from a practical perspective, the choice of enoyl−oxazolidinones seemed obvious.[3] Preliminary experiments using either catalyst **1** or [$Cp_2$-Zr(O$^t$Bu)THF][$BPh_4$] (**2**, 10 mol %) and acryloyloxazolidinone **3a** quickly revealed that these complexes did not sufficiently activate this substrate toward cycloaddition reactions with, e.g., cyclopentadiene (ca. 20% conversion after several hours at 25 °C). This may be due to the fact that complex **1** (or **2**) possesses 18 $e^-$ because of strong $\pi$-donation from the alkoxide ligand;[2a] bidentate coordination of **3a** may not be favorable under these circumstances.

Bosnich and co-workers had reported that Diels−Alder reactions could also be catalyzed by metallocene bis(triflate) complexes.[4] These are related to the cationic alkoxide complexes in that one (or more) of the triflate ligands is labile, particularly in polar solvents. Loss of one triflate ligand generates a species that is analogous to a cationic alkoxide complex with one important difference, the remaining triflate ligand will be an ineffective $\pi$-donor. Indeed, $Cp_2Zr(OTf)_2$ (**4**) was an effective catalyst for the Diels−Alder reaction of **3a** with cyclopentadiene (eq 3).




(3)

Herein, we report full synthetic and mechanistic details of the Diels−Alder reactions of enoyl−oxazolidinones catalyzed by zirconocene bis(triflate) catalysts.[5]

**Table 1. Diels−Alder Reactions between Dienophiles 3 and Cyclopentadiene Catalyzed by $Cp_2Zr(OTf)_2$[a]**

| entry | dienophile | solvent | *t* (h) | *endo*:*exo* |
|---|---|---|---|---|
| 1 | **3a** | $CH_2Cl_2$ | 1 | 4.6:1 |
| 2 | **3b** | $CH_2Cl_2$ | 2 | 4.5:1 |
| 3 | **3c** | $CH_2Cl_2$ | 5 | 1.3:1 |
| 4 | **3a** | 2-$NO_2$Pr | 0.5 | 5.0:1 |
| 5 | **3b** | 2-$NO_2$Pr | 1 | 5.4:1 |
| 6 | **3c** | 2-$NO_2$Pr | 4 | 1:1.1 |

[a] Conditions: 5 mol % $Cp_2Zr(OTf)_2$, $[\mathbf{3}]_o$ = 0.22 M, 2.2 equiv of cyclopentadiene, 0 °C. Reactions were quantitative with respect to conversion. Isolated yields of **5** were in excess of 90% following chromatography.

The use of chiral catalysts leads to efficient asymmetric induction in the products, particularly in polar solvents, and possible reasons for this behavior have been studied in some detail.[6]

## Results and Discussion

As indicated in eq 3, zirconocene bis(triflate) complexes were effective catalysts for Diels−Alder reactions of enoyl−oxazolidinones. Some of the results obtained are summarized in Table 1. Either **3a** or the crotonyl analogue **3b** reacted readily with cyclopentadiene in the presence of **4** (5 mol %) to provide excellent yields of the corresponding adducts *endo*-**5** and *exo*-**5** with enhanced *endo* selectivity. Although not synthetically interesting, even the normally unreactive methacryloyl substrate **3c** provided a mixture of *endo* and *exo* adducts in good yield under the conditions studied.

In general, these cycloaddition reactions proceeded more readily in polar solvents such as nitromethane or 2-nitropropane compared with dichloromethane. As can be appreciated from the results summarized in Table 1, the *endo*:*exo* selectivity is somewhat higher in nitroalkane than $CH_2Cl_2$ solution in reactions involving **3a** or **3b**.

In an attempt to study this issue from a fundamental perspective and also to gain support for bidentate activation of the dienophile with this system, we examined the binding of **3a** to **4** in $CD_3NO_2$ by $^1H$, $^{13}C$, and $^{19}F$ NMR spectroscopy. At a 1:1 stoichiometry in $CD_3$-$NO_2$, the binding of **3a** to **4** is nearly complete at −30 °C, and selected spectroscopic data for **3a**, **4**, and the complexes formed (**6a**, **6b**) are summarized in Table 2.

As shown in Figure 1a, the chemical shifts of the protons on, e.g., the double bond of the oxazolidinone (see Table 2 for free oxazolidinone) change dramatically on coordination to the metal center. Furthermore, as can be appreciated from Figure 1a, two doublets ($J$ = 16.3 Hz) in a ratio of 1.5:1 are present that can be assigned to $H_a$ (Table 2); this indicates that two different complexes are present. The $^{13}C$ NMR spectrum (Table 2, Figure 1b) provides convincing evidence for the formation of two complexes and also that both C=O groups of the oxazolidinone ligand are bound to the metal in both of these complexes as these signals are shifted downfield from those of **3a** (Table 2). Also the

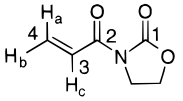
(3) For similar approaches employing other chiral catalysts and oxazolidinone-based dienophiles, see, inter alia: (a) Evans, D. A.; Miller, S. J.; Lectka, T. *J. Am. Chem. Soc.* **1993**, *115*, 6460. (b) Corey, E. J.; Imai, N.; Zhang, H.-Y. *J. Am. Chem. Soc.* **1991**, *113*, 728. (c) Narasaka, K.; Iwasawa, N.; Inoue, M.; Yamada, T.; Nakashima, M.; Sugimori, J. *J. Am. Chem. Soc.* **1989**, *111*, 5340 and references therein. For earlier work employing chiral oxazolidinone-based dienophiles and achiral alkylaluminum catalysts, see: (d) Evans, D. A.; Chapman, K. T.; Bisaha, J. *J. Am. Chem. Soc.* **1988**, *110*, 1238.

(4) (a) Odenkirk, W.; Bosnich, B. *J. Chem. Soc., Chem. Commun.* **1995**, 1181. (b) Hollis, T. K.; Robinson, N. P.; Bosnich, B.*Organometallics* **1992**, *11*, 2745. (c) Hollis, T. K.; Robinson, N. P.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 5464.

(5) Although we have completed analogous studies using titanocene bis(triflate) catalysts, these are less well understood from a mechanistic perspective than the zirconium systems discussed here, see: J. Guan, J. M.S. Thesis, University of Waterloo, 1994.

(6) Preliminary communication: Jaquith, J. B.; Guan, J.; Wang, S.; Collins, S.*Organometallics* **1995**, *14*, 1079.

**Table 2. NMR Spectroscopic Data for Compounds 3a, 4, 6a, and 6b in $CD_3NO_2$ at −30 °C[a]**




| compound | $^1$H (ppm) | $^{13}$C (ppm) | $^{19}$F (ppm) |
|---|---|---|---|
| **3a** | 7.42 (dd, $J$ = 10, 16 Hz, $H_c$), 6.43 (dd, $J$ = 16, 1.5 Hz, $H_a$), 5.90 (dd, $J$ = 10, 1.5 Hz, $H_b$), 4.45 (t, $CH_2O$), 4.02 (t, $CH_2N$) | 166.3 (C2), 155.3 (C1), 131.4 (C4), 128.3 (C3), 64.1 ($CH_2O$), 44.2 ($CH_2N$) | |
| **4** | 6.82 (sCpH) | | −77.5 |
| **6a** (major) | 7.10 (br d, $J$ = 16 Hz, $H_a$), 6.78 (dd, $J$ = 16, 10 Hz, $H_c$), 6.5−6.7 (s at 6.60 superimposed on m, CpH + $H_b$), 5.0 (t, $CH_2O$), 4.7 (t, $CH_2N$) | 169.5 (C2), 159.4 (C1), 141.8 (C4), 123.6 (C3), 119.2 (q, $J_{CF}$ = 319 Hz), 117.8 (q, $J_{CF}$ = 316 Hz),[b] 116.1 (Cp), 66.7 ($CH_2O$), 43.2 ($CH_2N$) | −77.9 |
| **6b** (minor) | 7.33 (br d, $J$ = 16 Hz, $H_a$), 6.75 (dd, $J$ = 16, 10 Hz, $H_c$), 6.5−6.7 (s at 6.60 superimposed on m, CpH + $H_b$), 5.0 (t, $CH_2O$), 4.7 (t, $CH_2N$) | 172.1 (C2), 157.0 (C1), 143.1 (C4), 123.6 (C3), 119.2 (q, $J_{CF}$ = 325 Hz), 117.8 (q, $J_{CF}$ = 312 Hz),[b] 116.3 (Cp−C), 66.6 ($CH_2O$), 43.4 ($CH_2N$) | −77.9 |

[a] Data were obtained at 500 or 200 MHz for $^1$H, 125 or 50 MHz for $^{13}$C, and 188 MHz for $^{19}$F. Chemical shifts reported with coupling constants and assignments in parentheses where applicable. [b] This is the chemical shift corresponding to free triflate ion in this solvent.



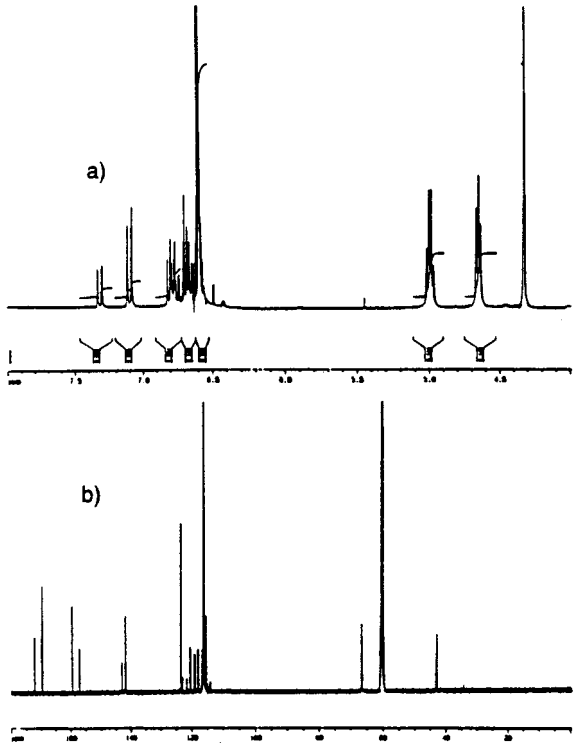
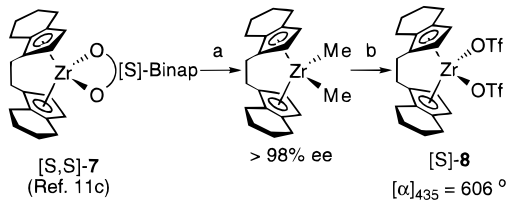



**Figure 1.** (a) $^1$H NMR spectrum of complexes **6a** and **6b** (500 MHz, $CD_3NO_2$, −30 °C). (b) $^{13}$C NMR spectrum of complexes **6a** and **6b** (125 MHz, $CD_3NO_2$, −30 °C).

$\beta$-carbon atom of the double bond is strongly deshielded relative to that of the free ligand in both complexes. Finally, two quartets are observed for the $CF_3$ carbon, and one of these is at the chemical shift of free triflate ion in this solvent. The $^1$H and $^{13}$C NMR spectral changes that occur on coordination of **3a** to Zr are similar to those reported for binding of this same substrate to Al (2 equiv of $AlEt_2Cl$, $CH_2Cl_2$) and are consistent with bidentate coordination to the metal and adoption of the s-cis geometry.[7] The $^{19}$F NMR spectrum of the mixture was less informative; at a 1:1 stoichiometry, a single, broad resonance was observed at − 77.9 ppm.[8] On the basis of all the spectral data, it is not possible to unambiguously determine what the structure of these two complexes are but, by analogy to a more detailed study employing metallocene catalyst **8** and **3a** (vide infra), we suspect that **6a** and **6b** are both five-coordinate, oxazolidinone monotriflate complexes.[9]

**Synthesis of Chiral Zirconocene Bis(triflate) Complex 8.** On the basis of these studies, which were consistent with bidendate coordination of **3a** to Zr, the synthesis of chiral versions of these catalysts was pursued. Of the various approaches to the synthesis of chiral metallocene complexes,[10] the original system developed by Brintzinger seemed most appropriate as the zirconocene dichloride complex can be prepared in large quantities, the synthetic route is short and uncomplicated by diastereomer separation, and the resolution is reasonably efficient.[11]

In practice, chiral zirconocene bis(triflate) [*S*]-**8** was prepared as shown in eq 4; optically pure [*S*,*S*]-**7**, prepared by the method of Buchwald and co-workers, was converted to the corresponding dimethyl derivative.[11c] The optical purity of this material could be




(4)

determined by reaction of 2 equiv of [*R*]-O-acetylman-

(7) (a) Castellano, S.; Dwight, W. J. *J. Am. Chem. Soc.* **1993**, *115*, 2986.

(8) At a 10:1 ratio of **3a**:**4**, two signals were present at −77.9 and −78.2 ppm in a 1:1.3 ratio, while at a 1:2 ratio of **3a**:**4**, two signals were present at −77.5 and −77.9 ppm in a 1:1.1 ratio. The signal at −77.5 corresponds to **4** in nitromethane at this temperature, while the signal at −78.2 is close to that of free triflate ion. Due to the limited temperature range available in this solvent, we were unable to characterize these complexes to the same extent as for those formed from **3a** and [*S*]-**8** (vide infra).

(9) For a discussion of bonding in five-coordinate, bent metallocene complexes, see: Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

(10) For a review, see: Halterman, R. L. *Chem. Rev. (Washington, D.C.)* **1992**, *92*, 965.

(11) (a) Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1982**, *232*, 233. (b) Collins, S.; Kuntz, B. A.; Hong, Y. *J. Org. Chem.* **1989**, *54*, 4154. (c) Grossman, R. B.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1991**, *113*, 2321.

**Table 3. Asymmetric Diels−Alder Reactions of 3a with Cyclopentadiene Catalyzed by [*S*]-8[a]**

| entry | dienophile | [*S*]-**8** (mol %) | solvent | *T* (°C) | *t* (h) | yield[b] (%) | *endo*:*exo*[c] | % ee[d] |
|---|---|---|---|---|---|---|---|---|
| 1 | **3a** | 1 | $CH_2Cl_2$ | −30 | 1 | 75 | 2.8:1 | 18[e] |
| 2 | **3a** | 10 | $CH_2Cl_2$ | −30 | 1 | 70 | 2.8:1 | 20 |
| 3 | **3a** | 1 | $CH_3NO_2$ | −30 | 1 | 94 | 5.4:1 | 69 |
| 4 | **3a** | 5 | $CH_3NO_2$ | −30 | 1 | 87 | 4.3:1 | 66 |
| 5 | **3a** | 10 | $CH_3NO_2$ | −30 | 1 | 85 | 4.2:1 | 58 |
| 6 | **3a** | 1 | $CH_2Cl_2$ | −78 | 1 | 88 | 5.3:1 | 30 |
| 7 | **3a** | 5 | $CH_2Cl_2$ | −78 | 1 | 91 | 5.3:1 | 34 |
| 8 | **3a** | 10 | $CH_2Cl_2$ | −78 | 1 | 89 | 5.5:1 | 23 |
| 9 | **3a** | 1 | 2-$NO_2$Pr | −78 | 1 | 83 | 11.5:1 | 91 |
| 10 | **3a** | 10 | 2-$NO_2$Pr | −78 | 1 | 98 | 10.3:1 | 88 |
| 11 | **3b** | 5 | $CH_2Cl_2$ | −30 | 24 | 37 | 3.4:1 | 70[e] |
| 12 | **3b** | 5 | $CH_3NO_2$ | −30 | 5 | 80 | 5.2:1 | 89 |
| 13 | **3b** | 5 | 2-$NO_2$Pr | −30 | 2 | 87 | 5.0:1 | 90 |
| 14 | **3c** | 5 | $CH_2Cl_2$ | −30 | 24 | 12 | 1.3:1 | 70[f] |
| 15 | **3c** | 5 | $CH_3NO_2$ | −30 | 48 | 88 | 1.1:1 | 78 |

[a] Conditions: $[\mathbf{3}]_o = 0.2$ M, 2.2 equiv of cyclopentadiene. [b] Isolated yields of pure material. [c] Determined from the $^1$H NMR spectra of the crude product. [d] Determined by HPLC analysis following purification by flash chromatography on silica gel. [e] The % ee is reported for the [2*R*]-*endo* stereoisomer. [f] The % ee is reported for the *exo* stereoisomer, configuration not determined.



delic acid in benzene-$d_6$.[12] By comparison to the spectrum of bis(mandelate) complexes derived from racemic material, the optical purity of this compound was determined to be better than 98% ee. Reaction of the dimethyl complex with 2 equiv of triflic acid in ether at low temperatures afforded optically pure, bis(triflate) complex **8** in 60−70% overall yield from **7**, following recrystallization from toluene. To show that protonolysis of the dimethyl complex does not induce racemization, the bis(triflate) complex was transformed to the dimethyl complex on treatment with MeLi in ether; $^1$H NMR spectra of the bis(acetylmandelate) derivative prepared from this material were identical to that obtained initially.

**Diels−Alder Reactions Catalyzed by Zirconocene Bis(triflate) Complex [*S*]-8.** A series of cycloaddition reactions between cyclopentadiene and oxazolidinones **3a**−**c** in the presence of various amounts of [*S*]-**8** were studied, and the results are summarized in Table 3. As shown in Table 3, our initial experiments using [*S*]-**8** involved the use of $CH_2Cl_2$ as the solvent, and although the *endo*:*exo* selectivity was good in most cases, the level of asymmetric induction was disappointingly low. However, by use of nitromethane as the solvent, a dramatic increase in enantioselectivity was observed. Interestingly, the diastereo- and enantioselectivity were dependent on catalyst concentration in nitroalkane solvent; both diastereo- and enantioselectivity tended to improve at *lower* catalyst loadings with this Zr-based catalyst.[13] Finally, by use of 2-nitropropane as the solvent at low temperatures, synthetically useful (i.e., >90% ee for **3a** and **3b**) levels of enantioselectivity were observed.

In both solvents, the sense of asymmetric induction was the same; the [2*R*]-*endo* enantiomer predominated in reactions of cyclopentadiene with either **3a** or **3b**. While this result is consistent with our initial analysis (eq 2), the observation that **3a** binds to **4** to form to isomeric complexes suggested more complex behavior; in particular, the pronounced solvent dependence was unexpected and not readily explained.

**Binding of 3a to Bis(triflate) Complex 8.** Analogous studies to those described earlier were performed using **3a** and (±)-**8** in both $CD_3NO_2$ and $CD_2Cl_2$ solvents at various temperatures. In $CD_3NO_2$ solvent at −30 °C, binding of **3a** to **8** is favorable ($K_{eq} = 33$) and two isomeric complexes **9a**,**b** are formed.[14] The temperature dependence for binding of **3a** to **8** was determined from $^1$H NMR spectra of a 4:3 mixture of the two, and the following thermodynamic parameters were obtained − $\Delta H_o = -9.8 \pm 1.0$ kcal mol$^{-1}$; $\Delta S_o = -33 \pm 3$ cal mol$^{-1}$ K$^{-1}$. The large, negative value of $\Delta S_o$ is consistent with complex formation involving a chelate structure; at room temperature, binding of **3a** to **8** is almost thermoneutral ($\Delta G_o \approx 0$).

Selected $^1$H and $^{13}$C NMR chemical shifts and assignments for the two complexes are summarized in Table 4. Some of the $^1$H assignments were confirmed by a 500 MHz $^1$H NMR TOCSY experiment; a portion of this spectrum is shown in Figure 2. As can seen from this figure, the doublet at $\delta$ 7.56 ($J = 17$ Hz, $H_a'$, Scheme 1) is correlated to a doublet of doublets at 6.77 ($H_c'$) and a doublet at 6.68 ($J = 11$ Hz, $H_b'$) in the major isomer; the corresponding signals in the minor isomer are found at 7.17, 6.92, and 6.82 ppm, respectively. Examination of the signals in the region $\delta$ 5.5−6.7 ppm was particularly instructive. In the major isomer, the doublet at $\delta$ 6.42 correlated with a doublet at 5.73 ($J = 2.7$ Hz) as did a doublet at 6.08 with that at 5.80. Evidently, these two pairs of signals are due to α and $\beta$ CpH protons on the two *different* Cp rings of this complex. The signals due to the minor isomer could be similarly assigned; the small doublet at 6.52 was correlated with that visible at 5.82 ppm, while the highly distorted, AB multiplet at 5.91 (integrating to 2 protons) represents the α and $\beta$ CpH protons of the other ring.[15]

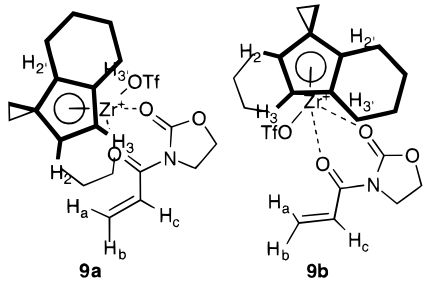
On the basis of these assignments, it proved possible to definitively determine the solution structures of the two isomeric complexes present. $^1$H-NOE difference

(12) Schafer, A.; Eberhard, K.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1987**, *328*, 87.

(13) Possible explanations could include competitive catalysis by dimeric species (i.e., $Zr_2$·**3**) at higher concentrations (although such species were not evident from the spectroscopic work, vide infra) or differences in the steady-state ratios of two isomeric monotriflate complexes (vide infra). It is interesting to note that the titanium analogue of [*S*]-**8** shows opposite behavior.[5]

(14) Identical behavior was exhibited by **3a** and optically pure [*S*]-**8**. Also, the ratio of **9a** to **9b** was invariant to changes in the concentration of either **3a** or **8** (and their ratio, vide infra), indicating that the formation of bimetallic complexes under these conditions is not significant.

**Table 4. Selected NMR Spectroscopic Data for Complexes 8, 9a, and 9b[a]**




| complex | $^1$H NMR | $^{13}$C NMR | $^{19}$F NMR |
|---|---|---|---|
| **8** | 6.82 (d, $J$ = 2.3 Hz, $H_3$), 6.09 (d, $J$ = 2.3 Hz, $H_2$) | 140.8 (4 °C), 139.5 (4 °C), 130.9, 120.1, 114.2 (br, 4 °C) | −76.8 (bound OTf) |
| **9a** | 7.17 (d, $J$ = 16.4 Hz, $H_a$), 6.92 (dd, $J$ = 16.4, 10.4 Hz, $H_c$), 6.82 (d, $J$ = 10.4 Hz, $H_b$), 6.52 (d, $J$ = 2.7 Hz, $H_3'$), 5.91 (AB m, 2H, $H_2$ + $H_3$), 5.82 (d, $J$ = 2.7 Hz, $H_2'$) | 173.5 (amide C═O), 161.4 (carbamate C═O), 144.8 ($\beta$-$CH_2$═), 129.3 (α-CH═), 69.2 ($CH_2O$), 45.7 ($CH_2N$) | −76.95 (bound OTf) −78.2 (free OTf) |
| **9b** | 7.56 (d, $J$ = 16.2 Hz, $H_a$), 6.77 (dd, $J$ = 16.2, 10.6 Hz, $H_c$),6.68 (d, $J$ = 10.6 Hz, $H_b$), 6.46 (d, $J$ = 2.7 Hz, $H_3'$ or $H_3$), 6.08 (d, $J$ = 2.7 Hz, $H_3$ or $H_3'$), 5.80 (d, $J$ = 2.7 Hz, $H_2$ or $H_2'$), 5.73 (d, $J$ = 2.7 Hz, $H_2'$ or $H_2$) | 174.2 (amide C═O), 160.5 (carbamate C═O), 146.0 ($\beta$-$CH_2$═), 126.1 (α-CH═), 69.5 ($CH_2O$), 45.9 ($CH_2N$) | −77.23 (bound OTf) −78.0 (free OTf) |

[a] Spectra were obtained in $CD_3NO_2$ solvent at −30 °C and at 500 MHz ($^1$H), 125 MHz, ($^{13}$C), and 188 MHz ($^{19}$F). Assignments of the Cp protons of **9b** are tentative; TOCSY spectra reveal that the signal at 6.46 is correlated with that at 5.73 and that at 6.08 with that at 5.80.



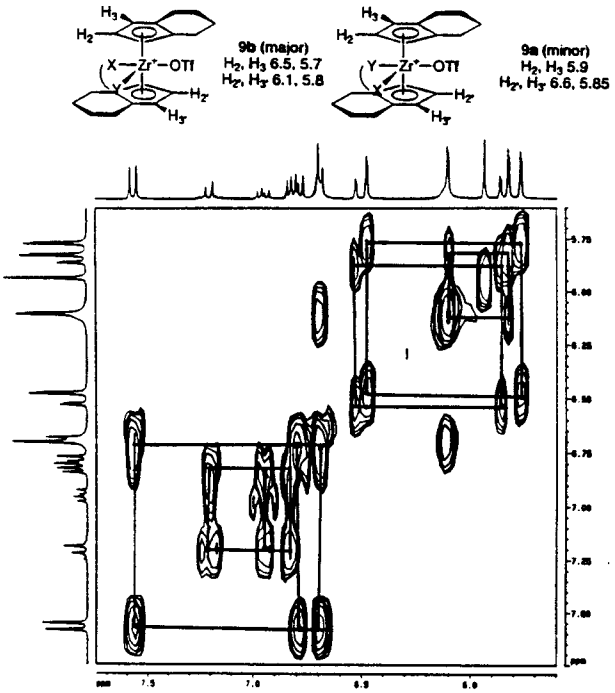
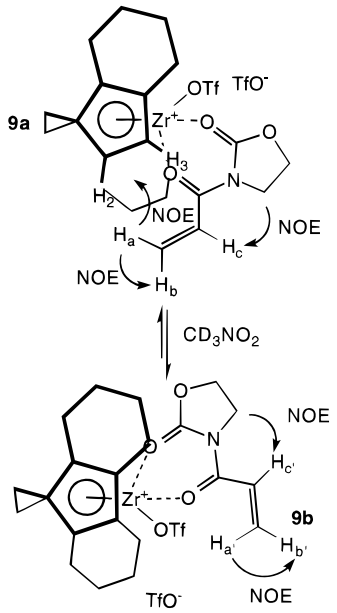



**Figure 2.** Partial TOCSY $^1$H NMR spectrum of complexes **9a** and **9b** (500 MHz, $CD_3NO_2$, −30 °C).

**Scheme 1**




spectra in $CD_3NO_2$:$CD_2Cl_2$ mixtures (ca. 5:1) at −60 °C[16] revealed that irradiation of the proton signals due to the N−$CH_2$ group in both complexes resulted in a small *negative* enhancement of the two vinylic ═CH protons in both complexes (see Supporting Information).[17] This demonstrates that in both complexes, the coordinated dienophile adopts the s-cis geometry. Irradiation of the signal at $\delta$ 7.56, due to a *trans*-$\beta$ proton ($J$ = 16 Hz) in the major isomer **9b** did not result in detectable NOE to protons other than those on the double bond. In contrast, irradiation of the signal at $\delta$ 7.15, due to the same proton in the minor complex, also led to enhancement of the AB multiplet at $\delta$ 5.9 corresponding to two Cp protons on a single Cp ring ($H_2$ and $H_3$).

These results are consistent with the structural assignment shown in Scheme 1; the major isomer possesses structure **9b**, in which the carbamate C═O group is laterally coordinated, while the minor isomer possesses structure **9a**, where this group is coordinated centrally. The difference in relative stability between **9a** and **9b** (1:2.4) and the less hindered system (**6a:6b** = 1.5:1) seems reasonable as the lateral coordination

(15) The astute reader will note that a prominent correlation exists between (broadened) signals at 6.7 and 6.1 ppm. These signals are due to the α and $\beta$ CpH protons of residual **8** and are line broadened, we suspect, due to triflate exchange (vide infra).

(16) The binding process is not significantly affected by the addition of small quantities of $CD_2Cl_2$. At this temperature, 2D-NOESY spectra indicated that exchange processes involving **9a** and **9b** were sufficiently slow that NOE difference spectra, free from exchange-related artifacts, could be obtained.

(17) The molecular weight of complexes **9** is 795 g mol$^{-1}$. When coupled with the high solvent viscosity of $CD_3NO_2$, it is apparent that slow tumbling conditions apply here. Consistent with this interpretation, the magnitude of the negative NOE *decreased* with increasing temperature and could not be (easily) observed at, e.g., −30 °C.

site is more sterically congested by the tetrahydroindenyl ligand, which should (selectively) destabilize the isomer where the C=C bond is located in this region.

Similar studies were performed in $CD_2Cl_2$ solvent. Binding of **3a** to **8** is less favorable under equivalent conditions in this solvent, with the extent of binding increasing with decreasing temperature (i.e., similar to that observed in nitromethane). Both $^1H$ and $^{19}F$ NMR spectra reveal the presence of two complexes, in addition to **8**, that appear to be equivalent to those observed in nitromethane solution (see Supporting Information). What is different between the two solvents is the ratio of **9a** to **9b** at a given temperature; at −30 °C, the ratio of **9a**:**9b** = 1:5.7 in $CD_2Cl_2$ while the ratio in $CD_3NO_2$ is 1:2.4.[18]

This finding, when coupled with the increase in enantioselectivity seen in nitroalkane solvent, and the sense of asymmetric induction observed (i.e., [2*R*]) suggests that the minor isomer **9a** may be reacting most rapidly and selectively with cyclopentadiene. Having said that, there is obvious cause for concern with this interpretation. If the rate at which these isomeric complexes interconvert is rapid with respect to the rate of the cycloaddition reaction, Curtin−Hammett conditions will apply. Under these conditions, it is the energy difference between transition states for product formation that will be paramount in governing the level of selectivity; the relative stability of the two isomers will be less important.

It is often assumed that the presence of (rapidly) interconverting isomers (in differing ratios under different conditions) is not very important to the level of enantioselectivity observed. This is not quite correct;[19] instead, the system is at equilibrium throughout the course of reaction, and while the level of selectivity will be chiefly determined by the differences in activation energies, this difference will be modulated by any change in the relative stability of the two isomers. In the present case, this will manifest itself as shown in Scheme 2. The situation is reminiscent of a nonlinear effect in asymmetric catalysis,[20] and it can be shown that the equations given in Scheme 2 apply, where $ee_{tot}$ is the observed selectivity, *g* is the relative reactivity of the two isomers, $ee_A$ and $ee_B$ are the inherent selectivities of the two isomers, and *K* is the equilibrium constant for their interconversion (we have assumed that **A** and **B** are the only significant catalyst species present during reaction). The final equation in Scheme 2 is also applicable to non-Curtin−Hammett conditions, but now *K* ([**B**]/[**A**]) will be a time-dependent quantity and thus the total enantioselectivity will not be constant during reaction.[21]

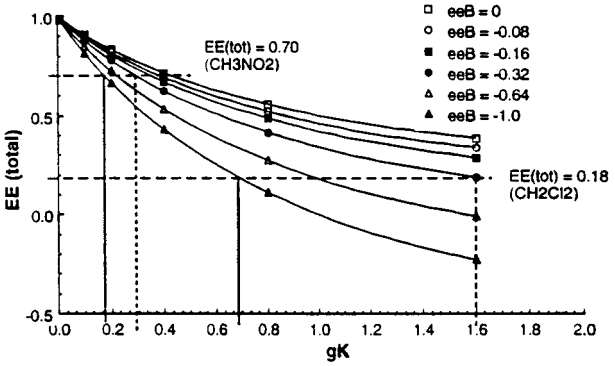
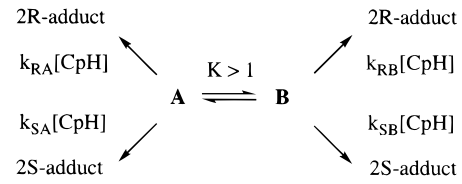



**Figure 3.** Plots of $ee_{tot}$ versus *gK* for various values of $ee_B$ assuming $ee_A = 1.0$ (see Scheme 2 for definitions).

**Scheme 2**




$$\frac{\partial[R-A]}{\partial t} = k_{RA}[A][CpH] + k_{RB}K[A][CpH]$$

$$\frac{\partial[S-A]}{\partial t} = k_{SA}[A][CpH] + k_{SB}K[A][CpH]$$

$$ee_{tot} = \frac{\partial[R-A]-\partial[S-A]}{\partial[R-A]+\partial[S-A]} = \frac{k_{RA}-k_{SA}+(k_{RB}-k_{SB})K}{k_{RA}+k_{SA}+(k_{RB}+k_{SB})K}$$

$$\text{let } ee_A = \frac{k_{RA}-k_{SA}}{k_{RA}+k_{SA}} \text{ and } ee_B = \frac{k_{RB}-k_{SB}}{k_{RB}+k_{SB}}$$

$$\text{with } g = \frac{k_{RB}+k_{SB}}{k_{RA}+k_{SA}} \text{ then } ee_{tot} = \frac{ee_A+(ee_B)gK}{1+gK}$$

Complete understanding of such a system, even under Curtin−Hammett conditions, requires that the instrinsic enantioselectivities as well as *K* be known; if one assumes that the former quantities are not altered by changing the solvent, it is instructive to examine the behavior to changes in *g* and *K*. Plots of $ee_{tot}$ vs *gK* for various values of $ee_B$ ($-1.0 \le ee_B \le 0.0$), assuming $ee_A = 1.0$ are shown in Figure 3. On the basis of the % ee observed in the two different solvents at −30 °C (70% and 18%, respectively), one can see from this figure that even in the unlikely event that $ee_B = -1.0$ (i.e., the major isomer is completely selective for the 2*S* enantiomer) that the observed change in % ee cannot be accounted for only by the change in *K* in the two different solvents. That is, *gK* has to change by a factor of at least 4 compared to *K* changing by a factor of 2.4; as the magnitude of the difference in selectivity between the two isomers decreases, Figure 3 shows that the reactivity differences between the isomers in the two solvents must become even more pronounced (i.e., the two isomers are closer in reactivity in dichloromethane compared to the situation in nitromethane). Having

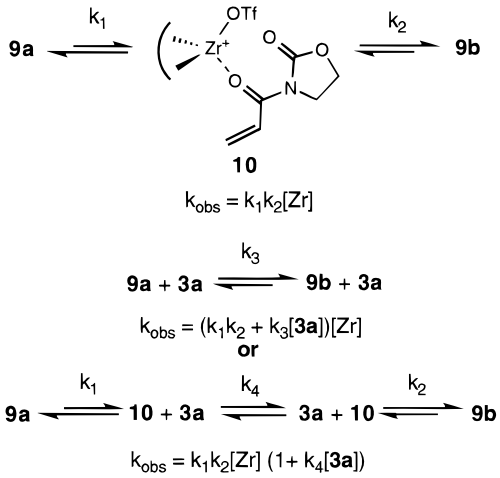
(18) Although we cannot exclude direct participation of the solvent (e.g., binding of nitromethane to Zr) in these experiments, $^1H$ and $^{13}C$ NMR spectra of **8** (or mixtures of **8** and **3a**) in $CD_2Cl_2$ containing small quantities of $CH_3NO_2$, are unchanged from those observed in pure $CD_2Cl_2$, and separate signals for, e.g., free and bound $CH_3NO_2$ are not observed at the lowest temperature/highest field strength accessible. Furthermore, in pure $CD_3NO_2$, there is no, significant, dissociation of triflate ion from **8** at −30 °C, suggesting nitromethane is a less effective ligand than triflate ion.

(19) See: Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper & Row: New York, 1981; p 212.

(20) Guillaneux, D.; Zhao, S.-H.; Samuel, O.; Rainford, D.; Kagan, H. B. *J. Am. Chem. Soc.* **1994**, *116*, 9430 and references therein.

(21) In addition, even under Curtin−Hammett conditions, the relative rates of interconversion of **A** and **B** compared to their reaction with CpH will be dependent on both relative and absolute concentrations of the species involved as the former is process is unimolecular and only depends on catalyst concentration while the latter depends upon both the catalyst concentration and [CpH]. For a discussion, see: Seeman, J. I. *Chem. Rev. (Washington, D.C.)* **1983**, *83*, 83 and references therein.

**Scheme 3**




said that, one is only talking about a change in reactivity differences (i.e., $g$) amounting to ~0.2 kcal mol$^{-1}$ at −30 °C, so that the solvent dependence, although dramatic in terms of enantioselectivity, should not be overinterpreted.

Under non-Curtin−Hammett conditions, complicated behavior is expected. For example, if isomer **A** is the more reactive (i.e., $g < 1$) but **B** is more stable ($K_{t=0} > 1$), qualitatively, one might expect $ee_{tot}$ to decrease with conversion since the steady-state value of $K$ ([**B**]/[**A**]) will be larger than the equilibrium value. However, the steady-state ratio of [**B**]/[**A**] will depend on both the relative rates at which the two isomers undergo cycloaddition (i.e., on $g$), the relative amounts of **A** and **B** initially present (i.e., on K), *and* the relative rates at which the two isomers will be formed from reaction of product complexes with free oxazolidinone **3a**. Thus, without detailed knowledge of this steady-state ratio, the behavior of $ee_{tot}$ with respect to conversion is difficult to interpret.

**Interconversion Mechanisms for 9a and 9b.** It is clear from the spectrum in Figure 2 that **9a** and **9b** are slowly exchanging on the NMR time scale at temperatures where the Diels−Alder reaction occurs at a significant rate. With this in mind, variable-temperature NMR studies on these complexes were performed to determine relevant interconversion mechanisms as well as associated activation parameters. The latter will provide insight into whether one is possibly dealing with a reaction under Curtin−Hammett conditions, along with experiments to be described later.

Two likely exchange processes could allow interconversion of these two isomers in solution (Scheme 3). A unimolecular exchange process involving dissociation of one of the C═O groups followed by reorganization of the bound oxazolidinone and recoordination of the C═O group would interconvert isomers. Alternatively, ligand exchange with free oxazolidinone provides an alternative pathway, which may be dynamically linked with the former, as illustrated in Scheme 3.

Two-dimensional $^1$H-EXSY spectra acquired at − 30 °C in the presence of excess **3a** (**3a**:**8** = 2:1) revealed that both exchange processes occur in nitromethane solvent (see Supporting Information). Variation of the mixing time established that the unimolecular process was the more rapid of the two under these conditions,

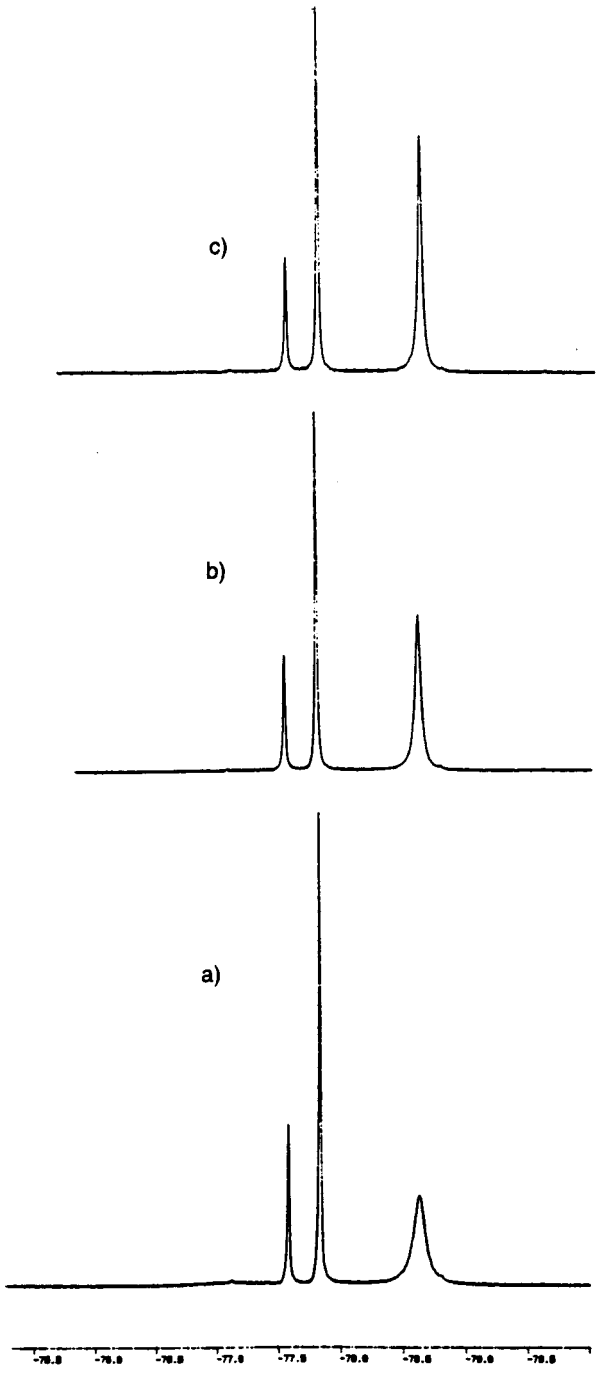



**Figure 4.** $^{19}$F NMR spectra (188 MHz, $CD_3NO_2$:$CD_2Cl_2$ ≈ 3:1 v/v, −26 °C) of (a) a 1:1 mixture of **3a** and **8**, (b) a 2:1 mixture of **3a** and **8**, and (c) a 5:1 mixture of **3a** and **8**.

based on the intensity of the cross peaks arising from exchange-related protons in the two complexes compared with those for **3a** and either **9a** or **9b**.

Variable-temperature $^{19}$F NMR spectra were obtained at various concentrations of **3a** at constant [**8**] with [**3a**]:[**8**] = 1:1, 2:1, and 5:1 at −26 °C. As shown in Figure 4, within experimental error, the line widths of the two signals due to **9a** and **9b** are independent of the amount of **3a** present at this temperature, again suggesting interconversion of these two complexes by exchange with free oxazolidinone is less important compared to the rate of their direct interconversion (i.e., Scheme 3, top mechanism).

It is also clear from the appearance of the signal due

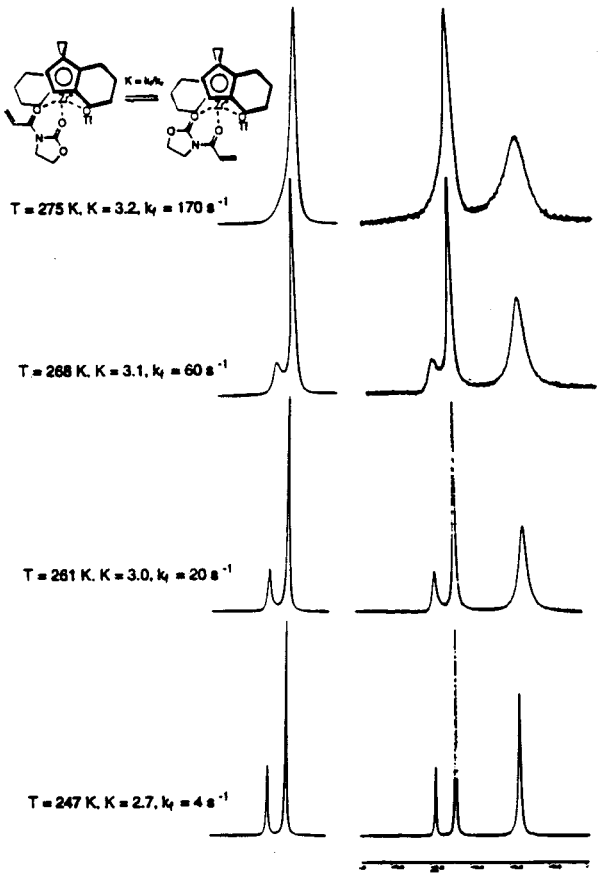



**Figure 5.** Experimental and simulated $^{19}F$ NMR spectra of a 5:1 mixture of **3a** and **8** at various temperatures in $CD_3NO_2$:$CD_2Cl_2$ ≈ 3:1 v/v.

to free triflate ion, depicted in Figure 4, that another dynamic process is occurring that does not involve either **9a** and **9b**. This process apparently involves free triflate ion and residual **8,** as the general features of these spectra could be reproduced by simply adding known amounts of [$^n$Bu$_4$N][OTf] to **8** in the absence of **3a** (see Supporting Information). Simulation of VT $^{19}F$ NMR spectra of mixtures of **8** at three different concentrations of [$^n$Bu$_4$N][OTf] demonstrated that the self-exchange process shown in eq 5 was rapid and involved an associative mechanism.

$$\mathbf{8} + \mathrm{TfO}^- \rightleftharpoons \mathrm{TfO}^- + \mathbf{8} \qquad (5)$$

$$\Delta H^{\ddagger} = 2.9 \pm 0.3 \text{ kcal mol}^{-1}, \Delta S^{\ddagger} = -26.8 \pm 2.7 \text{ eu}$$

Using this information and the temperature dependence of the equilibrium constant for binding of **3a** to **8** (vide supra), one could attempt to accurately simulate VT $^{19}F$ NMR spectra assuming two independent exchange processes—that shown in eq 5 as well as interconversion of **9a** and **9b** (Scheme 3). However, since the rate of the latter was basically insensitive to [**3a**], the spectra of **9a** and **9b**, obtained using a ratio of **3a**:**8** of 5:1, were simulated in that there is less interference from the effects of the triflate exchange process over a wider temperature range (i.e., there is very little residual **8** present under these conditions). It only proved possible to simulate these spectra (see Figure 5) by assuming that the equilibrium constant governing the isomerization of **9a** and **9b** was slightly dependent

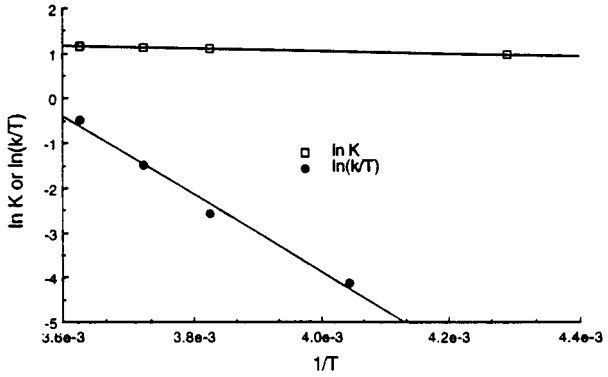



**Figure 6.** Arrhenius plots for the thermodynamics and kinetics of interconversion of **9a** and **9b** (eq 6).

on temperature, the major isomer **9b** being increasingly favored at higher temperature. Plots of both ln $K$ and ln($k_f/T$) vs 1/$T$ were linear over the temperature range studied (Figure 6), and the thermodynamic and kinetic parameters obtained are shown in eq 6.

$$\mathbf{9a} \underset{k_f}{\overset{k_f}{\rightleftharpoons}} \mathbf{9b} \qquad (6)$$

$$K = k_f/k_r > 1 \text{ with}$$

$$\Delta H_o = 610 \pm 60 \text{ cal mol}^{-1}, \Delta S_o = 4.5 \pm 0.5 \text{ eu}$$

$$\Delta H^{\ddagger} = 17.2 \pm 1.7 \text{ kcal mol}^{-1}, \Delta S^{\ddagger} = 13.9 \pm 1.4 \text{ eu}$$

Interestingly, the minor isomer **9a** is *more stable* from an enthalpy point of view, and it is the increase in entropy that appears to favor isomer **9b** overall ($\Delta G_{243}$ = −480 cal mol$^{-1}$).[22] Part of the increase in % ee observed at lower temperatures may be due to increased amounts of **9a** present at equilibrium.[23] The barrier ($\Delta G^{\ddagger}$) to interconversion at −30 °C in nitromethane is 13.8 kcal mol$^{-1}$ and will increase at lower temperatures as $\Delta S^{\ddagger} > 0$ (which is consistent with dissociation of a C═O group as postulated earlier). As this is a reasonably high activation energy compared to typical barriers to interconversion of conformers, it is not clear whether Curtin−Hammett conditions will be applicable (at all temperatures).

To determine whether interconversion of **9a** and **9b** is rapid compared to the rate(s) or their reaction with cyclopentadiene, we attempted to measure the rate of the latter process in mixed $CD_2Cl_2$:$CD_3NO_2$ solvent (ca. 1:3 v/v) at −45 °C using $^1H$ NMR spectroscopy. Under these conditions, this process was essentially complete by the time required for the first spectral acquisition following mixing (ca. 3 min), even at low loadings of substrate and catalyst (e.g., [**3a**] = [CpH] = 0.05 M with [**8**] = 5 × 10$^{-4}$ M!). More meaningful information was obtained from the following experiment: quenching two reactions in 2-nitropropane solvent at −78 °C at differ-

(22) MMX calculations on these two complexes also suggest that isomer **9a** is lower in enthalpy than **9b** by ca. 0.5 kcal mol$^{-1}$.

(23) Similar behavior was observed in 2-nitropropane and dichloromethane solvent. At lower temperatures in 2-nitropropane, increasing amounts of free triflate ion were observed (i.e., the ratio of (**9a** + **9b**): $TfO^-$ was no longer 1:1), suggesting formation of a dicationic complex (which would be expected to have similar enantioselectivity as **9a**).

ent times showed that the % ee (and the *endo*:*exo* ratio) varied somewhat with conversion (eq 7).

$$\text{[S]-}\mathbf{8}\ (3\ \text{mol\%}) + \mathbf{3a}\ (0.08\ \text{M}) \xrightarrow[2\text{-}NO_2Pr]{-78\ ^\circ C} \text{endo + exo-}\mathbf{5a} \qquad (7)$$

| t (min) | %conv. | endo:exo | 2R:2S endo |
|---|---|---|---|
| 0.50 | 30 | 12.5:1 | 9.4:1 |
| 3.00 | 79 | 11.70± 0.05:1 | 11.26 ± 0.04:1 |

Qualitatively, the behavior observed is different from what one might expect. However, as mentioned previously, the interpretation of these results requires knowledge of the instantaneous ratio of **9b**:**9a**, which could be initially greater than (or equal to) the equilibrium value (i.e., lower $ee_{tot}$) but could decline to a steady-state ratio which is less than the equilibrium value (higher $ee_{tot}$). The very rapid rates of reaction in 2-nitropropane at lower temperatures (eq 7) precluded meaningful analysis of this ratio by conventional NMR techniques.[24]

## Conclusions

Asymmetric Diels−Alder reactions involving cyclopentadiene and enoyl−oxazolidinone dienophiles are effectively and selectively catalyzed by chiral zirconocene bis(triflate) complexes, particularly in nitroalkane solvents at low temperatures. Detailed spectroscopic and kinetic studies have revealed that two isomeric complexes are formed on binding of substrate **3a** to **8**, and it seems that the minor isomer **9a** reacts most rapidly (and selectively) with cyclopentadiene. A variety of evidence points to the fact that these reactions occur under non-Curtin-Hammett conditions, and thus, the instantaneous ratio and relative reactivity of these isomers is important in determining the degree of diastereo- and enantioselectivity.[25] In particular, the dramatic changes in selectivity observed in nitroalkane vs dichloromethane solvent can be partially accounted for by changes in the relative stability of **9a** vs **9b** coupled with a difference in reactivity. Future work will focus on efforts to perturb the relative stability of these two complexes through either dienophile modification[26] and/or catalyst structure as well as the design of suitable catalysts where the issue of isomerism does not arise.

## Experimental Section

All reactions were performed under an atmosphere of nitrogen; exceptions are noted in the appropriate procedures. Air-sensitive solids were stored and weighed in a glovebox under a dried and deoxygenated nitrogen atmosphere. Standard techniques for dealing with air- and moisture-sensitive compounds were employed throughout.[27] All solvents were reagent grade chemicals obtained from commercial sources. Methylene chloride was distilled from $CaH_2$. Toluene, tetrahydrofuran, diethyl ether, and hexane were refluxed and distilled from sodium and benzophenone. Nitromethane and 2-nitropropane were distilled from $CaCl_2$ and stored over activated, 4 Å molecular sieves in amber glass bottles. Trifluoromethanesulfonic acid was distilled under reduced pressure from trifluoromethanesulfonic acid anhydride before use. Solutions of n-BuLi and MeLi were titrated before use.[28]

Routine $^1H$ and $^{13}C$ NMR spectra were recorded in $CDCl_3$ or $C_6D_6$ solution on either a Bruker AM-250 or AC-200 spectrometer; chemical shifts are referenced with respect to residual $CHCl_3$ or $C_6D_5H$. Low-temperature $^1H$, $^{13}C$, and $^{19}F$ spectra were recorded in $CD_2Cl_2$ or $CD_3NO_2$ solution using the above instruments or a Bruker AMX-500 spectrometer. Temperature calibration was determined from a 4% MeOH/$CD_3$-OD sample. $^{19}F$ chemical shifts are referenced with respect to internal $CFCl_3$ except where noted. IR spectra were recorded on a Bomem MB-100 FTIR spectrometer. Mass spectra were obtained using a Kratos MS-890 instrument at the University of Guelph. Elemental analyses were determined by M. H. W. Laboratories (Phoenix, AZ). HPLC analyses were conducted using a Waters 600E instrument equipped with a Waters 484 UV−vis detector set at 254 nm and interfaced to a Waters 745 data module.

**Preparation of Dienophiles 3.** *N*-Enoyl−2-oxazolidinones **3a**−**c** were prepared by acylation of 2-oxazolidinone according to a general method described by Evans et al.[3d]

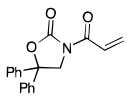
***N*-Acryloyl-2-oxazolidinone (3a).**[29] To a solution of 2-oxazolidinone (6.71 g, 77 mmol) in dry THF (50 mL), cooled to 0 °C, was added a solution of methylmagnesium bromide in THF (25 mL, 3.1 M). After 10 min at 0 °C, the mixture was cooled to −78 °C and acryloyl chloride (8.93 g, 99 mmol) was added. The mixture was stirred at −78 °C for 10 min and at 0 °C for 20 min. The reaction was quenched with 10 mL of saturated aqueous ammonium chloride solution and diluted with distilled ether (150 mL). The organic layer was washed with saturated aqueous ammonium chloride (10 mL) before being dried over magnesium sulfate, and a small amount of hydroquinone was added. The solvent was removed in vacuo. White crystals of **3a** were obtained upon recrystallization from diethyl ether or ethanol. Mp: 82 °C. $^1H$ NMR (250 MHz, $CD_3NO_2$, room temperature): $\delta$ 7.45 (dd, $J$ = 10.5, 17.0 Hz, 1H), 6.50 (dd, $J$ = 2.0, 17.0 Hz, 1H), 5.85 (dd, $J$ = 2.0, 10.5 Hz, 1H), 4.42 (t, $J$ = 5.0 Hz, 2H), 4.03 (t, $J$ = 5.0 Hz, 2H). $^{13}C$ NMR (62.5 MHz, $CD_3NO_2$, room temperature): $\delta$ 166.3, 155.4, 131.4, 128.8, 63.9, 43.8.

***N*-crotonyl-2-oxazolidinone (3b).**[30] To a solution of 2-oxazolidinone (0.87 g, 10 mmol) in dry THF (10 mL), at −78 °C, was added a solution of n-BuLi in hexanes (4 mL, 2.5 M). After 15 min of stirring, freshly distilled, crotonyl chloride (1.0 mL, 11 mmol) was added. The mixture was stirred at −78 °C for 30 min and at 0 °C for 15 min. The reaction was quenched

(24) Attempts were made to observe this ratio during catalysis by $^{19}F$ NMR spectroscopy at low temperatures in $CD_3NO_2$: $CD_2Cl_2$ solution by diffusing in small quantities of CpH.; at low conversion, there was minimal perturbation of the isomer ratio, but this experiment only proves than the interconversion of the two isomers is more rapid that the rate of diffusion of CpH under these conditions. The half-life of ca. 1 min at −78 °C (0.08 M in **3a**, 3 mol % [*S*]-**8**, eq 7) leads to an estimate of $k_{obs} = 0.2\ M^{-1}\ s^{-1}$ ($k$[Zr]$_o$) corresponding to an effective activation energy for cycloaddition of ∼12 kcal mol$^{-1}$ at this temperature, which is of similar magnitude to the barrier for interconversion of **9a** and **9b**, providing a further indication that non-Curtin−Hammett conditions apply.

(25) In addition, as alluded to earlier (ref 21), the relative rates for interconversion and chemical reaction will be concentration dependent. One would expect kinetic quenching to be valid at early conversions (i.e., lower ee) where $k$[CpH][Zr] ≥ $k'$[Zr] and a tendency towards C−H conditions (higher ee) at high conversion, but detailed study of this would require that the concentration dependence of all species on the ee be determined. We thank a referee for suggesting these experiments and bringing these features to our attention.

(26) For example, use of the more highly substituted oxazolidinone substrate shown below did perturb the equilibrium stability of the two complexes but not in the desired direction (**9a′**:**9b′** = 1:3.5 at −30 °C in $CD_3NO_2$). Predictably, the enantioselectivity of the Diels−Alder reaction with CpH was lower, ca. 56% ee (−30 °C, 1 mol % [*S*]−**8**). Jaquith, J. B. M.S. Thesis, University of Waterloo, 1995.

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with saturated aqueous ammonium chloride, diluted with diethyl ether, and washed with saturated aqueous sodium bicarbonate and then saturated aqueous sodium chloride. The organic phase was dried over magnesium sulfate and filtered. The solvent was removed under reduced pressure. The crude product was purified by recrystallization from diethyl ether to give the desired dienophile **3b** (0.6028 g, 39% yield). Mp: 38−39 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 7.36 (d, $J$ = 15.9 Hz, 1H), 7.20 (dt, $J$ = 6.3, 15.2 Hz, 1H), 4.54 (t, $J$ = 7.9 Hz, 2H), 4.18 (t, $J$ = 7.9 Hz, 2H), 2.08 (d, $J$ = 5.4 Hz, 3H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 164.9, 153.3, 146.2, 121.4, 61.9, 42.6, 18.1.

***N*-Methacryloyl-2-oxazolidinone (3c).**[31] Following the method described for the preparation of **3b**, dienophile **3c** was obtained in 80% yield. Mp: 56−57 °C. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 5.33 (s, 1H), 5.31 (s, 1H), 4.35 (t, $J$ = 7.8 Hz, 2H), 3.93 (t, $J$ = 7.8 Hz, 2H), 1.92 (s, 3H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 170.7, 152.6, 139.0, 120.4, 62.1, 42.8, 18.8.

**Preparation of $Cp_2Zr(OTf)_2$ (4).**[32] $Cp_2Zr(OTf)_2$ was prepared by the treatment of $Cp_2ZrMe_2$ with 2 equiv of triflic acid in dry diethyl ether at −80 °C. The crude product was collected by filtration under a nitrogen atmosphere and was further purified by recrystallization from $CH_2Cl_2$/hexane to yield **4** as a fine white powder in 75% yield. $^1$H NMR (250 MHz, $C_6D_6$): $\delta$ 5.86.

**Preparation of Racemic and [*S*]-ethylenebis($\eta^5$-tetrahydroindenyl)Zr(OTf)$_2$ (8).** A solution of either racemic or [*S*]-ethylenebis($\eta^5$-tetrahydroindenyl)$ZrMe_2$[11c] (263 mg, 0.682 mmol) in dry diethyl ether (10 mL) was cooled to −80 °C (diethyl ether/$CO_2$ bath), and a solution of triflic acid (505 $\mu$L, 2.7 M) in diethyl ether was added slowly. The solution was stirred at −80 °C for 3 h before the diethyl ether was removed in vacuo. The solid was dissolved in hot toluene (10 mL) and filtered through Celite (under nitrogen), washing with hot toluene (3 × 1 mL). The toluene was concentrated to 2−3 mL, heated to dissolve any solids, and allowed to cool to room temperature overnight. The solution was filtered, and the solid was washed with toluene (1 mL) and dry hexane (3 × 1 mL) to yield 343 mg of bright yellow crystals (77% yield). Lit.[6] $[\alpha]_{435}$ = +606° (0.18 g/100 mL, $CH_2Cl_2$). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 6.80 (d, $J$ = 3 Hz, 2H), 5.90 (d, $J$ = 3 Hz, 2H), 3.46 (s, 4H), 2.63 (m, 8H), 1.83 (m, 4H), 1.61 (m, 4H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 138.9, 137.4, 128.9, 118.8 (q, $J_{CF}$ = 320 Hz), 118.7, 112.5, 29.0, 24.0, 23.0, 21.6, 21.4. $^{19}$F NMR (188 MHz, $CDCl_3$): $\delta$ −77.2 (s). IR (KBr): 3112, 3076, 2950, 2912, 2865, 1677, 1649, 1493, 1469, 1441, 1353, 1314, 1291, 1236, 1197, 1152, 981, 818, 628 cm$^{-1}$. Anal. Calcd for $C_{22}H_{24}ZrO_6S_2F_6$: C, 40.42; H, 3.70. Found: C, 40.18; H, 3.89. MS (EI) $m/z$ 652 ($M^+$, $^{90}$Zr).

**General Conditions for Diels−Alder Reactions between *N*-Enoyl−2-oxazolidinones and Cyclopentadiene. Typical Procedure.** Oxazolidinone **3a** (141 mg, 1.0 mmol) and [*S*]-**8** (6.5 mg, 0.01 mmol) were combined and dissolved in $CH_3NO_2$ (2.0 mL). After the solution was cooled to −30 °C, cyclopentadiene (200−500 $\mu$L) was added via syringe. Reactions were monitored by TLC (silica gel, $CH_2Cl_2$). The mixture was quenched with saturated aqueous $NH_4Cl$ (2 mL) and diluted with $CH_2Cl_2$ (10 mL) and water (5 mL). The aqueous layer was washed with $CH_2Cl_2$ (2 × 5 mL), the combined organic layers were dried over anhydrous $Na_2SO_4$ and filtered, and solvent was removed in vacuo to provide the crude adduct in ca. 90% yield, substantially pure by $^1$H NMR spectroscopy. The adducts could be further purified by flash chromatography on silica gel (20 × 0.5 cm), eluting with $CH_2Cl_2$. The diastereomeric ratios were determined from $^1$H NMR spectra of the crude adduct mixture prior to chromatography. Enantiomeric excess (% ee) was determined by HPLC analysis of the purified adducts (vide infra).

***endo*- and *exo*- *N*-(Norborn-5-en-2-carboxyl)oxazolidinone 5a.**[28] *endo*-**5a**. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 6.18 (dd, $J$ = 3.0, 5.5 Hz, 1H, H6), 5.82 (dd, $J$ = 3.0, 5.5 Hz, 1H, H5), 4.40−4.32 (m, 2H, AB portion of an ABCD spin system for C10 protons), 4.01−3.86 (m, 3H, CD portion of an ABCD spin system for C11 protons overlapping with H2-*exo*), 3.26 (br s, 1H, H1), 2.89 (br s, 1H, H4), 1.90 (ddd, 1H, H3-*endo*), 1.49−1.31 (m, 3H, syn and anti H7 overlapping with H3-*exo*). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 174.6 (C9), 153.3 (C8), 137.9 (C6), 131.6 (C5), 61.9 (C10), 50.0 (C7), 46.3 (C11), 43.1 (C2), 42.9 (C1), 42.8 (C4), 29.5 (C3). $[\alpha]_{589}$ = +130° (2.2 g/100 mL; $CH_2Cl_2$, 86.8% ee). *exo*-**5a**. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 6.12 (br t, 2H, H5 and H6), 4.40−4.32 (m, 2H, AB portion of a ABCD spin system for C10 protons), 4.01−3.86 (m, 3H, CD portion of an ABCD spin system due to C11 protons overlapping with H2-*endo*), 3.26 (br s, 1H, H1), 2.89 (br s, 1H, H4), 1.90 (overlapping ddd, 1H, H3-*endo*), 1.49−1.31 (m, 3H, syn and anti H7 overlapping with H3-*exo*). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 176.0 (C9), 153.3 (C8), 138.1 (C6), 135.9 (C5), 61.9 (C10), 50.0 (C7), 46.7 (C11), 46.1 (C2), 42.9 (C1), 41.8 (C3), 30.3 (C3).

***endo*- and *exo*- *N*-(3-Methylnorborn-5-en-2-carboxyl)-oxazolidinone 5b.**[28] *endo*-**5b**. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 6.33 (dd, $J$ = 3.1, 5.6 Hz, 1H), 5.75 (dd, $J$ = 2.7, 5.6 Hz, 1H), 4.37 (t, $J$ = 8.0 Hz, 2H, AB portion of an ABCD spin system for C10 protons), 3.94 (m, 2H, AB portion of an ABCD spin system for C11 protons), 3.50 (t, $J$ = 3.7 Hz, 1H, H2-*exo*) 3.24 (br s, 1H, H1), 2.50 (br s, 1H, H4), 2.07 (overlapping ddd, 1H, H3-*endo*), 1.67 (d, $J$ = 8.6 Hz, 1H, bridgehead proton), 1.43 (d, $J$ = 8.6 Hz, 1H, bridgehead proton), 1.09 (d, $J$ = 7.0 Hz, 3H, C2 methyl protons). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 175.6 (C9), 153.4 (C8), 139.6 (C6), 131.0 (C5), 61.83 (C10), 51.3, 49.5, 47.4, 47.1, 43.0, 36.5, 20.3. $[\alpha]_{589}$ = +167° (0.310 g/100 mL; $CH_2Cl_2$, 92% ee). *exo*-**5b**. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 6.28 (dd, $J$ = 3.1, 5.5 Hz, 1H), 6.12 (dd, $J$ = 2.8, 5.6 Hz, 1H), 4.37 (t, $J$ = 8.0 Hz, 2H, AB portion of an ABCD spin system for C10 protons), 3.94 (m, 2H, AB portion of an ABCD spin system for C11 protons), 3.50 (t, $J$ = 3.7 Hz, 1H, H2-*exo*), 2.83 (m, 1H, H1), 2.66 (m, 1H, H4), 2.07 (overlapping ddd, 1H, H3-*endo*), 1.63 (d, $J$ = 8.5 Hz, 1H, bridgehead proton), 1.34 (d, $J$ = 8.5 Hz, 1H, bridgehead proton), 0.82 (d, $J$ = 7.0 Hz, 3H, C2 methyl protons).$^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 174.4 (C9), 153.4 (C8), 136.9 (C6), 135.5 (C5), 61.77 (C10), 50.6, 49.5, 47.5, 46.7, 43.05, 37.4, 18.8.

***endo*- and *exo*- *N*-(2-Methylnorborn-5-en-2-carboxyl)-oxazolidinone 5c.** *endo*-**5c** + *exo*-**5c**. IR ($CHCl_3$): 3060, 2966, 2872, 1778, 1694, 1480, 1454, 1381, 1325, 1292, 1224, 1120, 1097, 1038 cm$^{-1}$. Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.16; H, 6.78. Found: C, 65.17; H, 6.69. *endo*-**5c**. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 6.21 (dd, $J$ = 3.0, 5.7 Hz, 1H), 6.03 (dd, $J$ = 3.0, 5.7 Hz), 4.36 (m, 2H, AB portion of an ABCD spin system for C10 protons), 4.00 (m, 2H, AB portion of an ABCD spin system for C11 protons), 3.30 (br s, 1H, H1), 2.74 (br s, 1H, H4), 2.09 (dd, $J$ = 3.9, 12.9 Hz, 1H, H3-*endo*), 1.45 (m, 1H, bridgehead proton), 1.40 (dd, $J$ = 2.9, 12.9 Hz, 1H, bridgehead proton), 1.32 (dd, $J$ = 2.9, 12.9 Hz, 1H, H2-*exo*), 1.21 (s, 3H, C2 methyl protons). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 187.6 (C9), 152.2 (C8), 139.1 (C6), 133.5 (C5), 61.95 (C10), 51.6, 50.4, 49.2, 44.4, 43.0, 39.5, 22.1. *exo*-**5c**. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 6.04 (s, 2H), 4.30 (m, 2H, AB portion of an ABCD spin system for C10 protons), 3.88 (m, 2H, AB portion of an ABCD spin system for C11 protons), 3.03 (br s, 1H, H1), 2.74 (br s, 1H, H4), 1.82 (dd, $J$ = 3.5, 12.8 Hz, 1H, H3-*endo*), 1.69 (dd, $J$ = 2.5, 12.8 Hz, 1H, H3-*exo*), 1.54 (m, 2H, bridgehead protons), 1.53 (s, 3H, C2 methyl protons). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 177.6 (C9), 152.2 (C8), 137.24 (C6), 137.17 (C5), 62.0 (C10), 53.1, 51.1, 45.7, 44.1, 42.0, 40.3, 24.8.

**HPLC Analysis of Diels−Alder Adducts 5a−c.** Diels−Alder adducts were separated by HPLC using a Chiralcel OD

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(32) Siedel, A. R.; Newmark, R. A.; Glenson, W. B.; Lamanna, W. M. *Organometallics* **1990**, *9*, 1290.

(25.0 cm × 4.6 mm) column, eluting with hexane:$^{i}$PrOH at 1.0 mL/min at 25 °C. Conditions and assignments are noted below, where the assignments marked with an asterisk are tentative.

| adduct | $C_6H_{14}$:$^{i}$PrOH | $t_R$ (min) (assignment) |
|---|---|---|
| **5a** | 98:2 | 45 ([2*S*]-*exo**), 48 ([2*R*]-*exo**), 51 ([2*S*]-*endo*), 55 ([2*R*]-*endo*) |
| **5b** | 99:1 | 43 ([2*R*] + [2*S*]-*exo*), 49 ([2*S*]-*endo*), 53 ([2*R*]-*endo*) |
| **5c** | 99:1 | 37 ([2*S*]-*exo**), 40 ([2*R*]-*exo**), 43 ([2*R*] + [2*S*]-*endo*) |

**Chemical Correlation of Diels−Alder Adducts 5a and 5b.** Pure samples of the adducts *endo*-**5a** and -**5b** (87% and 91% ee, respectively) could be obtained by flash chromatography of the *endo*:*exo* mixtures on silica gel eluting with $CH_2Cl_2$:hexane. They were separately converted to the corresponding benzyl esters *endo*-**11a** and *endo*-**11b** respectively, according to the following procedure:[3d] To a solution of 2.0 equiv of benzyl alcohol in anhydrous THF (∼0.2 M) at −78 °C was added 1.5 equiv of *n*-BuLi. A solution of the adduct in anhydrous THF (1.0 equiv, ∼1 M) was added via cannula, and the mixture was stirred at 0 °C for 3 h. The mixture was then quenched with saturated ammonium chloride and extracted with $CH_2Cl_2$. The organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuo. The resultant oily product was purified by preparative TLC chromatography, eluting with 20:1 hexane/ethyl acetate, to provide the desired benzyl ester as colorless oils in yields of 50−60%.

The benzyl ester prepared from *endo*-**5a** had an optical rotation of $[\alpha]_{589} = +109.5°$ (1.25 g/100 mL; $CH_2Cl_2$) corresponding to the [2*R*] enantiomer with an optical purity of 84%.[11c] The benzyl ester prepared from *endo*-**5b** had an optical rotation of $[\alpha]_{589} = +123°$ (1.37 g/100 mL; $CH_2Cl_2$) corresponding to the [2*R*] enantiomer with an optical purity of 95%.[3d]

***endo*- and *exo*-Norborn-5-ene-2-carboxylic Acid Benzyl Ester 11a.**[3d] *endo*-**11a**. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 7.34 (m, 5H), 6.18 (dd, $J$ = 3.0, 5.6 Hz, 1H), 5.87 (dd, $J$ = 2.8, 5.6 Hz, 1H), 5.10 (d, $J$ = 12.5 Hz, 1H), 5.03 (d, $J$ = 12.5 Hz, 1H), 3.22 (br s, 1H), 2.99 (overlapping ddd, 1H), 2.90 (br s, 1H), 1.91 (overlapping ddd, 1H), 1.35 (t, $J$ = 3.1 Hz, 1H), 1.42 (d, $J$ = 7.5 Hz, 1H), 1.26 (d, $J$ = 7.5 Hz, 1H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 174.4, 137.7, 136.4, 135.3, 132.3, 128.5, 128.0, 65.9, 49.6, 45.8, 43.2, 42.6, 29.3. *exo*-**11a**. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 7.34 (m, 5H), 6.11 (m, 2H), 5.16 (s, 2H), 3.06 (br s, 1H), 2.90 (br s, 1H), 2.28 (dd, $J$ = 4.4, 10.1 Hz, 1H), 1.92 (ddd, $J$ = 4.0, 4.5, 10.1 Hz, 1H), 1.62 (m, 1H), 1.37 (m, 1H). $^{13}$C NMR (62.5 MHz, $CDCl_3$) $\delta$ 175.9, 138.1, 135.7, 135.3, 128.5, 128.2, 69.6, 66.2, 46.6, 46.4, 43.2, 41.7, 30.4.

***endo*- and *exo*-3-Methylnorborn-5-ene-2-carboxylic Acid Benzyl Ester 11b.**[3d] *endo*-**11b**: $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 7.33 (m, 5H), 6.26 (dd, $J$ = 3.1, 5.7 Hz, 1H), 5.95 (dd, $J$ = 2.8, 5.7 Hz, 1H), 5.10 (d, $J$ = 12.5 Hz, 1H), 5.04 (d, $J$ = 12.5 Hz, 1H), 3.13 (br s, 1H), 2.47 (br s, 1H), 2.43 (dd, $J$ = 4.4, 8.0 Hz, 1H), 1.87 (m, 1H), 1.71 (dd, $J$ = 1.8, 4.9 Hz, 1H), 1.66 (m, 1H), 0.92 (d, $J$ = 6.9 Hz, 3H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 174.4, 138.7, 136.5, 135.3, 133.3, 128.5, 127.9, 69.7, 65.8, 52.6, 48.9, 46.0, 37.9, 20.9. *exo*-**11b**. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 7.33 (m, 5H), 6.20 (dd, $J$ = 3.1, 5.6 Hz, 1H), 6.10 (dd, $J$ = 2.9, 5.7 Hz, 1H), 5.16 (s, 2H), 2.98 (br s, 1H), 2.17 (br s, 1H), 2.38 (m, 1H), 1.87 (m, 1H), 1.53 (d, $J$ = 8.6 Hz, 1H), 1.42 (m, 1H), 1.18 (d, $J$ = 7.0 Hz, 3H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ 175.9, 138.7, 136.6, 135.3, 133.3, 128.6, 128.0, 69.7, 66.1, 51.4, 48.1, 47.3, 39.2, 19.0.

**Triflate Exchange with *rac*-8 in 3:1 $CD_3NO_2$:$CD_2Cl_2$.** *rac*-**8** (9.6 mg, 0.0153 mmol) was dissolved in 0.700 mL of solvent in an NMR tube. A stock solution of $[Bu_4N][OTf]$ (123 mg, 0.306 mmol in 1.0 mL, 0.306 M) was prepared. Variable-temperature NMR spectra were recorded after the addition of 50 (1 equiv), 100 (2 equiv), and 200 $\mu$L (4 equiv) total volume of the $[Bu_4N][OTf]$ solution. The corresponding signal intensities for catalyst-triflate:free-triflate were 2:1, 1:1, and 1:2 at low $T$. Signals were observed at −76.57 (*rac*-**8**) and −78.16 ppm (OTf) relative to $CFCl_3$ at 225 K, and the frequency difference (300 Hz) was essentially invariant with temperature in the absence of exchange. Spectra were simulated using the program DNMR4[33] to give rate constants ($k_{obs}$) for the exchange between bound and free triflate (eq 8). This rate constant is related to $k$ (eq 9) by the relationship $k = k_{obs}/(K_{eq}[rac\text{-}\mathbf{8}])$, where $K_{eq} = [OTf_{free}]/[OTf_{bound}]$. $K_{eq}$ is thus equal to 0.5, 1, and 2 for the 50, 100, and 200 $\mu$L runs, respectively. $T_2$* values were estimated for both $^{19}$F signals from the width at half-height at 225 K of separate solutions of *rac*-**8** and $[Bu_4N][OTf]$ as the slow exchange limit could not be attained over the temperature range accessible. Each signal had a width of ∼2.25 Hz and, hence, a $T_2$* of 0.14 s.

$$OTf_{bound} \underset{k_{obs}^{-1}}{\overset{k_{obs}}{\rightleftharpoons}} OTf_{free} \tag{8}$$

$$rac\text{-}\mathbf{8} + {}^{-}OTf \underset{k^{-1}}{\overset{k}{\rightleftharpoons}} rac\text{-}\mathbf{8} + {}^{-}OTf \tag{9}$$

The rate constants showed a first-order dependence on the concentration of $[Bu_4N][OTf]$, indicating an associative exchange mechanism. Eyring plots yielded the activation parameters for the exchange between bound and free triflate: $\Delta G^{\ddagger}(298\ K) = 44.1 \pm 0.6$ kJ mol$^{-1}$, $\Delta H^{\ddagger} = 12 \pm 2$ kJ mol$^{-1}$, $\Delta S^{\ddagger} = 108 \pm 8$ J mol$^{-1}$ K$^{-1}$.

**Thermodynamics of Coordination of Oxazolidinone 3a to *rac*-8.** This study used a 3:4 ratio of **3a**:*rac*-**8** in a solvent mixture consisting of 3:1 $CD_3NO_2$:$CD_2Cl_2$. This allowed for the observation of both bound and free oxazolidinone signals over the entire temperature range of the experiment. *rac*-**8** (20 mg, 0.030 mmol) was weighed into a 1.00 mL volumetric flask. To this flask was added 250 $\mu$L (0.023 mmol) of a solution of **3a** (26 mg, 0.184 mmol in 2.00 mL, 0.092 M). The 1.00 mL volumetric flask was then filled to the mark, and this solution was used in the NMR study ($[Zr]_o = 0.030_6$ M and $[ox]_o = 0.023_0$ M). The ratio of free to bound **3a** was determined by the ratio of the total integrals of the methylene oxazolidinone signals ($\delta$ 4.01 and 4.46 for free and $\delta$ 4.70 and 5.06 for bound **3a** at 226 K). The intensity of the $^{13}$C satellite of $CD_2HNO_2$ (0.55% of the main signal) was subtracted from the intensity of the signal at $\delta$ 4.01. Spectra were measured over the temperature range 226−282 K; at higher temperatures, the spectra were significantly broadened by exchange, and accurate integration was not possible (see Supporting Information).

The equilibrium constant at various temperatures for the equilibrium depicted in eq 10 were determined from the standard expression for the equilibrium constant (eq 11). Simplification gives an expression (eq 12) which requires only initial concentrations of *rac*-**8** and **3a** as well as the concentration of bound oxazolidinone ($x$). The thermodynamic parameters are $K_{eq}$ (−30 °C) = 33.1; $\Delta G$ (226 K) = −9 kJ mol$^{-1}$; $\Delta G$°

$$\mathbf{3a} + rac\ \mathbf{8} \rightleftharpoons \mathbf{91} + \mathbf{9b} + {}^{-}OTf \tag{10}$$

$$K_{eq} = \frac{[\mathbf{9a} + \mathbf{9b}][OTf]}{[rac\text{-}\mathbf{8}][\mathbf{3a}]} \tag{11}$$

$$K_{eq} = \frac{x^2}{x^2 - x(Zr_o + L_o) + Zr_oL_o} \tag{12}$$

(33) Binsch, G., Kleier, D. A. *DNMR Version 4.0, General NMR Line-Shape Program with Symmetry and Magnetic Equivalence Factoring*; Department Of Chemistry, University Of Notre Dame: Notre Dame, IN. Revised by L. J. Letendre and J. A. Brunelle, Department Of Chemistry, Worcester Polytechnic Institute, Worcester, MA. Latest revision by Stephen H. Fleischman, Department Of Chemistry, University Of Vermont, Burlington, VT.

$= 1 \pm 5$ kJ mol$^{-1}$; $\Delta H = -41 \pm 3$ kJ mol$^{-1}$; $\Delta S = -140 \pm 14$ J mol$^{-1}$ K$^{-1}$.

**Variable-Temperature NMR Study of Interconversion of 9a and 9b.** To determine the effect of [**3a**] on the rate of interconversion, variable-temperature NMR experiments were conducted at *rac*-**8**:**3a** ratios of 1:1, 1:2, and 1:5 in 3:1 $CD_3NO_2$:$CD_2Cl_2$ solution at the same total concentration of *rac*-**8**. The $^{19}$F NMR spectra at any given temperature for these three samples were essentially identical, indicating that an oxazolidinone-mediated exchange process was minor compared to direct interconversion. The $^{19}$F signals of the two isomers (**9a** −77.79 ppm, **9b** −78.02 ppm relative to $CFCl_3$ at 233K) show no further sharpening below 247 K ($T_2$* for both isomers = 0.085 s). Due to interference from the broad lines resulting from the much faster triflate exchange process, it was not possible to accurately simulate the exchange process between **9a** and **9b** at higher temperatures for the 1:1 and 1:2 samples, because of the temperature dependence for binding of **3a** to *rac*-**8** (vide supra). Spectra obtained for the 1:5 mixture could be accurately simulated by DNMR4,[33] and both the experimental and simulated spectra are depicted in Figure 4. An Eyring plot gave the following activation parameters: $\Delta H^{\ddagger} = 72.0 \pm 3.8$ kJ mol$^{-1}$, $\Delta S^{\ddagger} = 58.2 \pm 2.9$ J mol$^{-1}$ K$^{-1}$ for the exchange process and as the equilibrium constant (for **9a** ⇄ **9b**) was also temperature dependent, as deduced from the simulated spectra, an Arrhenius plot gave $\Delta H_o = 2.55 \pm 0.25$ kJ mol$^{-1}$, $\Delta S_o = 18.8 \pm 2.1$ J mol$^{-1}$ K$^{-1}$.

**Determination of Enantioselectivity as a Function of Conversion for 3a and Cyclopentadiene.** Stock solutions of **3a** (53.3 mg, 0.35 mmol in 4.3 mL of 2-nitropropane, 0.082 M) and [*S*]-**8** (6.5 mg, 0.01 mmol in 540 $\mu$L, $0.018_5$ M) were prepared under nitrogen in a glovebox. Two milliliters of the solution of **3a** and 250 $\mu$L of the solution of [*S*]-**8** were added to two, round-bottomed flasks. After the mixture was cooled to −78 °C with vigorous stirring, 25 $\mu$L of CpH was added to each flask. The reactions were quenched after 30 and 180 s by the addition of 500 $\mu$L of pH 7 buffer. The mixtures were warmed to room temperature, and each was filtered through a short plug of silica gel, washing with diethyl ether. The filtrates were concentrated in vacuo, and the crude product mixtures were analyzed by $^1$H NMR spectroscopy to determine % conversion. The % ee was determined by HPLC on the crude samples; three replicates of the second sample were used to determine integration errors, and the results are summarized in eq 7.

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**Supporting Information Available:** $^1$H NMR NOE difference spectra of **9a** and **9b** obtained at 500 MHz in $CD_3NO_2$:$CD_2Cl_2$ solution at −45 °C, 2D $^1$H-EXCSY and 1D $^1$H, $^{13}$C, and $^{19}$F NMR spectra of **9a** and **9b**, experimental and simulated $^{19}$F NMR spectra for mixtures of *rac*-**8** and [$^n$Bu$_4$N][OTf] in $CD_3NO_2$ solution, and Eyring and Arrhenius plots for the triflate exchange process and for binding of **3a** to *rac*-**8**, respectively (14 pages). Ordering information is given on any current masthead page.

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