Asymmetric Induction in the Diels–Alder Reaction Using Chiral Metallocene Catalysts

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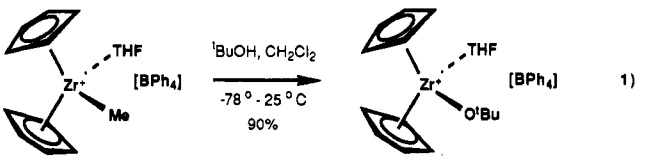
Summary: The Diels–Alder reaction between cyclopentadiene and various dienophiles is efficiently catalyzed by cationic zirconocene compounds (e.g. [Cp$_2$Zr(O^{t}Bu)-THF][BPh$_4$] (2)). The use of catalytic amounts of optically pure (S)-[ethylenebis(η^5-tetrahydroindenyl)]-zirconium tert-butoxide tetrahydrofuran tetraphenylborate (3) resulted in modest enantioselectivity in this C–C bond-forming process. Compound (S)-3 crystallizes in the hexagonal space group P6$_1$: a = 11.607(2) Å, c = 55.363(9) Å, V = 6459(2) Å^3, Z = 6 with R = 0.0278, R$_w$ = 0.0273 for 2534 observed reflections with F > 6.0σ(F). A model for the facial selectivity observed is presented on the basis of the structure of compound (S)-3.

Introduction

The chemistry of cationic metallocene compounds of the group 4 transition elements is the focus of much current research.[1] Most efforts have been directed toward the study of alkyl derivatives 1. We recently described the preparation of a cationic alkoxide derivative 2 which is an effective catalyst for the Diels–Alder reaction (eq 1).[2,3]



1) 1 → 2

In this paper, we present a more extensive study of the Diels–Alder reactions catalyzed by compound 2, the preparation of chiral catalysts of this type (i.e. 3), and the utility of this compound for effecting catalytic, asymmetric Diels–Alder reactions.

Results and Discussion

Since chiral, [1,2-ethylenebis(η^5-tetrahydroindenyl)]-zirconium dichloride (4) is readily available in large quantities from cheap starting materials,[4] we elected to study the utility of this compound as a precursor to Diels–Alder catalyst 3. Compound 4 was resolved using the procedure described by Buchwaid et al.,[5] by reaction of the racemate with 0.5 equiv of (S)-binaphthol (Scheme I). The cyclic (S,S)-binaphtholate derivative 5 so obtained, was converted to the dimethyl derivative 6 in 85% yield without difficulty. The optical purity of this material was 97.8% ee as determined by conversion to the bis((R)-O-acetyl mandelate) derivative.[6]

Preparation of cationic *tert*-butoxide derivative 3 was accomplished in 85% overall yield by treatment of compound 6 with 1.0 equiv of *tert*-butanol in toluene followed by in situ protonolysis with [Et$_3$NH][BPh$_4$] in THF (Scheme I, $[\alpha]_{435} = +540°$ ($c = 6.2$ mg/100 mL, THF)).

Single crystals of compound (S)-3 could be obtained by liquid diffusion of hexane into saturated THF solutions. Compound (S)-3 crystallizes in the chiral, hexagonal space group P6$_1$. Crystallographic data and selected bond lengths and angles appear in Tables I and II, respectively. A molecular plot of the cationic unit of compound 3 appears in Figure 1.[7] Unlike compound 2, substantial bending at the oxygen atom of the *tert*-butoxide ligand is observed (C(9)–O(1)–Zr(1) = 161.9(4) vs ca. 175°) and is accompanied by a significant increase in the Zr(1)–O(1) bond length (1.929(3) vs ca. 1.89 Å). This distortion is undoubtedly due, in part, to steric repulsion between the *tert*-butyl group and the six-membered ring of the tetrahydroindenyl ligand. Qualitatively, compound 3 appears to be as effective a catalyst as 2 *despite* the increase in steric hindrance at the metal center in the former compound. This feature may be related to the structural distortion that is evident in the alkoxide ligand.

The ansa ligand of compound 3 adopts the "forward" conformation[8] despite the presence of the bulky *tert*-butoxide ligand (Figure 2); presumably, the steric interaction between the *tert*-butyl group and the six-membered ring of the tetrahydroindenyl ligand is reduced by bending at oxygen in the manner indicated, and the in-plane coordination of the THF moiety also serves to reduce steric interactions between this group and the ansa ligand. Furthermore, the ansa ligand adopts a skewed, asymmetric conformation[9] with respect to the two equatorial ligands; presumably, this also avoids steric repulsion between the *tert*-butoxide groups and the six-membered ring of the tetrahydroindenyl ligand.

(1) For a recent review see: Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325.

(2) Collins, S.; Koene, B. E.; Ramachandran, R.; Taylor, N. J. *Organometallics* **1991**, *10*, 2092.

(3) The use of achiral, titanium- and zirconium-based catalysts somewhat analogous to those discussed here (and in ref 2) for use in the Diels–Alder reaction has recently been reported. (a) Hollis, T. K.; Robinson, N. P.; Bosnich, B. B. *J. Am. Chem. Soc.* **1992**, *114*, 5464. (b) Hollis, T. K.; Robinson, N. P.; Bosnich, B. *Organometallics* **1992**, *11*, 2745. On the basis of data presented in the latter reference, these catalysts possess comparable activity to those reported here although they do not appear to be suitable for use with acrylate dienophiles.

(4) (a) Wild, F. R. W. P.; Wasiucionek, M.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1985**, *288*, 63. (b) Collins, S.; Kuntz, B. A.; Taylor, N. J.; Ward, D. G. *Ibid.* **1988**, *342*, 21.

(5) Grossman, R. B.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1991**, *113*, 2321. We thank Prof. Buchwald for a copy of the supplementary material describing this process.

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

(7) The geometry of the tetraphenylborate counterion is unexceptional; see the supplementary material for details.

(8) For a discussion of *ansa*-metallocene conformations see: (a) Collins, S.; Hong, Y.; Ramachandran, R.; Taylor, N. J. *Organometallics* **1991**, *10*, 2349. (b) Burger, P.; Diebold, J.; Gutmann, S.; Hund, H.-U.; Brintzinger, H.-H. *Ibid.* **1992**, *11*, 1319.

(9) This type of conformation has been observed previously in *ansa*-metallocenes with bulky substituents on the cyclopentadienyl rings: See ref 8 and: (a) Collins, S.; Hong, Y.; Taylor, N. J. *Organometallics* **1990**, *9*, 2695.

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Scheme I

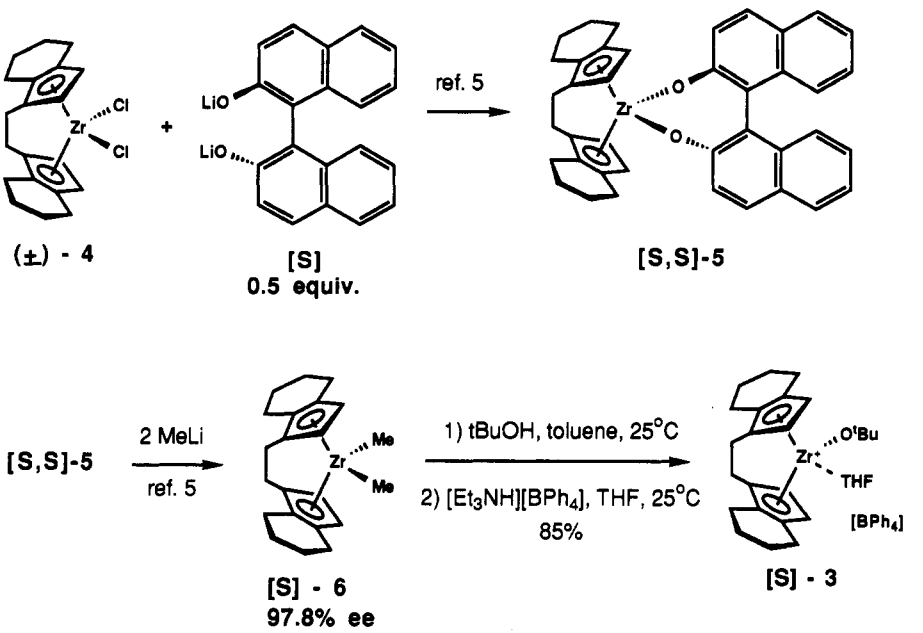


Table I. Summary of Crystallographic Data for Compound (*S*)-3[a]

emp form	$C_{52}H_{61}BO_2Zr$	λ (Å)	0.710 73
cryst col; habit	colorless hexagonal needle fragment	ads coeff (cm^{-1})	2.95
		2θ range (deg)	4.0–45.0
cryst size (mm)	0.22 {001} × 0.22 {00$\bar{1}$} × 0.23 {100}[b]	scan type	ω
		scan range (ω) (deg)	0.70
cryst syst	hexagonal	no. of measd rflns	3244
space group	$P6_1$	no. of ind. rflns	2856
T (K)	175	no. of obsd. rflns ($F > 6.0\sigma(F)$)	2534
a (Å)	11.607(2)	R (%)	2.78
c (Å)	55.363(9)	R_w (%)	2.73
V (Å^3)	6459(2)	GOF	1.81
Z	6		
ρ_{calc} (g/cm^3)	1.265		

[a] For full details see the supplementary material. [b] Distances from a common center.

Table II. Selected Bond Lengths (Å) and Angles (deg) for Compound (*S*)-3[a,b]

bond lengths (Å)[c]		bond angles (deg)[c]	
Zr(1)–O(1)	1.929(3)	cent–Zr(1)–cent'	123.3(2)
Zr(1)–O(2)	2.268(4)	O(1)–Zr(1)–O(2)	93.8(1)
Zr(1)–cent	2.243(6)	C(9)–O(1)–Zr(1)	161.9(4)
Zr(1)–cent'	2.223(6)	Zr(1)–O(2)–C(13)	118.9(2)
O(1)–C(9)	1.453(5)	Zr(1)–O(2)–C(16)	130.9(4)
		C(13)–O(2)–C(16)	107.3(4)

[a] For a complete listing see the supplementary material. [b] For the numbering scheme please see Figure 1; cent and cent' are the two centroids of the cyclopentadienyl rings. [c] Estimated standard deviations in parentheses.

A series of Diels–Alder reactions between cyclopentadiene and various dienophiles were studied in the presence of 2–5 mol % of compound **2** or **3**, and the results are summarized in Table III.

In the case of methyl acrylate (entries 1–3), high endo selectivity is observed at room temperature and the selectivity improves with decreasing temperature using catalyst **2**. The reaction between methyl methacrylate and cyclopentadiene was catalyzed by compound **2** (entry 4); however, the catalyzed reaction was not very stereoselective. In this case, using 2.5 equiv of cyclopentadiene, the catalyzed reaction afforded the Diels–Alder adduct in

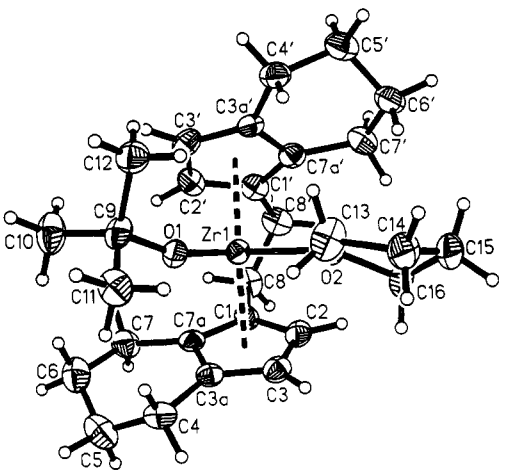


Figure 1. Molecular structure of the cationic unit of compound (*S*)-**3** with 50% probability thermal ellipsoids depicted.

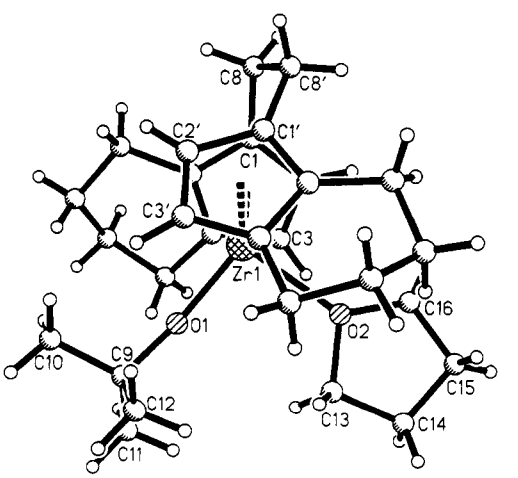
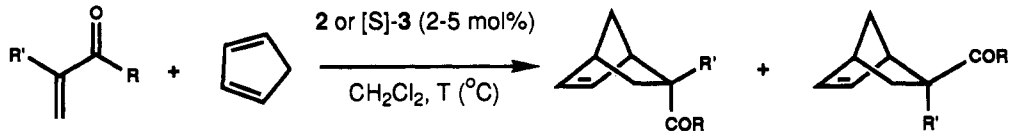


Figure 2. View of the structure of compound (*S*)-**3** orthogonal to the plane defined by O(1)–Zr(1)–O(2) without thermal ellipsoids depicted.

54% yield (100% conversion yield based on unreacted dienophile) after 3 h at room temperature as revealed by GC. By this time, most of the cyclopentadiene had

Table III. Diels–Alder Reactions Catalyzed by Compound 2 and (*S*)-3[a]



entry	catalyst (mol %)	R	R′	*T* (°C)	time (h)	yield (%)[b]	endo:exo[c]	(2*R*):(2*S*) (endo or exo)[d]
1	**2** (5.0)	OMe	H	25	1.0	95	11:1	
2	**2** (5.0)	OMe	H	0	3.0	90	15:1	
3	**2** (5.0)	OMe	H	–45	9.0	76	22:1	
4	**2** (5.0)	OMe	Me	25	3.0	55	~1:1	
5	**2** (2.0)	H	H	25	*e*	100	3.2:1	
6	**2** (2.0)	H	H	–78	1.0	96	4.5:1	
7	**2** (2.0)	H	Me	–78	3.0	94	1:15.6	
8	**3** (5.0)	OMe	H	25	0.5	98	7.0:1	1.08:1
9	**3** (5.0)	OMe	H	0	3.0	97	8.7:1	1.21:1
10	**3** (5.0)	OMe	H	–45	9.0	87	17.4:1	1.72:1
11	**3** (2.0)	H	H	–78	3.0	93	4.8:1	1:3.21
12	**3** (2.0)	H	Me	0	1.0	93	1:12.6	1.45:1[f,g]
13	**3** (2.0)	H	Me	–78	3.0	94	1:25.1	1.92:1[f,g]

[a] All reactions were conducted in CH_2Cl_2 solution (3.0 mL) using 2.5 mmol of cyclopentadiene, 1.0 mmol of dienophile and 0.02–0.05 mmol of compound **2** or **3**. [b] Determined by GC using an internal standard (*n*-decane). [c] Determined by GC and/or ^{1}H NMR spectroscopy. [d] Ratio of enantiomers determined by GC on a 30-m J&W Scientific Cyclodex-B column unless otherwise noted. Absolute configurations based on optical rotations as compared to literature values.[21,22] [e] Instantaneous on mixing. [f] Ratio of enantiomers determined by ^{1}H NMR spectroscopy in the presence of (+)-Eu(hfc)$_3$. [g] The major enantiomer formed is (2*R*)-exo.

Table IV. Selected ^{13}C and ^{1}H NMR Chemical Shift Data for the *p*-Tolualdehyde Complex of Compound 2[a]

[$Cp_2ZrOtBu(THF)$][BPh_4] (**2**)	**2** + 1.0 equiv of *p*-tolualdehyde[b]	*p*-tolualdehyde
^{1}H NMR[b]	^{1}H NMR	^{1}H NMR
6.35 (s, CpH)	9.45 (s, CHO)	9.96 (s, CHO)
3.48 (m, bound THF)	7.78 (d, *J* = 8.0 Hz, *o*-ArH)	7.82 (d, *o*-ArH)
1.88 (m, bound THF)	7.45 (d, *J* = 8.0 Hz, *m*-ArH)	7.43 (d, *m*-ArH)
1.28 (s, tBu)	6.32 (s, CpH)	2.52 (s, *p*-CH_3)
	3.56 (m, free THF)	
	2.50 (s, *p*-CH_3)	
	1.81 (m, free THF)	
	1.29 (s, tBu)	
^{13}C NMR[b]	^{13}C NMR	^{13}C NMR
114.6 (s, Cp)	197.5 (ArCHO)	191.7 (CHO)
83.0 [s, $OC(CH_3)_3$, quaternary C]	149.4 (ipso-C–CHO, ArChO)	145.3 (ipso-C–CHO)
78.1 (s, bound THf, α-C)	132.2 (ipso-C–CH_3, ArCHO)	134.0 (ipso-C–CH_3)
31.6 [s, $OC(CH_3)_3$, primary C]	131.4 (br, ortho-CH, ArCHO)	129.6 (*o*-CH)
25.8 (s, bound THF, β-C)	130.2 (*m*-CH, ArCHO)	129.5 (*m*-CH)
	67.5 (free THF)	21.6 (*p*-CH_3)
	25.6 (free THF)	
	22.2 (*p*-CH_3, ArCHO)	

[a] In CD_2Cl_2 solvent at –89 °C at 200 MHz (for ^{1}H) and 50 MHz (for ^{13}C). [b] Resonances for the tetraphenylborate counterion have been omitted for clarity and are unaffected by the addition of aldehyde.

dimerized and thus accounts for the diminished yield of product seen with this relatively unreactive dienophile.

Aldehyde dienophiles react rapidly and cleanly with cyclopentadiene in the presence of cation **2**; reactions are usually complete after 1–3 h at –78 °C. High exo selectivity was observed in the cycloaddition of methacrolein and cyclopentadiene (entry 7), whereas in the case of acrolein (entries 5 and 6), the endo adduct predominated but the level of selectivity was somewhat reduced compared to the uncatalyzed reaction (~4:1 at 25 °C).

The reaction of metallocene **2** with 1 equiv of *p*-tolualdehyde was studied by variable-temperature ^{1}H and ^{13}C NMR spectroscopy in CD_2Cl_2 in an attempt to address the mode(s) of complexation of a carbonyl compound to the metal center. Under these conditions, displacement of coordinated THF is highly favored and signals characteristic of the coordinated aldehyde and free THF are observed (Table IV).

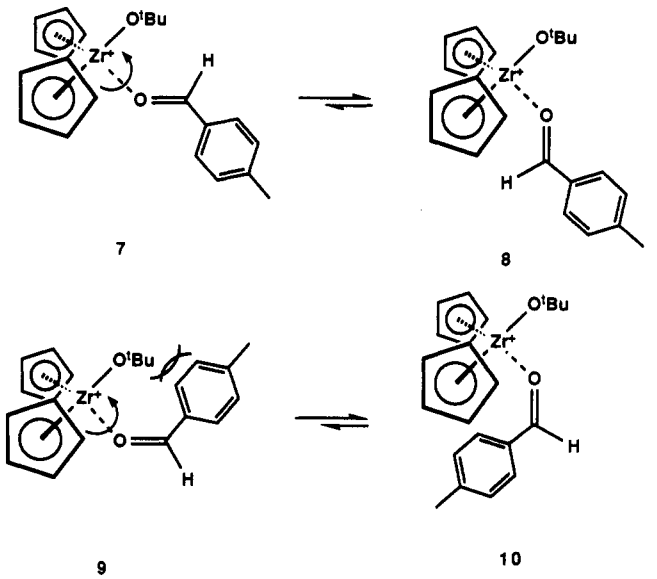
Particularly noteworthy of the spectral characteristics of the complexed aldehyde is the *upfield* shift of ca. 0.5 ppm of the aldehyde proton and the downfield shift of the carbonyl carbon (to ca. 197.5 from 191.7 ppm). The latter behavior is expected on complexation whereas the former result suggests that the aldehyde proton is located within a shielding region of the metallocene complex.[10] Of the two possible modes of complexation (i.e. syn to aldehyde H or anti), only syn complexation is expected to lead to this result (structures **7** and **8**, Scheme II). In support of this hypothesis, the chemical shifts of the ortho aromatic protons are essentially unaffected by complexation; anti complexation (i.e. structures **9** and especially **10**) should lead to perturbation of the chemical shifts of the aromatic protons of the aldehyde.

For syn complexation of the aldehyde, there are two possible conformers that maximize electronic stabilization of the metal center[11] while minimizing steric interactions between the metal ligands and the aromatic ring of the aldehyde (structures **7** and **8**, Scheme II). At the lowest temperature studied (–89 °C), there is no evidence from either the ^{13}C or ^{1}H NMR spectra for the presence of two

(10) For a discussion of chemical shift anisotropy in the ^{1}H NMR spectra of titanocene and zirconocene complexes see: (a) Paquette, L. A.; Moriarty, K. J.; Rogers, R. D. *Organometallics* **1989**, *8*, 1506 and references therein.

(11) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

Scheme II



conformers of this type, although we cannot rule out very rapid interconversion.

Low-temperature NOE difference ^{1}H NMR spectra were recorded while the aldehyde proton was irradiated. This led to a large enhancement of the signal due to the ortho aromatic protons of the aldehyde (ca. 8%) as expected, and as well, small but measurable enhancements of the *tert*-butyl (1.4%) and Cp resonances (1.9%) of complex **2** were observed. This result seems consistent with conformer **7** being highly favored on a time-averaged basis.[12]

The stereochemical results observed using catalyst **2** and aldehyde dienophiles can be partially rationalized with reference to possible structure(s) of the dienophile–metallocene complex (Scheme III). Syn coordination of the dienophile in its s-trans conformation, exposes the double bond to attack by the diene. In the case of acrolein (structure **11**) the electronically favored endo approach is sterically less favorable than the exo approach and this may account for the somewhat low endo selectivity observed. The exo selectivity observed in the reaction of methacrolein with cyclopentadiene is to be expected;[14] in this case the inherent exo selectivity of this dienophile is likely to be augmented by the sterically more favorable approach of the diene to either the s-cis or s-trans conformer of the coordinated dienophile (structures **12** and **13**).[15]

It is expected, on the basis of other studies concerned with ester ligation of Lewis acids,[16] that coordination anti to ester oxygen will be favored. The high endo selectivity observed in the cycloaddition of methyl acrylate could stem from both the electronically and sterically favored approach of the diene to the coordinated dienophile in its s-trans conformation (structure **14**).[15]

Similar trends in the endo:exo selectivity are seen when (*S*)-**3** is used as the catalyst (Table III, entries 8–13). The level of enantioselectivity observed using this catalyst is modest. Under optimal conditions (entry 10), methyl acrylate and cyclopentadiene furnished the (2*R*)-endo adduct in 26.5% ee. As entries 8–10 demonstrate, the increase in endo selectivity that is observed as the temperature is decreased is approximately matched by a corresponding increase in the level of enantioselectivity.

Reaction of acrolein with cyclopentadiene occurred with an opposite sense of facial selectivity and provided the (2*S*)-endo product with an optical purity of 52.4% ee (entry 11). Finally, the (2*R*)-exo adduct (31.5% ee) predominates in the reaction between methacrolein and cyclopentadiene (entry 13).

The results obtained using this catalyst are also consistent with the models proposed in Scheme III. As acrolein and methyl acrylate coordinate to the metal center in a manner that exposes the opposite enantioface to incoming diene, one expects a reversal in the sense of asymmetric induction using a chiral catalyst (e.g. structures **15** and **16**). Clearly, the energy differences involved between the two possible approaches of the diene are minimal even at low temperatures.[15]

A view orthogonal to that depicted in Figure 1 is shown in Figure 2. It is evident from this picture that the six-membered rings of the tetrahydroindenyl ligand only extend as far as C(13) of the coordinated THF moiety. In the putative dienophile–cation complexes this would roughly correspond to the location of the carbonyl carbon. Thus the modest facial selectivity observed in the Diels–Alder reaction may be related to the imperfect shielding of the C=C bond of the dienophile by the six-membered rings.

Conclusions

The Diels–Alder reaction between cyclopentadiene and various dienophiles is efficiently and cleanly catalyzed by cationic alkoxide complexes. The use of a chiral catalyst led to a modest level of asymmetric induction in this C–C bond-forming process. While some caution should be exercised in interpreting these results, a simple model based on the interaction of the dienophile with the metal center appears to account for them. Future studies will concentrate on the influence of an increase in steric hindrance at the metal center on the level and sense of asymmetric induction and on the use of conformationally well-defined dienophiles.

Experimental Section

All solvents and chemicals were reagent grade and purified as required. Tetrahydrofuran and toluene were dried by distillation from sodium–benzophenone ketyl. Dichloromethane was distilled from CaH_2 under nitrogen. Triethylammonium tetraphenylborate was prepared and purified using a literature procedure.[17] [Ethylenebis(η^5-tetrahydroindenyl)]zirconium dichloride (**4**) was prepared as described previously.[4b] (±)-2,2′-Binaphthol was resolved using the method of Kazlauskas.[18] The

(12) Additional support for conformer **7** being the most stable one is derived from molecular mechanics calculations on this complex and that of **8**.[13] The difference in the MMX energy calculated is 0.99 kcal/mol favoring complex **7**.

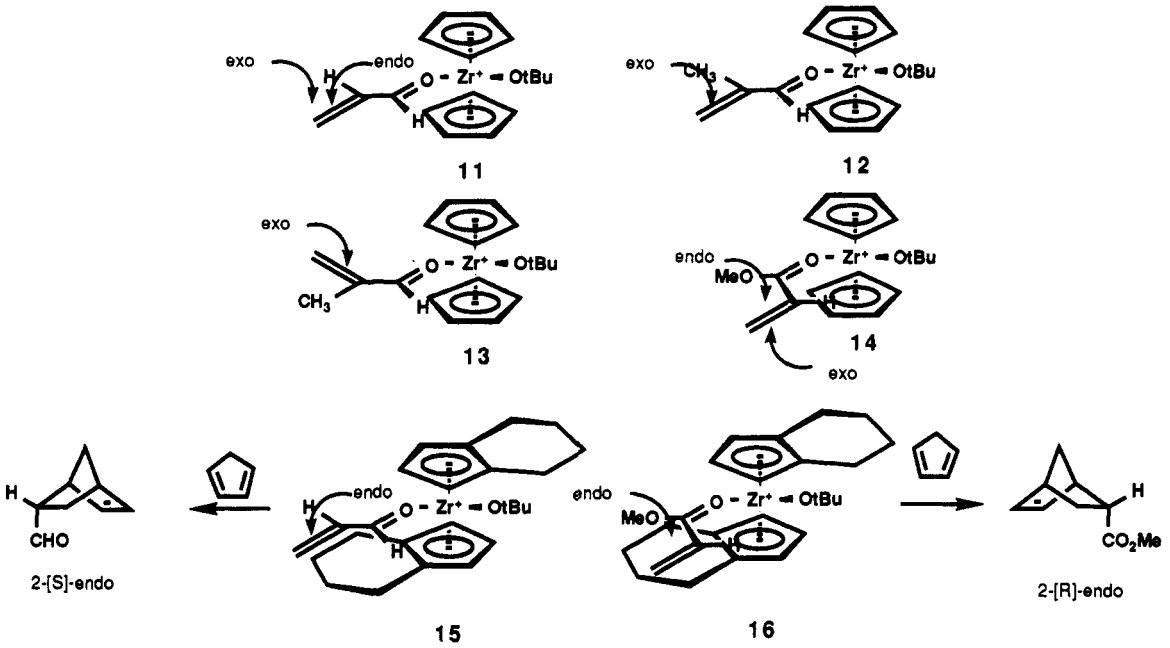
(13) The X-ray geometry of complex **2** was employed and the geometry of the complex minimized using the MMX force field contained within the program PCModel (Serena Software Inc.). Since the MMX force field does not contain parameters appropriate for the sp-hybridized oxygen of the *tert*-butoxide ligand in **2**, the *x*, *y*, *z* coordinates of the quaternary carbon of this ligand, the oxygen atom, the metal center, and the aldehyde oxygen were kept fixed at the values observed in the X-ray structure of the THF adduct, and all other atoms were allowed to minimize. Full details of these calculations are available on request.

(14) The tendency of α-alkyl-substituted dienophiles to undergo exo additions to cyclopentadiene is well-known. See ref 22 and also: Berson, J. A.; Hamlet, Z.; Mueller, W. A. *J. Am. Chem. Soc.* **1962**, *84*, 297.

(15) This analysis is also supported by MMX calculations on dienophile complexes and the Diels–Alder transition states derived from them. For details, see ref 13.

(16) Hawkins, J. M.; Loren, S. *J. Am. Chem. Soc.* **1991**, *113*, 7794 and references therein.

Scheme III



method of Buchwald was used to resolve compound 4 without modification.[5] (*R*)-*O*-Acetyl mandelate was prepared from (*R*)-mandelic acid using a literature procedure.[19]

^1H and ^{13}C NMR spectra were recorded on a Bruker AM-250 or AC-200 spectrometer; chemical shifts are referenced with respect to residual undeuterated solvent. Low-temperature NMR spectra were obtained in CD_2Cl_2 solution; temperatures were determined using a standard sample of methanol (4% in methanol-d_4). IR spectra were obtained using a Bomem MB-100 FTIR instrument. Optical rotations were recorded using a JASCO DIP-360 automatic polarimeter. Gas chromatography was performed on a Hewlett-Packard 5890 instrument equipped with FID detectors and a 0.25-mm × 30-m J&W Scientific DB-1701 capillary column or with a 0.25-mm × 30-m J&W Scientific Cyclodex-B column. HPLC analyses were conducted on a Waters 600E chromatograph equipped with a Waters 480 UV–vis detector and a 4.6-mm × 25-cm Regis Pirkle Covalent leucine or Pirkle Covalent naphthylalanine column; hexane–2-propanol was used as eluent. Elemental analyses were determined by M. H. W. Laboratories of Phoenix, AZ.

Preparation of Compound 2.[2] A suspension of $[Cp_2ZrMe(THF)][BPh_4]$[20] (1.256 g, 2.0 mmol) in CH_2Cl_2 (40 mL) was *prepared* at −78 °C. A solution of dry *tert*-butanol in CH_2Cl_2 (2.0 mL of 1.05 M, 2.1 mmol) was added dropwise via syringe. The mixture was allowed to warm to room temperature over 1 h and stirred at room temperature for 3 h. The yellow solution gradually faded to provide a very pale yellow solution. The solvent was removed in vacuo (10^{-2} mmHg) and the white, solid residue dissolved in a minimal volume of dry THF (ca. 20 mL). Hexanes (20 mL) were slowly added at room temperature to precipitate the title compound. The mixture was filtered, washing with additional hexanes, and the fine, white solid was dried in vacuo (1.235 g, 90% yield). This material is sufficiently pure for use as a catalyst; the only contaminant is a small amount of free THF (usually less than 10 mol %). An analytical sample can be obtained by liquid diffusion of hexanes into a saturated solution of this compound in THF. ^1H NMR (200 MHz, CD_2Cl_2, 25 °C): δ 7.46 (br m, 8 H), 7.15 (t, J = 7.0 Hz, 8 H), 7.00 (t, J = 7.0 Hz, 4 H), 6.32 (s, 10 H), 3.23 (m, 4 H), 1.82 (m, 4 H), 1.32 (s, 9 H) ppm. ^{13}C NMR (50 MHz, CD_2Cl_2, 25 °C): δ 162.6 (four lines, $^1J_{CB}$ = 49.2 Hz), 135.4 (meta carbons), 125.7 (four lines, $^2J_{CB}$ = 2.4 Hz), 121.7 (para carbons), 114.6 (C_5H_5), 82.95 [$OC(CH_3)_3$], 77.96 [$O(CH_2CH_2)_2$], 31.35 [$OC(CH_3)_3$], 25.69 [$O(CH_2CH_2)_2$] ppm. IR (Nujol) 1480, 1427, 1365, 1174, 1002, 843, 820, 811, 741, 735, 707 cm^{-1}. Anal. Calcd for $C_{42}H_{47}BO_2Zr$: C, 73.55; H, 6.91. Found: C, 73.37; H, 7.12.

Low-Temperature NMR Experiments. A solution of compound **2** (68.6 mg, 0.05 mmol) in CD_2Cl_2 (0.5 mL) in a screw top NMR tube fitted with a septum was cooled to −89 °C in the probe of a Bruker AC-200 spectrometer. The ^1H and ^{13}C NMR spectra were recorded (see Table IV), and to the cold, colorless solution was added 12.0 μL of *p*-tolualdehyde (0.05 mmol) via syringe. The solution changed to bright yellow, was shaken briefly to mix, and then was returned to the probe at −89 °C. The ^1H and ^{13}C NMR spectra were recorded (see Table IV). Only signals due to free THF and complexed aldehyde were observed in the ^1H NMR spectrum of the mixture; at this temperature self-exchange of THF is slow on the NMR time scale and thus separate signals for **2** (THF) and free THF should have been observable.[2] Therefore, an estimate for equilibrium constant for the formation of the aldehyde complex is ~20. At −89 °C, aside from viscosity-induced line-broadening, the only evidence of a dynamic process was observed in the ^{13}C NMR spectrum. The signal due to the ortho carbons of the complexed aldehyde was the only one that was line broadened—a result that may be attributed to hindered rotation about the C(aryl)–CHO bond in the complexed aldehyde.

Difference NOE ^1H NMR spectra were recorded at −89 °C while the signal of the aldehyde proton was irradiated. Eight FIDs were acquired using a 30° pulse width with on-resonance low-power decoupling and a delay of 10 s (to allow buildup of NOE) and then eight FIDs were acquired with off-resonance low-power decoupling under the same conditions. The experiments were averaged for a total of 16 cycles (or 128 FIDs). The enhancements are as follows: ortho protons, 8.3%, Cp protons, 1.9%, *tert*-butyl protons, 1.4%.

Optical Purity of (*S*)-[Ethylenebis(η⁵-tetrahydroindenyl)]zirconium Dimethyl (6). A solution of compound (*S*)-**6** [38.8 mg, 0.100 mmol, $[\alpha]_D$ = +169 ± 3° (c = 0.04 g/mL, CH_2Cl_2)] in dry $CDCl_3$ (2.0 mL) was treated in one portion with (*R*)-*O*-acetyl mandelate (42.7 mg, 0.22 mmol, >99.5% ee by HPLC; Pirkle Covalent leucine, hexane:2-propanol 85:15) at room temperature. After gas evolution had ceased (15 min), the ^1H NMR (250-MHz) spectrum of the solution was recorded. The area ratio of the doublet (CpH) at 5.18 (due to the (*S,R,R*) diastereomer)[6] to that at 5.36 (due to the (*R,R,R*) diastereomer)[6] ppm was 89.2:1 corresponding to an optical purity of 97.8%.

Preparation of Compound 3. To a solution of (*S*)-[ethyl-

(17) Amorose, D. M.; Lee, R. A.; Petersen, J. L. *Organometallics* **1991**, *10*, 2191.
(18) Kazlauskas, R. J. *Org. Synth.* **1991**, *70*, 60.
(19) Breithole, E. G.; Stammer, C. H. *J. Org. Chem.* **1974**, *39*, 1311.
(20) Jordan, R. F.; Bajgur, C. S. *J. Am. Chem. Soc.* **1986**, *108*, 7410.

enebis(η^5-tetrahydroindenyl)]zirconium dimethyl (565.6 mg, 1.47 mmol) in dry toluene (14.0 mL) under nitrogen was added *tert*-butanol (140 μL, 1.0 equiv) by syringe. After 3 h at room temperature, the solution was concentrated to dryness in vacuo. The white solid was dissolved in 10 mL of dry THF and cooled to −78 °C, and a solution of $[Et_3NH][BPh_4]$ (617.9 mg, 1.47 mmol) in THF (15 mL) was added via syringe. The syringe was rinsed with 2 × 5 mL of THF to complete the transfer. The mixture was warmed to room temperature (30 min) and then stirred at room temperature for 2 h. The very pale yellow solution was concentrated to ca. 5 mL and then diluted with ca. 20 mL of dry toluene with vigorous stirring. The mixture was concentrated to dryness under high vacuum (0.01 mmHg) to provide a solid foam. The foam was slurried in toluene (10 mL) with vigorous stirring to give a white powder which was filtered, washing with toluene (10 mL) and then hexane (2 × 10 mL) prior to drying in vacuo (1.025 g, 85% yield). This material is sufficiently pure (NMR) for subsequent use as a catalyst. An analytical sample can be obtained by slow diffusion of hexane into a THF solution of this compound. $[\alpha]_{435} = +540°$ (c = 6.2 mg/100 mL, THF). ^{1}H NMR (300 MHz, THF-d_8): δ 7.25 (br m, 8 H), 6.83 (t, J = 7.8 Hz, 8 H), 6.68 (t, J = 7.8 Hz, 4 H), 6.50 (d, J = 1.9 Hz, 1 H), 5.87 (d, J = 1.9 Hz, 1 H), 5.70 (d, J = 1.9 Hz, 1 H), 5.66 (d, J = 1.9 Hz, 1 H), 3.2–2.8 (m, 4 H), 2.70 (dt, 1 H), 2.7–2.4 (complex m, 6 H), 2.18 (dt, 1 H), 1.9–1.7 (m, 4 H), 1.7–1.4 (m, 4 H), 1.32 (s, 9 H) ppm. ^{13}C NMR (75.5 MHz, THF-d_8): δ 165.2 (1:1:1:1 q, J_{CB} = 49.8 Hz, ipso C, BPh_4), 137.2 (BPh_4 + quaternary Cp C), 136.9 (quaternary Cp C), 136.6 (quaternary Cp C), 135.9 (quaternary Cp C), 132.8 (quaternary Cp C), 125.8 (1:1:1:1 quartet, J_{CB} = 4.9 Hz, ortho C, BPh_4), 123.8 (quaternary Cp C), 121.9 (BPh_4), 115.7 (tertiary Cp C), 113.7 (tertiary Cp C), 111.4 (tertiary Cp C), 109.0 (tertiary Cp C), 83.2 [$OC(CH_3)_3$], 79.5 (5 lines, bound THF-d_8), 33.4 [$OC(CH_3)_3$], 29.1 (CH_2 bridge), 28.2 (CH_2 bridge), 24.8, 24.5, 24.4, 24.2 (all CH_2 adjacent to Cp rings), 23.5 (2 C), 23.34, 23.32 (remaining CH_2 groups) ppm. IR (Nujol mull): 3030, 1579, 1463, 1360, 1169, 965, 839, 802, 746, 731, 704, 622 cm^{-1}. Anal. Calcd for $C_{52}H_{61}BO_2Zr$: C, 76.16; H, 7.50. Found: C, 76.24; H, 7.32.

X-ray Diffraction Studies on Compound 3. Single crystals of **3** suitable for X-ray diffraction studies were grown by liquid diffusion of hexane into a saturated THF solution: A needle fragment of dimensions 0.22 {100} × 0.22 {00$\bar{1}$} × 0.23 {100} mm was mounted on a Nicolet-Siemens R3m/V diffractometer. Intensity data were collected using graphite-monochromated, Mo Kα radiation (λ = 0.710 73 Å) at 175 K. Accurate unit cell dimensions were determined using 25 general reflections ($21 < 2\theta < 29°$) well distributed in reciprocal space. Background measurements were made at the beginning and end of each scan for a total time equal to half the scan time. Crystal stability was monitored by measuring two standard reflections every 100 measurements. Due to the cell dimensions (long c-axis), a small percentage of weak data was rejected due to overlap problems. Absorption corrections to the data were made using a face-indexed numerical method (transmission factors 0.8815–0.8926).

The structure was solved by Patterson and Fourier techniques using Siemens SHELXTL-PLUS software running on a DEC 3100 computer. Isotropic refinement of all non-hydrogen atoms converged with R = 0.0583. Anisotropic refinement of all non-hydrogen atoms converged with R = 0.0527. Hydrogen atoms were included in the final refinement in calculated positions with fixed isotropic thermal parameters; R = 0.0278; R_w = 0.0273 with $w^{-1} = \sigma^2(F)$. The highest residual electron density was 0.30 e A^{-3} whereas the largest difference hole was −0.43 e A^{-3}.

A summary of the crystal, collection, and refinement data appears in Table I, and a list of selected bond lengths and angles, in Table II. Full details of the crystal, collection, and refinement data are summarized in the supplementary material along with tables of atomic coordinates and isotropic thermal parameters (Table 1), bond lengths and angles (Tables 2 and 3, respectively), anisotropic thermal parameters (Table 4) and H-atom coordinates and isotropic thermal parameters (Table 5). A molecular plot of the structure of the tetraphenylborate anion has also been deposited.

As the space group $P6_1$ lacks a unique origin, solution in the enantiomorphic cell $P6_5$ was also attempted: Refinement as described above converged with R = 0.0287 and R_w = 0.0285, clearly indicating that $P6_1$ is the correct enantiomorphic cell.

Diels–Alder Reactions Catalyzed by 2 or 3. A solution of the catalyst (0.02 or 0.05 mmol) in 3.0 mL of dry CH_2Cl_2 was prepared at −78 °C. The solution was warmed to the temperature of the reaction (see Table I), and n-decane (100 μL), freshly cracked cyclopentadiene (2.5 mmol), and the dienophile (1.0 mmol) were added consecutively by syringe. The solution was kept at the reaction temperature until the dienophile had been consumed (GC). The yields and endo:exo ratios could be determined by GC analysis on a Hewlett-Packard 5890 instrument equipped with a 30-m J&W Scientific DB-1701 column.

Optical purities could be determined by analysis of the mixtures on a 30-m J&W Scientific Cyclodex-B column. Assignments, retention times, and conditions are as follows.

Methyl (2*R*)-*endo*-Bicyclo[2.2.1]hept-5-ene-2-carboxylate (14.75 min, 100 °C, Isothermal), Methyl (2*S*)-*endo*-Bicyclo-[2.2.1]hept-5-ene-2-carboxylate (15.16 min, 100 °C, Isothermal), (2*R*)-*endo*-Bicyclo[2.2.1]hept-5-ene-2-carboxaldehyde (28.64 min, 80 °C, Isothermal), and (2*S*)-*endo*-Bicyclo[2.2.1]-hept-5-ene-2-carboxaldehyde (28.96 min, 80 °C, Isothermal). To isolate the products, the addition of n-decane was eliminated and, after the reaction was complete, the mixture was diluted with pentane (10 mL) and stirred over silica gel (1 g) to remove the catalyst. The mixture was filtered, washing with ether, and the filtrate concentrated in vacuo (100 mmHg) at 0 °C to provide crude product (>85% purity, contaminated with small amounts of dicyclopentadiene) which could be further purified by bulb-to-bulb distillation at 20 mmHg.

The optical purity of *exo*-2-methylbicyclo[2.2.1]hept-5-ene-2-carboxaldehyde could be determined by ^{1}H NMR spectroscopy in $CDCl_3$ solvent at 200 MHz in the presence of 5–10 mol % (+)-Eu(hfc)$_3$ by comparing the *intensities* of the two partially resolved signals due to the aldehyde protons of the diastereomeric complexes: (2*R*) δ = 10.27 ppm; (2*S*) δ = 10.29 ppm.

Optical rotations and ^{1}H NMR spectra of the purified products were recorded, and the data are summarized below.

Methyl (2*R*)-*endo*-Bicyclo[2.2.1]hept-5-ene-2-carboxylate. $[\alpha]_D = +38.2°$ (95% EtOH) [lit.[21] $[\alpha]_D = -141°$ (95% EtOH) for the (2*S*) enantiomer]. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.23 (dd, 1 H), 5.97 (dd, 1 H), 3.62 (s, 3 H), 3.18 (br s, 1 H), 2.98 (t, 1 H), 2.94 (br s, 1 H), 1.93 (two overlapping dd, 2 H), 1.37 (complex m, 1 H), 1.16 (dt, 1 H).

(2*S*)-*endo*-Bicyclo[2.2.1]hept-5-ene-2-carboxaldehyde. $[\alpha]_D = -44.0°$ (EtOH) [lit.[22] $[\alpha]_D = -83.3°$ (EtOH)]. ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.42 (d, 1 H), 6.23 (dd, 1 H), 6.03 (dd, 1 H), 3.78 (t, 1 H), 3.26 and 3.05 (br s, total 2 H), 2.94 (complex m, 1 H), 1.75 (complex m, 1 H), 1.37 (dt, 1 H), 1.13 (complex m, 1 H).

(2*R*)-*exo*-2-Methylbicyclo[2.2.1]hept-5-ene-2-carboxaldehyde. $[\alpha]_D = -7.29°$ (EtOH) [lit.[22] $[\alpha]_D = +23.3°$ (EtOH) for the (2*S*) enantiomer]. ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.74 (s, 1 H), 6.28 (dd, 1 H), 6.04 (dd, 1 H), 2.83 and 2.76 (br s, total 2 H), 2.21 (dd, 1 H), 1.88 (AB multiplet, 2 H), 1.02 (s, 3 H), 0.76 (dt, 1 H).

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Supplementary Material Available: Tables of crystallographic data, atomic coordinates and isotropic thermal parameters, bond lengths and angles, anisotropic thermal parameters, and H-atom coordinates and isotropic thermal parameters and an ORTEP diagram for **3** (11 pages). Ordering information is given on any current masthead page.

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(21) Berson, J. A.; Walla, J. S.; Remanick, A.; Suzuki, S.; Reynolds-Warnhoff, P.; Willner, D. *J. Am. Chem. Soc.* **1961**, *83*, 3986.
(22) Hashimoto, S.; Komeshima, N.; Koga, K. *J. Chem. Soc., Chem. Commun.* **1979**, 437 and references therein.