of signals in the product from signals due to polyethylene. However, ICP analysis for tin from an acid-digested sample showed that some tin had been introduced at a level of 0.45 mmol of $SnBu_2Cl$/g of oligomer. Similar procedures using diphenyltin dichloride and tin tetrachloride yielded oligomer **3** and a 1:1 mixture of oligomers **6** and **7**, respectively, which were analyzed and shown to have 0.62 mmol of $-SnPh_2Cl$/g of oligomer and 0.58 mmol of "Sn"/g of oligomer. Oligomer **3** was further characterized by ^1H NMR spectroscopy and shown to have a molecular weight of 1423 on the basis of integration of the $-CH_3$ signal versus 1,1,2,2-tetrachloroethane as an internal standard. ^{119}Sn NMR spectroscopy showed these oligomers to have the following tin signals: **2**, δ 137.2; **3**, δ −74.1; **6**, δ 139.2; **7**, δ 119.6.

Preparation of Polystyrene-Bound Di-*n*-butyltin Chloride (4). A 500-mL round-bottomed three-necked flask equipped with a 125-mL pressure-equalized addition funnel and a magnetic stirring bar was flame dried and purged with nitrogen three times. After the apparatus cooled, it was placed in an acetone–dry ice bath under a static nitrogen pressure. THF (100 mL) was added, and the mixture cooled to −78 °C. Then 2 mL of a 1.6 N *n*-butyllithium solution in hexane was added. The oligomerization was carried out by dropwise addition of 10.81 g (104 mmol) of styrene as a solution in 10 mL of THF. The product dark red solution was stirred for 1 h at −78 °C, and then di-*n*-butyltin dichloride was added as a THF solution. After the mixture was warmed to room temperature and stirred for 2 h, the solvent was removed at reduced pressure. Dissolution of the residue in chloroform and filtration removed some insoluble impurities. Removal of the solvent left 10 g of a crude tin-containing oligomer that was characterized by ^{119}Sn NMR ($CDCl_3$) δ 155. ICP analysis of this oligomer showed it to have 0.26 mmol of Sn/g of oligomer.

Preparation of polystyrene *n*-butyltin dichloride (5) was accomplished by a procedure analogous to that used for **4** with the only difference being the use of $BuSnCl_3$ as the stannylating agent. The product **4** so prepared had a ^{119}Sn NMR spectrum with a peaks at δ 70 and 76. The presence of more than one peak was presumably the result of the presence of more than one diastereomeric center in the polystyrene oligomer. GPC analysis showed this oligomer had a molecular weight of 1250, and ICP analysis showed that it contained 0.3 mmol of $-SnBuCl_2$/g of oligomer.

Digestion of Oligomer Samples. The procedure used was a modification of Shanina's.[19] To a 20-mL quartz crucible was added 0.2 g of the oligomer sample and 4 mL of concentrated H_2SO_4. The oligomer mixture was gently heated on a hot plate until the oligomer sample was completely decomposed. Then, 10 mL of concentrated HNO_3 was added dropwise to the decomposed oligomer sample, followed by further heating on the hot plate for an additional 24 h with occasional shaking. A brownish homogeneous solution was finally obtained after this acidic digestion. After this solution was cooled to 25 °C, it was diluted with distilled water in a 25-mL volumetric flask and analyzed for tin content by atomic absorption spectroscopy by the Agricultural Analytical Services Laboratory at Texas A&M University. Control analyses for tin using the same amount of reagents excluding the oligomer sample were also carried out.

Reduction of Alkyl Halides with Polyethylene-Bound Tin. Toluene (20 mL), 2 mmol of the organic halide, 0.2 mmol of benzo-15-crown-5, a 6-fold excess of sodium borohydride, and 500 mg of **2** were mixed together at 25 °C under a nitrogen or argon atmosphere to form a suspension. No reaction occured with this suspension at room temperature, but on heating to reflux (110 °C) a solution formed. After 16–18 h of reflux, GC analysis showed that no starting material remained. Cooling the reaction mixture at this point re-formed the suspension of a polyethylene-bound tin reagent, which was recovered by filtration. This recovered tin catalyst could be reused by washing it with 2-propanol and acetone and air drying it. Analysis of a concentrated sample of the filtrate by ICP showed that >99.9% of the starting tin reagent had been recovered from solution. Specifically, in the case of using 1.5 g of $PESnPh_2Cl$ in a synthetic reaction, the filtrate contained less than 9×10^{-3}% of the starting tin compound. Similarly, the filtrate from a reaction using 1.5 g of $PESnBu_2Cl$ as a catalyst contained less than 3×10^{-2}% of the starting tin reagent.

Acknowledgment. Support of this research by the Robert A. Welch Foundation and the National Science Foundation (DMR-8605941) is gratefully acknowledged. S.A.W. also acknowledges fellowship support from the NIH MARC program and from Procter and Gamble through the National Organization of Black Chemists and Chemical Engineers.

(19) Shanina, T. M.; Gel'man, N. E.; Mikhailovskaya, V. S.; Kabaeva, N. M. *Zh. Anal. Khim.* **1981**, *36*, 414–417.

Asymmetric Induction during the Reactions of Dienyl–Iron and Diene–Molybdenum Complexes with Chiral *N*-Acyloxazolidinone Enolates

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The addition of chiral *N*-acyloxazolidinone enolates to diene–molybdenum and dienyl–iron complexes gives enantiomeric excesses as high as 80%. The oxazolidinone derived from valinol adds preferentially to the *pro-S* terminus of the diene/dienyl complex while the oxazolidinone derived from norephedrine adds to the *pro-R* terminus. A rationalization of these experimental results is attempted based on Seebach's topological rules for the Michael addition of enamines to nitro olefins.

Introduction

The use of transition metal stabilized diene and dienyl complexes as intermediates for the synthesis of natural products has been of continuing interest in our research group.[1] We have demonstrated that the cyclohexadiene–$Mo(CO)_2Cp$ complex **1** can be converted to the 1,3-cis-disubstituted π-allyl complex **2** and thence to the acyclic molecule **3**, which corresponds to a right-hand subsection of macrolide antibiotics such as tylosin (**4**).[2] We have also shown that the cycloheptadiene–$Mo(CO)_2Cp$ complex **5** can be converted to lactone **7** via complex **6**.[3]

(1) Pearson, A. J. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Ed.; John Wiley & Sons: Chichester, 1987; Vol. 4, Chapter 10.

(2) Pearson, A. J.; Khan, M. N. I.; Clardy, J. C.; Cun-heng, H. *J. Am. Chem. Soc.* **1985**, *107*, 2748.

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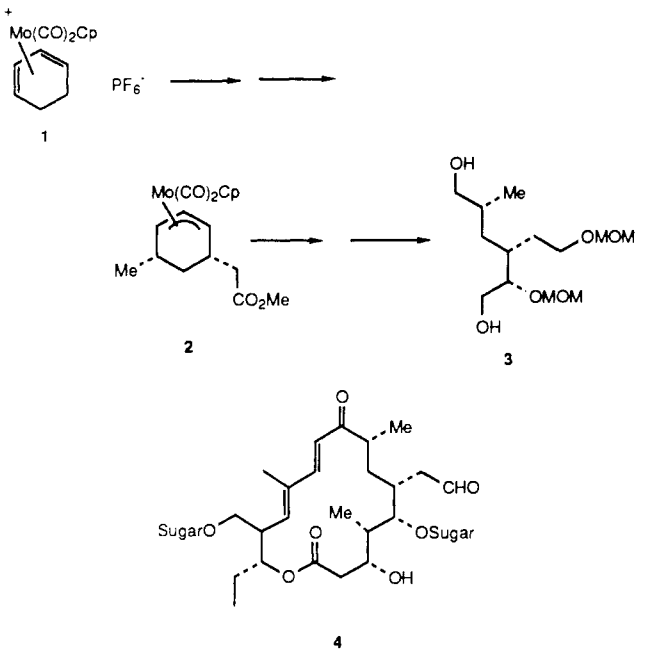
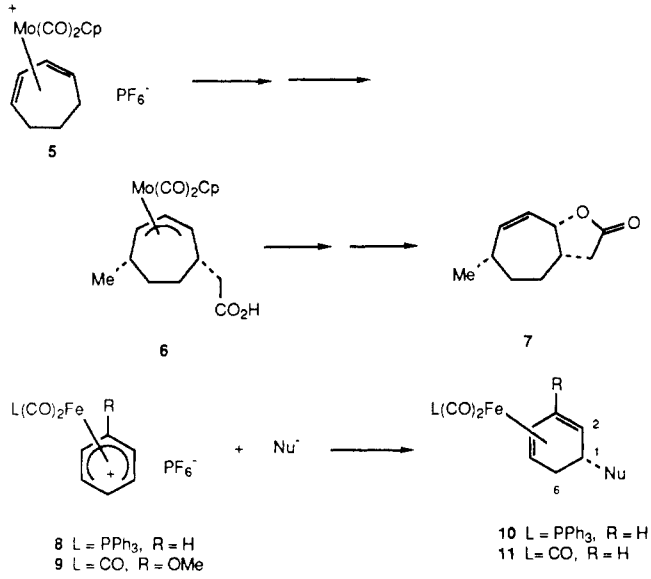
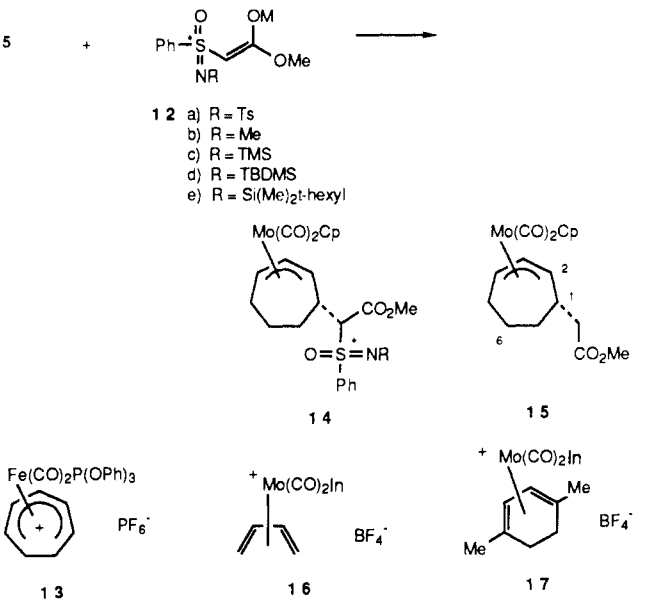


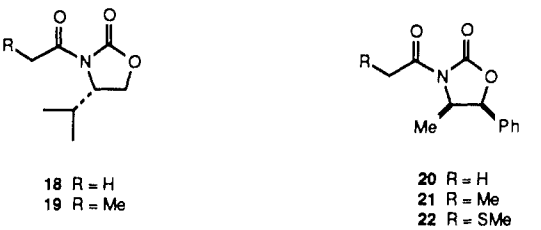
Unfortunately, the use of complexes **1** and **5**, as well as the iron complexes **8** and **9**, in natural products synthesis is limited by the fact that these molecules possess a plane of symmetry, so that the products **2**, **6**, **10**, and **11** were unavoidably obtained in racemic form.



Recently, we reported the addition of chiral sulfoximinyl esters (**12**) to complexes **1**, **5**, **8**, and **13** which allowed the preparation of, e.g., the ester **15** in 89% enantiomeric excess (ee). However, with complexes **1**, **8**, and **13** lower ee's were obtained (generally less than 78%).[4,5] Furthermore, the use of sulfoximine as a chiral auxiliary is severely limited by the fact that resolution is necessary for its production, and that it is completely destroyed during its subsequent removal. In an attempt to address these problems, we have investigated the chiral *N*-acyloxazolidinone nucleophiles (**18**–**22**) developed by Evans



and co-workers, which are known to give high enantiomeric excesses during aldol reactions.[6] They offer an advantage over the sulfoximine esters in that they possess a recoverable chiral auxiliary and they are obtained from commercially available and inexpensive amino acid derivatives.



Herein, we report the asymmetric induction obtained during the addition of chiral oxazolidinone enolates to complexes **1**, **5**, **8**, **9**, **16**, and **17**.[8]

Results

Our studies centered on the addition of oxazolidinones **18**–**22** to complexes **1**, **5**, **8**, **9**, **16**, and **17** which are all obtained via established procedures.[6a,9] Deprotonation of the *N*-acyloxazolidinone (LDA, THF, −78 °C) followed by reaction with the desired transition metal complex yielded complexes **23**–**28**, except for the reaction of **22** with iron complexes, which gave no observable addition products. This unexpected phenomenon was not further investigated. ^{1}H NMR (200 MHz) spectral analysis of these adducts revealed, in some cases, mixtures of diastereomers, usually with one predominating, but no conclusive information concerning asymmetric induction was evident. Diastereomer ratios, in cases where these could be reliably measured, are listed in Table I. The chiral auxiliary was removed (NaOMe, MeOH, room temperature)[6a] to yield

(3) Pearson, A. J.; Khan, M. N. I. *J. Org. Chem.* **1985**, *50*, 5276.
(4) Pearson, A. J.; Blystone, S. L.; Nar, H.; Pinkerton, A. A.; Roden, B. A.; Yoon, J. *J. Am. Chem. Soc.* **1989**, *111*, 134.
(5) Sulfoximine ester enolate additions to complex **9** yielded only moderate enantiomeric excesses (%ee's < 35%): Holden, M., unpublished results, this laboratory.

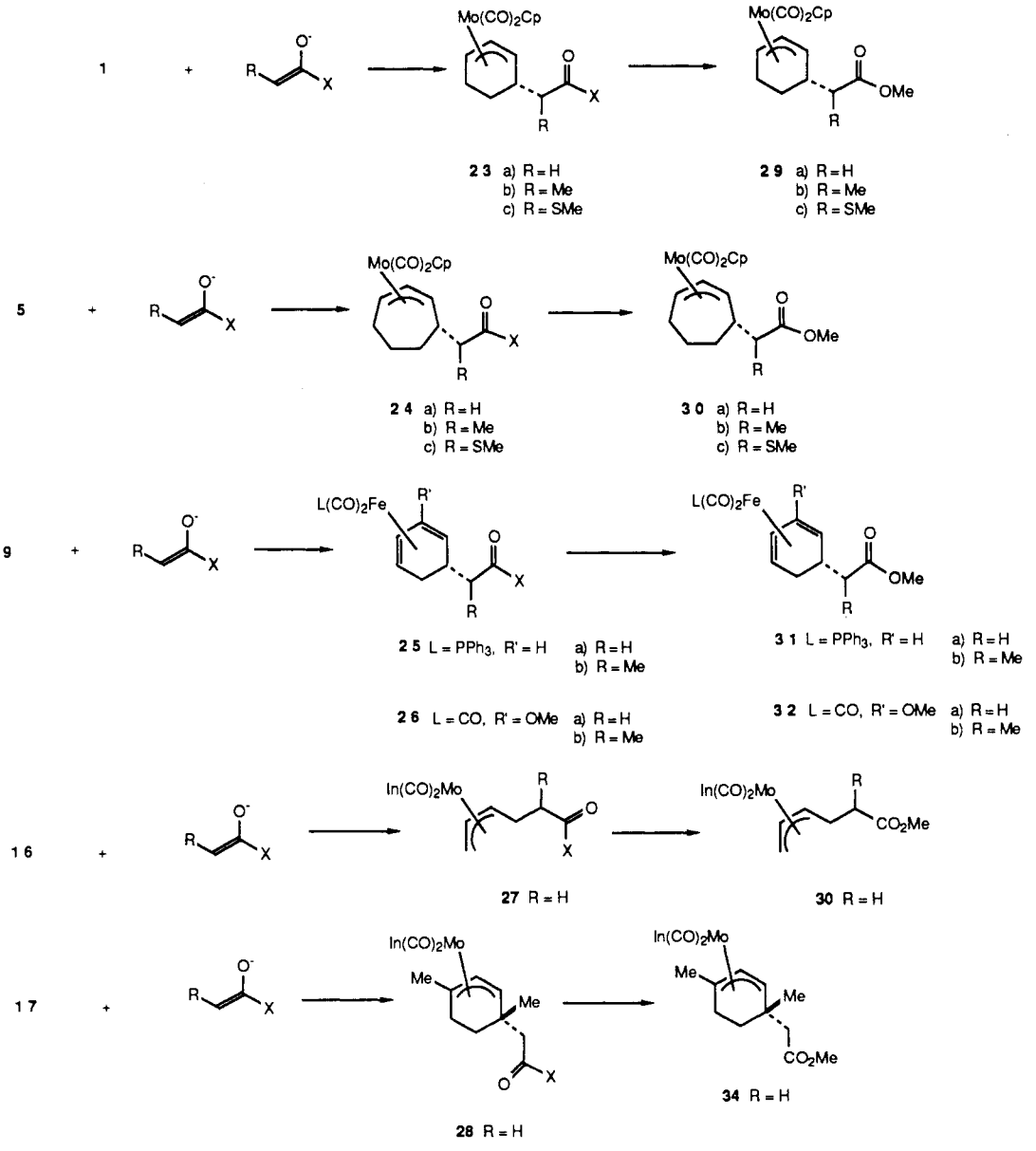
(6) (a) Evans, D. A.; Bartroli, J.; Shih, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 2127. (b) Evans, D. A.; Ennis, M. D.; Mathre, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 1737. (c) Evans, D. A. *Aldrichimica Acta* **1982**, *15*, 23, and references cited therein. (d) Evans, D. A.; Sjorgen, E. B.; Bartroli, J.; Dow, R. L. *Tetrahedron Lett.* **1986**, *27*, 4957.
(7) Johnson, C. R.; Schroek, C. W. *J. Am. Chem. Soc.* **1973**, *95*, 7418. Johnson, C. R. *Aldrichimica Acta* **1985**, *18*, 3 and references cited therein.
(8) The addition of chiral oxazolidinone enolates to diene–molybdenum complexes has been previously attempted; however, no selectivity was reported: Green, M.; Greenfield, S.; Kersting, M. *J. Chem. Soc., Chem. Commun.* **1985**, 18.
(9) Newman, M. S.; Kutner, A. *J. Am. Chem. Soc.* **1951**, *73*, 4199.

Table I. Results of Oxazolidone Enolate Additions

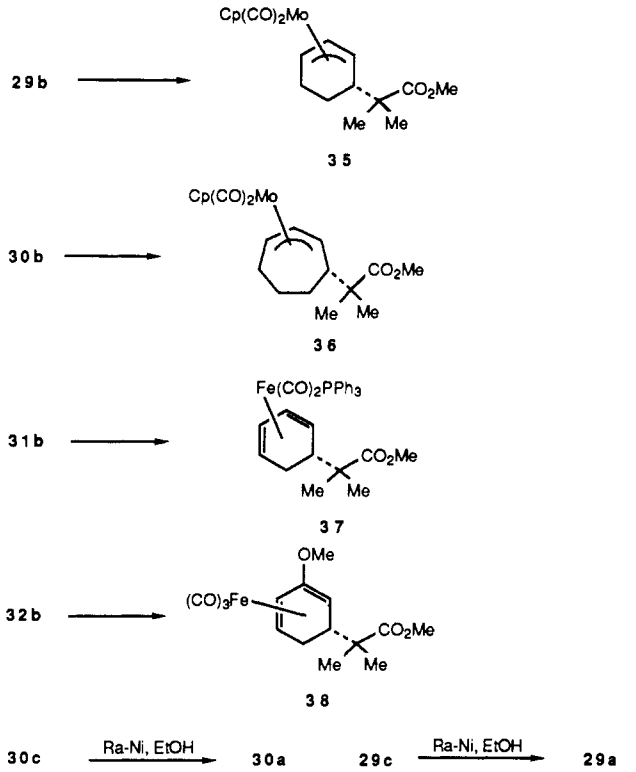
entry	oxazolidone	complex	yield,[a] %	diastereomeric excess,[b] %	$[\alpha]_D$, deg	enantiomeric excess, %
1	**18**	**1**	79	*e*	+45.5	65 (*S*)
2	**19**	**1**	70[c]	*e*	+104.3	85 (*S*)
3	**20**	**1**	74	62.0	-51.8	65 (*R*)
4	**21**	**1**	60[c]	63.0	-102.1	80 (*R*)
5	**22**	**1**	57[d]	20.0	-4.2	8 (*R*)
6	**18**	**5**	65	0.0	+14.0	15 (*S*)
7	**19**	**5**	65[c]	50.0	+65.0	30 (*S*)
8	**20**	**5**	76	0.0	-6.0	10 (*R*)
9	**21**	**5**	60	0.0	-69.0	32 (*R*)
10	**22**	**5**	52[d]	48.0	-5.3	10 (*R*)
11	**18**	**8**	78	*e*	+1.8	37 (*S*)
12	**19**	**8**	64	*e*	+4.9	19 (*S*)
13	**20**	**8**	63	*e*	-1.6	33 (*R*)
14	**21**	**8**	54	*e*	-5.5	20 (*R*)
15	**18**	**9**	71	*e*	-9.4	60 (*S*)
16	**19**	**9**	68	6.4	-1.2	11 (*S*)
17	**20**	**9**	77	53.0	+8.3	57 (*R*)
18	**21**	**9**	70	*e*	+2.0	15 (*R*)
19	**20**	**16**	69	0	0.0	0
20	**20**	**17**	43	50.0	–[f]	50

[a] After methanolysis, unless otherwise noted. [b] Based on ^{1}H NMR analysis. [c] Prior to methylation. [d] After desulfurization. [e] Unable to determine. [f] Not measured.

Scheme I



methyl esters **29–34**, generally in good overall yield. In the case of the *N*-acetyl derivatives (**a**, R = H) the complexes were directly submitted to NMR determination of optical purity. In the case of the *N*-propionyl adducts (**b**, R = Me) and the *N*-methylthio acetyl derivatives (**c**, R = SMe) diastereomeric mixtures still existed, requiring further manipulation prior to reliable determination of enantiomeric excess. For complexes **29b**, **30b**, **31b**, and **32b** treatment with LDA (–78 °C) followed by addition of MeI (–78 °C to room temperature) yielded the isobutyrate complexes **35**, **36**, **37**, and **38**, while treatment of complexes **29c** and **30c** with Ra-Ni (EtOH, reflux)[10] yielded the simple monoester complexes **29a** and **30a**, and all of these complexes could now be analyzed for optical purity.



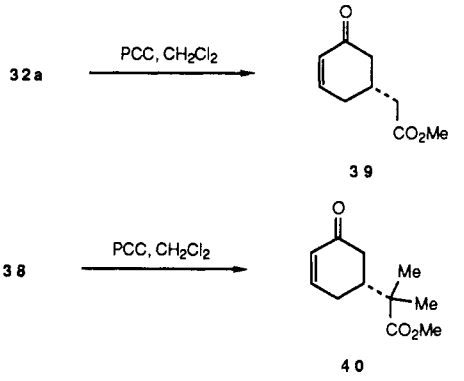
All of the monoester derivatives obtained in this fashion showed optical activity in varying degrees. The extent of asymmetric induction was determined by ^{1}H NMR spectroscopy at 200 MHz in the presence of the chiral lanthanide shift reagent (+)-tris[(heptafluorobutyryl)camphorato]europium(III) [Eu(hfbc)$_3$]. For complexes **29**, **30**, **32**, **33**, and **34** the methyl ester singlet was shifted to lower field and split into two peaks separated by approximately 0.03 ppm while for compound **30**, the Cp singlet was shifted downfield and split into two peaks separated by approximately 0.02 ppm. The results of these studies are given in Table I, in which the ee is estimated from peak areas of the split resonances.

It was observed that complexes obtained from oxazolidinones **18** and **19** gave opposite enantiomers compared to oxazolidinones **20**, **21**, and **22**, as expected. For the molybdenum complexes **1** and **5** the *N*-propionyloxazolidinones give greater asymmetric induction than their *N*-acetyl counterparts, but the opposite trend is observed for the iron complexes **8** and **9**, the *N*-propionyloxazolidinones giving lower enantiomeric excesses compared to the *N*-acetyloxazolidinones. It is also noted that the *N*-[(methylthio)acetyl]oxazolidinones react satisfactorily with the molybdenum–diene complexes but not the iron–dienyl complexes, but we can offer no explanation for this at present.

The asymmetric induction observed for complexes **1** or **8** is better than that previously reported using the sulfoximine esters (80% and 30%, respectively), whereas that obtained for complex **5** is not as encouraging.[4] In the case of complex **9**, the asymmetric induction is also higher using the oxazolidinones compared with sulfoximine **12** (23–35% ee).[5]

The absolute stereochemistry of complexes **29**, **30**, and **31** was assigned by comparison with previous studies of these systems using Mosher's method, which have been confirmed by X-ray crystallographic analysis[4] (1*S* stereochemistry is depicted in the structures). The absolute stereochemistry of complex **32** is inferred from the above data, a positive rotation now corresponding to the 1*R* derivative. The change in sign of rotation is probably due to the presence of MeO on the diene ring.

In order to assess the utility of these complexes for asymmetric synthesis, it is necessary to show that further manipulation does not cause racemization of the newly formed chiral center. We have already demonstrated this for complexes **29**, **30**, and **31**. In the case of **32a**, demetalation via the method of Birch et al.[11] (PCC, CH_2Cl_2, room temperature, 4 h) yielded enone **39** in high yield, with no loss of enantiomeric purity as determined by NMR chiral shift analysis. Similarly, demetalation of complex **38** yielded enone **40** with no loss of optical purity.



Discussion

We now attempt to give some rationalization of the chiral recognition observed during the above transformations. The reactions of chiral oxazolidinone-derived enolates with alkyl halides and with aldehydes is well understood, addition of electrophile taking place at the enolate face trans to the substituents on the oxazolidinone ring.[12,6a] While the aldehyde reactions most closely resemble those reported here, the electrophilic moiety being a double bond, the Zimmerman–Traxler transition state commonly used to explain diastereoselective aldol reactions is inappropriate for reactions of transition metal–olefin complexes, since there is obviously no opportunity for association of enolate and electrophile via chelation through the lithium cation. The transition metal moiety clearly does not play an active role here, since all enolate additions to 18-electron complexes occur stereospecifically anti to the metal. Consequently, those factors that destabilize a six-membered ring transition state may or may not be important in these reactions.

Seebach has proposed a set of topological rules for reactions that involve open transition states, exemplified by

(10) Pettit, G. R.; van Tamelen, E. E. *Org. React.* **1966**, *12*, 356.

(11) Kelley, L. F.; Dahler, P.; Narula, A. S.; Birch, A. J. *Tetrahedron Lett.* **1981**, *22*, 1433.

(12) Evans, D. A.; Takacs, J. M. *Tetrahedron Lett.* **1980**, *21*, 4233.

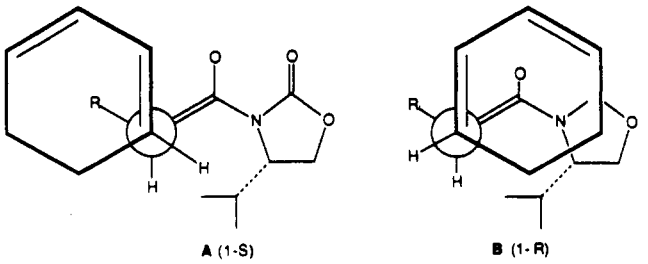


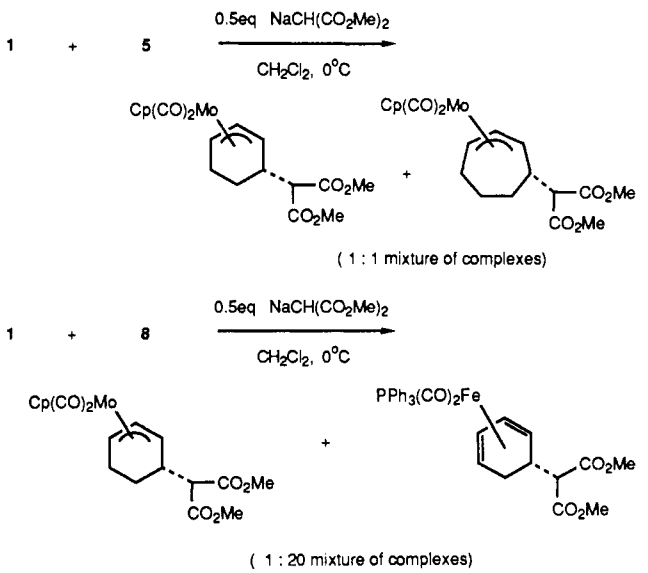
Figure 1. Possible limiting arrangements for cyclohexadiene–$Mo(CO)_2Cp$ and enolate nucleophile, representing the transition state during C–C bond formation. (The metal is omitted for clarity; it is imagined to sit atop the diene.)

the Michael addition of enamines to nitro olefins.[13] The open transition-state model used for these reactions preserves some of the characteristics of the Zimmerman–Traxler model, most notably the synclinal orientation of π-systems for the nucleophile–electrophile combination. This model was used by us to rationalize the asymmetric induction observed during the addition of sulfoximinyl ester enolates to olefin–metal complexes,[4] and by Rosenblum to explain diastereoselectivity during enolsilane additions to (vinyl ether)–Fp complexes,[16] although it was stated that an anti transition state is also compatible with their results.

Figure 1 depicts two limiting synclinal arrangements for an olefin–metal complex interacting with enolate. For convenience, we have chosen the cyclohexadiene–molybdenum system, in which the metal (sitting atop the diene) is omitted for clarity, reacting with the enolate from the oxazolidinone **18** (or **19**). Transition state A is expected to be energetically favored over B due to greater steric compression in the latter, and this is consistent with the observed absolute stereochemistry of the products from this reaction.

We cannot offer a convincing explanation for the results of addition of **19** vs **18** and of **21** vs **20** to complexes **1**, **5**, **8**, and **9**, especially in view of the observation that asymmetric induction is enhanced by methyl substitution during reactions with the diene–molybdenum systems, while the dienyl–iron complexes give poorer enantioselectivity with *N*-propionyl vs *N*-acetyl derivatives. Competition studies show that while complexes **1** and **5** are equally reactive toward dimethyl sodiomalonate, the dienyl–iron systems are 20 times more reactive than the diene–molybdenum derivatives (see the Experimental Section), but this represents a very small difference in activation energy. This may be a result of there being a lower energy LUMO for the iron systems, therefore leading to a stronger frontier orbital interaction between this system and the enolate, compared with the molybdenum complexes. This being the case, reactions of complexes **8** and **9** may involve a greater contribution from a Mulzer-type eclipsed transition state.[14] Since methyl substitution (R in Figure 1) is expected to destabilize all possible transition states, these effects require further experimental support before complete rationalization is possible.

The butadiene complex **16** gives essentially no stereoselectivity during its reaction with the enolate of **20**.



Presumably, this reflects the fact that removal of the ring methylene groups leads to a lowering of the energy difference between A and B, due to removal of the major steric interactions.

Conclusions

We have presented here a method for asymmetric induction in diene–molybdenum and dienyl–iron complexes. This method offers promise over other methods in that the oxazolidinones give acceptably high enantiomeric excesses as well as a recoverable chiral auxiliary. Furthermore, coupling of this synthetic method with previously established manipulations of the resultant π-allyl–molybdenum and diene–iron complexes provide a valuable tool for the asymmetric synthesis of natural products. A partial explanation of the observed enantioselectivity is offered, but clearly further experimentation is necessary before a complete understanding of this phenomenon can emerge.

Experimental Section

General Procedures. Infrared spectra were recorded with a Perkin-Elmer 1420 instrument, and optical rotations were recorded on a Perkin-Elmer 251 digital polarimeter at room temperature in a 1-mL cell. NMR spectra were recorded in deuteriochloroform solution unless otherwise stated, using a Varian XL-200 instrument, and mass spectra were obtained in-house on a Kratos MS-25A instrument. Molecular ions are given for ^{96}Mo for molybdenum complexes. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN. All reactions were performed under inert atmosphere (dry, O_2-free, argon) unless otherwise noted. Solvents were purified by distillation as follows: tetrahydrofuran from sodium benzophenone, methanol and dichloromethane from calcium hydride.

Preparation of Lithiodiisopropylamine (LDA). A stock solution of LDA was prepared as follows: In a flame-dried 250-mL three-neck flask, filled with dry, oxygen-free argon, equipped with a pressure-equalizing dropping funnel, argon bubbler, and rubber septum, was placed 20 mL of THF and 7 mL (5 g, 49.5 mmol) of diisopropylamine. The solution was cooled to 0 °C and stirred while 35 mL (49.5 mmol) of MeLi was added dropwise. After the reaction was complete, the solution was transferred via cannula to an oven-dried flask for storage (under argon, equipped with rubber septum). An aliquot of the solution was titrated against 101.2 mg (0.647 mmol) of menthol in 1 mL of THF with a small crystal of 1,10-phenanthroline present until the red color persisted. The calculated molarity was 0.76 M.

Addition of Oxazolidinone Enolates to Metal Complexes. General Procedure. The desired oxazolidinone (1.2 mmol) was dissolved in 10 mL of THF in a flame-dried flask under argon and cooled to −78 °C. To this was added 1.2 mmol of LDA

(13) Seebach, D.; Golinski, J. *Helv. Chim. Acta* **1981**, *64*, 1413. For alternative open transition state models, see ref 14 and 15.
(14) Mulzer, J.; Zippel, M.; Brüntrup, G.; Segner, J.; Finke, J. *Justus Liebigs Ann. Chem.* **1980**, 1108.
(15) (a) Noyori, R.; Nishida, I.; Sakata, B. *J. Am. Chem. Soc.* **1981**, *103*, 2106. (b) Noyori, R.; Nishida, I.; Sakata, J.; Nishizawa, M. *J. Am. Chem. Soc.* **1980**, *102*, 1223.
(16) Chang, T. C. T.; Coolbaugh, T. S.; Foxman, B. M.; Rosenblum, M.; Simms, N.; Stockman, C. *Organometallics* **1987**, *6*, 2394.

(prepared as above), and the mixture was stirred at −78 °C for 15 min (solution turns pale yellow). At this time 1 mmol of the appropriate metal complex was added, and the solution was stirred until the THF insoluble complex dissolved, yielding a bright yellow solution (ca. 30 min). The solution was warmed to room temperature, quenched with 10 mL of saturated aqueous NH_4Cl, and the organics were extracted with ether (2 × 20 mL). The combined ether layers were washed with water (10 mL) and saturated aqueous NaCl (10 mL) followed by drying ($MgSO_4$). Removal of the ether in vacuo yielded a yellow oil in all cases. Extensive purification was avoided in order to prevent fractionation of diastereomers, which could lead to false estimates of enantiomeric excesses.

Spectroscopic data for selected adducts is given below:

(4′*R*,5′*S*)-Dicarbonyl(η⁵-cyclopentadienyl)[3′-[2-(2-4-η-cyclohex-2-enyl)acetyl]-4′-methyl-5′-phenyl-2′-oxazolidinone]molybdenum (23a) was obtained as a mixture of diastereomers. IR ($CHCl_3$): ν_{max} 1940, 1860, 1730, 1690 cm^{-1}. ^1H NMR ($CDCl_3$), major diastereomer: δ 7.35 (5 H, m, Ph), 5.67 (1 H, d, $J_{4',5'}$ = 7.3 Hz, 5′-H), 5.29 (5 H, s, Cp), 4.75 (1 H, m, 4′-H), 4.18 (1 H, t, $J_{2,3} = J_{3,4}$ = 7.1 Hz, 3-H), 3.75 (1 H, m, 2-H), 3.65 (1 H, m, 4-H), 3.18 and 3.02 (2 H, ABX, J_{AB} = 14.5 Hz, J_{AX} = 6.0 Hz, J_{BX} = 6.4 Hz, CH_2CON), 2.35 (1 H, m, endo-5-H), 1.65 (1 H, m, exo-5-H), 0.88 (3 H, d, $J_{4',Me}$ = 6.5 Hz, 4′-CH_3), 0.87 (1 H, m (obscured), endo-6-H), 0.6 (1 H, m, exo-6-H). HRMS: calcd for $C_{25}H_{25}MoNO_5$ *m/z* 517.0967, found *m/z* 517.0981.

(4′*R*,5′*S*)-Dicarbonyl(η⁵-cyclopentadienyl)[3′-[2-(2-4-η-cyclohept-2-enyl)acetyl]-4′-methyl-5′-phenyl-2′-oxazolidinone]molybdenum (24a) was obtained as a mixture of diastereomers. IR ($CHCl_3$): ν_{max} 1940, 1860, 1730, 1690 cm^{-1}. ^1H NMR ($CDCl_3$), major diastereomer: δ 7.31 (5 H, m, Ph), 5.66 (1 H, d, $J_{4',5}$ = 7.3 Hz, 5′-H), 5.23 (5 H, s, Cp), 4.77 (1 H, m, 4′-H), 4.12 (1 H, t (br), $J_{3,4}$ = 7.3 Hz, 4-H), 3.8 (1 H, d, $J_{2,3}$ = 8.5 Hz, 3-H), 3.75 (1 H, t, $J_{2,3} = J_{3,4}$ = 8.5 Hz, 3-H), 3.1 (2 H, m, CH_2CON), 1.7 (1 H, m, endo-1-H), 2.2 (2 H, m, endo-7-H and endo-5-H), 1.3 (2 H, m, endo-6-H and exo-5-H), 0.89 (3 H, d, $J_{4',Me}$ = 6.5 Hz, 4′-CH_3), 0.88 (1 H, m (obscured), exo-5-H), 0.5 (1 H, m, exo-6-H). HRMS: calcd for $C_{26}H_{27}MoNO_5$ *m/z* 531.0944, found *m/z* 531.0935.

(4′*R*,5′*S*)-Dicarbonyl[3′-[2-(2-5-η-cyclohexa-2,4-dienyl)-acetyl]-4′-methyl-5′-phenyl-2′-oxazolidinone](triphenylphosphine)iron (25a) was obtained as a mixture of diastereomers undistinguishable from its ^1H NMR spectrum. IR ($CHCl_3$): ν_{max} 3020, 1970, 19190, 1775, 1690 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.4 (20 H, m, CHPh and PPh_3), 5.58 (1 H, d, $J_{4',5'}$ = 7.1 Hz, 5′-H), 4.87 (2 H, m, 3-H, 4-H), 4.67 (1 H, m, 4′-H), 2.7 (3 H, m, CH_2CON and endo-1-H), 2.38 (2 H, m, 2-H and 5-H), 2.15 (1 H, m, endo-6-H), 1.12 (1 H, m, exo-6-H), 0.81 (3 H, d, $J_{4',Me}$ = 6.5 Hz, 4′-CH_3). HRMS: calcd for (M^+ − 2CO) $C_{38}H_{34}FeNO_5P$ *m/z* 615.1625, found *m/z* 615.1604.

(4′*S*)-Tricarbonyl[3′-[3-(2-5-η-3-methoxycyclohex-2,4-dienyl)propionyl]-4′-isopropyl-2′-oxazolidinone]iron (26a) was obtained as a mixture of diastereomers. IR ($CHCl_3$): ν_{max} 2050, 1975, 1775, 1690 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.11 (1 H, d (br), $J_{4,5}$ = 7 Hz, 4-H, both diastereomers), 4.39 (2 H, m, 4′-H, both diastereomers), 4.19 (4 H, m, 5′-H, both diastereomers), 3.61 (3 H, s, OMe, one diastereomer), 3.58 (3 H, s, OMe, one diastereomer), 3.27 (1 H, m, 2-H, one diastereomer), 3.21 (1 H, m, 2-H, one diastereomer), 2.89 (2 H, m, CHMe, both diastereomers), 2.56 (2 H, m, 5-H, both diastereomers), 2.26 (2 H, m, $CHMe_2$, both diastereomers), 2.87 (2 H, m, endo-6-H, both diastereomers), 1.07 (3 H, d, J = 6.7 Hz, $CH(CH_3)_2$, one diastereomer), 0.97 (3 H, d, *J* = 6.7 Hz, $CHCH_3$, one diastereomer), 0.88 (6 H, d, *J* = 7 Hz, $CH(CH_3)_2$, one diastereomer), 0.85 (6 H, d, *J* = 7 Hz, $CH(CH_3)_2$, one diastereomer). HRMS: calcd for M^+ − CO) $C_{18}H_{23}FeNO_6$ *m/z* 405.0874, found *m/z* 405.0881.

(4′*R*,5′*S*)-Dicarbonyl(η⁵-indenyl)[3′-[2-(2-4-η-1,4-dimethylcyclohex-2-enyl)acetyl]-4′-methyl-5′-phenyl-2′-oxazolidinone]molybdenum (28a)[17] was obtained as a mixture of diastereomers. IR ($CHCl_3$): ν_{max} 2930, 1930, 1850, 1775, 1690 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.36 (5 H, m, Ph), 7.09 (4 H, m, indenyl), 6.02 (1 H, m, indenyl), 5.75 (1 H, d, $J_{4',5'}$ = 7.3 Hz, 5′-H), 5.55 (1 H, t, *J* = 2.6 Hz, indenyl), 4.75 (1 H, m, 4′-H), 3.32 (1 H, d, J_{gem} = 14.2 Hz, CHHCON), 2.75 (1 H, dd, $J_{2,3}$ = 7.5 Hz, *J* = 1.5 Hz, 2-H), 2.43 (1 H, d, J_{gem} = 14.2 Hz, CHHCO), 1.7 (2 H, m, endo-5-H, exo-5-H), 1.52 (3 H, s, 4-methyl), 1.14 (3 H, s, 1-methyl), 1.1 (1 H, m, endo-6-H), 0.86 (3 H, d, $J_{4',Me}$ = 6.6 Hz, 4′-Me), 0.25 (1 H, m, exo-6-H), −0.37 (1 H, d, $J_{2,3}$ = 7.5 Hz, 3-H). HRMS: calcd for $C_{31}H_{31}MoNO_5$ *m/z* 595.1257, found *m/z* 595.1179.

(4′*R*,5′*S*)-Dicarbonyl(η⁵-indenyl)[3′-(4-6-η-hex-4-enyl)-4′-methyl-5′-phenyl-2′-oxazolidinone]molybdenum (27a) was obtained as a mixture of diastereomers. IR ($CHCl_3$): ν_{max} 1945, 1860, 1780, 1700 cm^{-1}. ^1H NMR ($CDCl_3$), both diastereomers: δ 7.33 (5 H, m, Ph), 7.04 (4 H, m, indenyl), 5.98 (2 H, m, indenyl), 5.62 (1 H, d, $J_{4',5'}$ = 7.3 Hz, 5′-H), 5.59 (1 H, t, *J* = 2.9 Hz, indenyl), 4.68 (1 H, m, 4′-H), 3.15 (1 H, m, 4-H), 2.8 (2 H, m, 2-H), 2.26 (1 H, ddd, $J_{5,6trans}$ = 7.9 Hz, J_{gem} = 2.6 Hz, $J_{4,6trans}$ = 1.5 Hz, 6-H_{trans}), 2.12 (1 H, m, 3-H), 1.46 (1 H, dd, $J_{5,6cis}$ = 11.7 Hz, J_{gem} = 2.6 Hz, 6-H_{cis}), 0.85 ($^1/_2$ H, d, $J_{4',Me}$ = 6.6 Hz, 4′-H), 0.84 ($^1/_2$ H, d, $J_{4',Me}$ = 6.6 Hz, 4′-H), 0.25 (1 H, m, 3-H), −0.41 (1 H, dt, $J_{2,6cis}$ = 11.7 Hz, $J_{2,6trans} = J_{4,5}$ = 7.9 Hz, 5-H). HRMS: calcd for $C_{27}H_{25}MoNO_5$ *m/z* 541.0788, found *m/z* 541.0780.

Removal of the Oxazolidinone Chiral Auxiliary. General Procedure. Freshly cut sodium metal (5 mmol) was added in portions to MeOH (9 mL) in a dry 25-mL 3-neck flask equipped with rubber septa, under argon, at 0 °C. When the reaction had ceased, the solution was warmed to room temperature, and 1 mmol of the oxazolidone adduct in 1 mL of MeOH was added. The solution immediately turned bright yellow and was stirred until the reaction was judged to be complete by TLC (silica gel, 30% EtOAc/Hexane; ca. 15 min). The solution was acidified with 10% HCl and extracted with ether (3 × 20 mL). The combined organic layers were washed with H_2O (10 mL) and brine (10 mL) and dried ($MgSO_4$). The ether was removed in vacuo to yield the appropriate methyl ester complex, which could be further purified by flash chromatography (silica gel, 30% EtOAc/hexane). In cases where diastereomers existed, extensive purification was avoided to prevent fractionation of diastereomers.

Dicarbonyl(η⁵-cyclopentadienyl)[methyl 2-(2-3-η-cyclohept-2-enyl)propionate]molybdenum (30b). IR ($CHCl_3$): ν_{max} 1940, 1852, 1720 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.23 (5 H, s, Cp, minor diastereomer), 5.21 (5 H, s, Cp, major diastereomer), 4.13 (4 H, m, 4-H, 2-H, both diastereomers), 3.70 (2 H, t, $J_{2,3} = J_{3,4}$ = 8.7 Hz, 3-H), 3.65 (6 H, s, CO_2CH_3, both diastereomers), 2.52 (2 H, m, endo-7-H, both diastereomers), 2.14 (2 H, m, endo-5-H, both diastereomers), 2.08 (2 H, m, $Me(CH)CO_2Me$, both diastereomers), 1.98 (4 H, m, endo-6-H, exo-5-H, both diastereomers), 1.17 (3 H, d, $J_{8,Me}$ = 9 Hz, $CHCH_3$, major diastereomer), 1.05 (3 H, d, $J_{8,Me}$ = 7.7 Hz, $CHCH_3$, minor diastereomer), 0.86 (2 H, m, exo-6-H, both diastereomers). HRMS: calcd for $C_{18}H_{22}MoO_4$ *m/z* 398.3302, found *m/z* 398.0725.

Dicarbonyl[methyl 2-(2-5-η-cyclohexa-2,4-dienyl)-propionate](triphenylphosphine)iron (31b). IR ($CHCl_3$): ν_{max} 1905, 1965, 1720 cm^{-1}. ^1H NMR ($CDCl_3$) (1:1 mixture of diastereomers, partial characterization): δ 7.31 (30 H, m, Ph, both diastereomers), 4.80 (4 H, m, 3-H, 4-H, both diastereomers), 3.50 (3 H, s, CO_2CH_3, one diastereomer), 3.47 (3 H, s, CO_2CH_3, one diastereomer), 2.15 (2 H, m, 2-H or 5-H, both diastereomers), 2.14 (2 H, m, 2-H, 5-H, both diastereomers), 0.88 (3 H, d, *J* = 6.9 Hz, $CHCH_3$, one diastereomer), 0.86 (3 H, d, *J* = 6.9 Hz, $CHCH_3$). HRMS: calcd for $C_{29}H_{29}FeO_3P$ (M − CO) *m/z* 512.1048, found *m/z* 512.1190.

Tricarbonyl[methyl (2-5-η-3-methoxycyclohexa-2,4-dienyl)acetate]iron (32a). IR ($CHCl_3$): ν_{max} 2060, 19790, 1730 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.14 (1 H, d (br), $J_{4,5}$ = 7.6 Hz, 4-H), 3.63 (3 H, s, CO_2CH_3), 3.59 (3 H, s, OCH_3), 3.31 (1 H, m, 2-H), 2.55 (1 H, m, 5-H), 2.23 (2 H, t, $J_{1,7}$ = 6.7 Hz, CH_2CO_2Me), 2.47 (1 H, m, endo-1-H), 1.90 (1 H, ddd, *J* = 7.8 Hz, *J* = 5.2 Hz, *J* = 2.2 Hz, endo-6-H), 1.17 (1 H, m, exo-6-H). HRMS: calcd for $C_{12}H_{14}FeO_5$ (M − CO) *m/z* 294.0033, found *m/z* 294.0190.

Tricarbonyl[methyl (2-5-η-3-methoxycyclohexa-2,4-dienyl)propionate]iron (32b). IR ($CHCl_3$): ν_{max} 2035, 1958, 1713 cm^{-1}. ^1H NMR ($CDCl_3$) (1:1 mixture of diastereomers): δ 5.11 (2 H, m, H-4, both diastereomers), 3.65 (3 H, s, CO_2CH_3, one diastereomer), 3.62 (3 H, s, CO_2CH_3, one diastereomer), 3.60 (3 H, s, OCH_3, one diastereomer), 3.59 (3 H, s, OCH_3, one diastereomer), 3.31 (1 H, dd, $J_{1,2}$ = 3 Hz, $J_{2,4}$ = 1.2 Hz, H-2, one diastereomer), 3.16 (1 H, dd, $J_{1,2}$ = 3 Hz, $J_{2,4}$ = 1.2 Hz, H-2, one diastereomer), 2.58 (2 H, m, H-5, both diastereomers), 2.37 (2 H,

(17) For preparation of complex 17, see: Pearson, A. J.; Khetani, V. D. *J. Org. Chem.* **1988**, *53*, 3395.

m, endo-1-H, both diastereomers), 2.24 (2 H, m, $CHMeCO_2Me$, both diastereomers), 1.80 (1 H, ddd (obs), J_{gem} = 3 Hz, $J_{5,6endo}$ = 4 Hz, endo-6-H, one diastereomer), 1.74 (1 H, ddd (obs), J_{gem} = 13 Hz, $J_{5,6endo}$ = 4 Hz, endo-6-H, one diastereomer), 1.09 (3 H, d, $J \approx 7$ Hz, $CHCH_3$, one diastereomer), 1.01 (3 H, d, J = 7 Hz, $CHCH_3$, one diastereomer), 0.86 (2 H, m, exo-6-H, both diastereomers). HRMS: calcd for (M^+ – CO) $C_{15}H_{20}FeO_5$ m/z 308.0347, found m/z 308.0339.

Dicarbonyl(η^5-indenyl)(methyl 4–6-η-hex-4-enolate)molybdenum (33a). IR ($CHCl_3$): ν_{max} 1940, 1860, 1725 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.04 (4 H, m, indenyl), 5.98 (2 H, m, indenyl), 5.6 (1 H, t, J = 1.9 Hz, indenyl), 3.6 (3 H, s, CO_2CH_3), 3.09 (1 H, m, 4-H), 2.3–1.9 (5 H, m, 2-H, 3-H, 6-H_{trans}), 1.41 (1 H, dd, $J_{5,6cis}$ = 11.7 Hz, J_{gem} = 2.6 Hz, 6-H_{cis}), –0.42 (1 H, dt, $J_{5,6cis}$ = 11.7 Hz, $J_{5,6trans}$ = $J_{5,6trans}$ = $J_{4,5}$ = 7.9 Hz, 5-H). HRMS: calcd for $C_{18}H_{18}MoO_4$ m/z 396.0260, found m/z 396.0267.

Dicarbonyl(η^5-indenyl)[methyl 2-(2–4-η-1,4-dimethylcyclohex-2-enyl)acetate]molybdenum (34a). Racemic sample, produced as described in reference 17. IR ($CHCl_3$): ν_{max} 1930, 1850, 1720 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.1 (4 H, m, indenyl), 6.0 (1 H, m, indenyl), 5.75 (1 H, m, indenyl), 5.55 (1 H, t, J = 2.9 Hz, indenyl), 3.61 (3 H, s, CO_2CH_3), 2.59 (1 H, dd, J = 7.4 Hz, J = 1.7 Hz, 2-H), 2.20 and 2.08 (2 H, AB qd, J_{AB} = 12.9 Hz, CH_2CO_2Me), 1.65–1.5 (2 H, m, endo-5-H and exo-5-H), 1.51 (3 H, s, 4-Me), 1.09 (3 H, s, 1-Me), 0.94 (1 H, dd, J = 14 Hz, J = 6 Hz, endo-6-H), 0.24 (1 H, m, exo-6-H), –0.36 (1 H, d, J = 7.4 Hz, 3-H). HRMS: calcd for $C_{22}H_{24}MoO_4$ m/z 450.0730, found m/z 450.0719.

Methylation of Methyl Propionate Complexes. General Procedure. The desired complex (1 mmol) was dissolved in 10 mL of THF and placed a dry, argon-filled 25-mL three-neck flask, equipped with rubber septa, and cooled to –78 °C. LDA (5 mmol) was added slowly via syringe. The mixture was stirred for 15–30 min at –78 °C followed by addition of 10 mmol of MeI. Stirring was continued at –78 °C for 30 min; the mixture was warmed to room temperature and stirred for an additional 30 min. The reaction was quenched with saturated aqueous NH_4Cl (10 mL) followed by extraction with ether (2 × 20 mL). The combined organic layers were washed with water (10 mL) and saturated aqueous NaCl (10 mL) and dried ($MgSO_4$). Removal of ether in vacuo yielded the desired methyl isobutyrate complexes, which could be purified by flash chromatography (silica gel, 30% EtOAc/hexane).

Dicarbonyl(η^5-cyclopentadienyl)[methyl 2-(2–4-η-cyclohept-2-enyl)isobutyrate]molybdenum (36). Yellow solid, mp 127–129 °C. IR ($CHCl_3$): ν_{max} 1940, 1850, 1715 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.22 (5 H, s, Cp), 4.18 (1 H, dm, $J_{3,4}$ = 7 Hz, 4-H), 3.71 (1 H, t, $J_{2,3}$ = $J_{3,4}$ = 7 Hz, 3-H), 3.67 (3 H, s, CO_2CH_3), 3.52 (1 H, dm, $J_{2,3}$ = 7 Hz, 2-H), 2.48 (1 H, dm, $J_{1,2}$ = 7 Hz, 1-H), 2.12 (2 H, m, endo-5-H, endo-7-H), 1.20 (3 H, s, Me), 1.17 (3 H, s, Me), 1.32 (2 H, m (obscured), endo-6-H, exo-5-H), 1.10 (1 H, m, exo-7-H), 0.84 (1 H, m, exo-6-H). Anal. Calcd for $C_{19}H_{24}MoO_4$: C, 54.38; H, 5.86. Found: C, 54.46; H, 5.89.

Dicarbonyl[methyl 2-(2–5-η-cyclohexa-2,4-dienyl)isobutyrate](triphenylphosphine)iron (37). IR ($CHCl_3$): ν_{max} 1905, 1965, 1720 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.36 (15 H, m, Ph), 4.93 (1 H, m, 3-H), 4.81 (1 H, m, 4-H), 3.53 (3 H, s, CO_2CH_3), 2.48 (1 H, dt, $J_{4,5}$ = 11.4 Hz, $J_{5,6endo}$ = 3.8 Hz, 5-H), 2.24 (1 H, m, 2-H), 2.18 (1 H, m, 1-H), 1.82 (1 H, ddd, J_{gem} = 14.7 Hz, $J_{1,6endo}$ = 11 Hz, $J_{5,6endo}$ = 3.8 Hz, endo-6-H), 0.91 (3 H, s, Me), 0.89 (3 H, s, Me). HRMS: calcd for $C_{30}H_{31}FeO_3P$ (M – CO) m/z 526.1203, found m/z 526.1339.

Tricarbonyl[methyl 2-(2–5-η-3-methoxycyclohexa-2,4-dienyl)isobutyrate]iron (38). IR ($CHCl_3$): ν_{max} 2035, 1958, 1713 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.09 (1 H, dd, $J_{4,5}$ = 7.0 Hz, $J_{2,4}$ = 2.1 Hz, 4-H), 3.62 (3 H, s, CO_2CH_3), 3.60 (3 H, s, OCH_3), 3.16 (1 H, dd, $J_{1,2}$ = 3.1 Hz, $J_{2,4}$ = 2.1 Hz, 2-H), 2.57 (1 H, ddd, $J_{4,5}$ = 7.0 Hz, $J_{5,6endo}$ = 4.1 Hz, $J_{5,6exo}$ = 2.1 Hz, 5 H), 2.43 (1 H, ddd, $J_{1,6endo}$ = 10.6 Hz, $J_{1,6exo}$ = 4.6 Hz, $J_{1,2}$ = 3.2 Hz, 1-H), 1.68 (2 H, ddd, J_{gem} = 14.8 Hz, $J_{1,6endo}$ = 10.6 Hz, $J_{5,6endo}$ = 4.0 Hz, endo-6-H), 1.07 (3 H, s, Me), 1.00 (3 H, s, Me). HRMS: calcd for $C_{15}H_{18}FeO_6$ m/z 350.0452, found m/z 350.0449.

Desulfurization of Methylthio Complexes. General Procedure. The methylthioacetyloxazolidinone adduct (1 mmol) was taken up in 10 mL of dry ethanol and placed in a dried 25-mL flask equipped with a reflux condensor, under argon. To this was added 3 mL of Raney Nickel suspended in water. This was refluxed until the reaction was complete by TLC (silica gel, 20% EtOAc/hexane). The reaction was cooled to room temperature and filtered through a plug of cotton wool. The eluent was taken up in ether and washed with water (1 × 10 mL) and brine (1 × 10 mL), and the organic layer was dried ($MgSO_4$) and concentrated in vacuo. Purification via flash chromatography (20% EtOAc/hexane) yielded the desired monoester complexes, which have been previously characterized.

Demetalation of Iron Complexes. General Procedure. The appropriate complex (1 mmol) was taken up in dichloromethane (25 mL) and placed in a dried 50-mL flask under argon. To this was added in one portion pyridinium chlorochromate (5 mmol), and the reaction mixture was stirred until complete by TLC (silica gel, 30% EtOAc/hexane; ca. 4 h). Filtration through silica gel with 20% EtOAc/hexane as eluent followed by removal of the solvent in vacuo yielded pure enone as a clear oil.

Methyl (3-Oxocyclohex-4-enyl)acetate (39). Yield 80%. IR ($CHCl_3$): ν_{max} 1720, 1668 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.92 (1 H, ddd, $J_{4,5}$ = 10 Hz, J = 5.3 Hz, J = 2.7 Hz, 5-H), 6.01 (1 H, dm, $J_{4,5}$ = 10 Hz, H-4), 3.64 (3 H, s, CO_2CH_3), 2.55 (2 H, m, α-6-H), 2.48 (2 H, m, β-6-H), 2.36 (2 H, d, $J_{1,7}$ = 6.8 Hz, CH_2CO_2Me), 2.24 (2 H, m, 2-H), 0.86 (1 H, m, 1-H). HRMS: calcd for $C_9H_{12}O_3$ m/z 168.0786, found m/z 168.0798.

Methyl 2-(3-oxocyclohex-4-enyl)isobutyrate (40). Yield 82%. IR ($CHCl_3$): ν_{max} 1720, 1668 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.97 (1 H, ddd, $J_{4,5}$ = 10 Hz, J = 5.4 Hz, J = 2.6 Hz, 5-H), 6.01 (1 H, d (br), $J_{4,5}$ = 10 Hz, 4-H), 3.64 (3 H, s, CO_2CH_3), 2.30 (2 H, m, 6-H), 2.01 (2 H, m, 2-H), 1.17 (3 H, s, Me), 1.164 (3 H, s, Me), 0.85 (1 H, m, 1-H). HRMS: calcd for ($C_{11}H_{16}O_3$ + H) m/z 197.1178, found m/z 197.1180.

Competition Study between Complexes 1 and 5. In a flame-dried 25-mL flask filled with argon, 27.4 mg (0.57 mmol) of NaH (50% dispersion in mineral oil) was added and washed with THF (2 × 5 mL). The flask was then charged with 10 mL of THF and cooled to 0 °C. Then 75 mg (0.57 mmol) of $CH_2(CO_2Me)_2$ was added. At this time, 25 mg (0.057 mmol) of complex 1 and 26 mg (0.057 mmol) of complex **5** was dissolved in 50 mL of CH_2Cl_2 and cooled to 0 °C. This mixture was then treated with 1.92 mL of the $NaCH(CO_2Me)_2$/THF solution. The reaction was stirred for 2 h at 0 °C until we were confident that all malonate was consumed. The reaction was warmed to room temperature, and the bulk of the CH_2Cl_2 was removed in vacuo. Water (10 mL) was added, and the organics were extracted with ether (2 × 25 mL). The ether layer was dried ($MgSO_4$) and concentrated in vacuo to yield a yellow oil (22 mg). ^1H NMR ($CDCl_3$) analysis of the crude product mixture indicated a 1:1 mixture of the two adducts as determined by integration of the two Cp resonances (5.27 and 5.23 ppm).

Competition Study between Complexes 1 and 8. In an analogous fashion, a mixture of 25 mg (0.057 mmol) of complex 1 and 31 mg (0.057 mmol) of complex 8 in 50 mL of CH_2Cl_2 was treated with 1.92 mL of $NaCH(CO_2Me)_2$/THF solution. When the reaction was complete (2 h) the CH_2Cl_2 was removed in vacuo, the resultant yellow oil was treated with 10 mL of H_2O, and the organics were extracted with ether (2 × 25 mL). The combined ether layers were dried ($MgSO_4$) and concentrated in vacuo to yield a brown oil (31 mg). ^1H NMR ($CDCl_3$) analysis of the crude product indicated a 20:1 mixture favoring the iron adduct by comparison of the integration of the Cp singlet (5.27 ppm) of the Mo adduct vs integration of 3-H resonance (4.93 ppm) of the iron adduct.

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Supplementary Material Available: ^1H NMR spectra of compounds **23a**, **24a**, **25a**, **26a**, **27a**, **28a**, **30b**, **31b**, **32a**, **32b**, **33a**, **34a**, **37–40** (16 pages). Ordering information is given on any current masthead page.