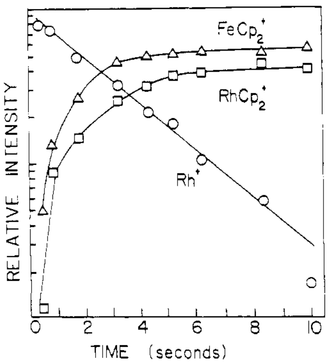

Figure 2. Temporal variation of ion abundance for the $\mathrm{Rh^+}$–ferrocene system. The pressure is ~10^{-7} torr.

Table I. Relative Product Distributions for the Primary Reactions of $\mathrm{Ti^+}$ and $\mathrm{Rh^+}$ with Ferrocene and Nickelocene

reaction		rel product dist, %	
$\mathrm{M^+}$	$\mathrm{M'Cp_2}$	$\mathrm{MCp_2^+}$ [a]	$\mathrm{M'Cp_2^+}$ [b]
$\mathrm{Ti^+}$	$\mathrm{FeCp_2}$	63	37
$\mathrm{Ti^+}$	$\mathrm{NiCp_2}$	40	60
$\mathrm{Rh^+}$	$\mathrm{FeCp_2}$	43	57
$\mathrm{Rh^+}$	$\mathrm{NiCp_2}$	83	17

[a] Metal switching. [b] Charge Exchange.

desorption are prone to adsorb neutrals which are vaporized by the next laser shot.[10] This produces a localized high-pressure gradient in the cell that varies from shot to shot. So that representative pressures could be recorded, several rapid laser pulses were used to remove surface-adsorbed gases, followed by a single laser pulse from which the Fourier transform mass spectrum was recorded.

The primary reaction trends for the four systems investigated are similar. In all cases the two metallocene products come up together in time and dominate after a few seconds, as exemplified by Figure 2. Reaction 1 dominated in the $\mathrm{Rh^+/NiCp_2}$ and $\mathrm{Ti^+/FeCp_2}$ cases while reaction 2 prevailed in the $\mathrm{Rh^+/FeCp_2}$ and $\mathrm{Ti^+/NiCp_2}$ cases. Product distributions are listed in Table I. The reactions with $\mathrm{Rh^+}$ are in general greater than 3 times faster than the corresponding $\mathrm{Ti^+}$ reactions and range from about 10^{-10} cm^3 molecule^{-1} s^{-1} for $\mathrm{Rh^+}$ with $\mathrm{FeCp_2}$ to about 10^{-9} cm^3 molecule^{-1} s^{-1} for $\mathrm{Rh^+}$ with $\mathrm{NiCp_2}$, compared to the Langevin rate constant for both of these reactions of 1.5×10^{-9} cm^3 molecule^{-1} s^{-1}. The observed rate constants are only good within a factor of 2, however, due to the uncertainty in the pressure. The observation of only minor amounts of $\mathrm{MCp^+}$ or $\mathrm{M'Cp^+}$ provides evidence for the stability of these gas-phase metallocene complexes. The $\mathrm{TiCp_2^+}$ is observed to react further with ferrocene and nickelocene to form the mixed dimer species $\mathrm{TiFeCp_4^+}$ and $\mathrm{TiNiCp_4^+}$, whereas the analogous reactions are not observed for $\mathrm{RhCp_2^+}$.

The reaction of $\mathrm{Fe^+}$ with $\mathrm{FeCp_2}$ to form $\mathrm{FeCp_2^+}$ was previously confirmed by ICR[7] and probably results from charge exchange. Similarly, in our experiments $\mathrm{Fe^+}$ reacts with nickelocene to give only the charge-exchange product $\mathrm{NiCp_2^+}$. This result is not unusual since Fe has a higher ionization potential (IP = 7.87 eV)[11] than either $\mathrm{FeCp_2}$ (IP = 7.0 eV)[11] or $\mathrm{NiCp_2}$ (IP = 6.8 eV).[11] In the case of Ti (IP = 6.82 eV)[11] reaction 2 suggests that some $\mathrm{Ti^+}$ may be formed either in an electronically excited state or with excess kinetic energy since its ground-state ionization potential is lower than that of either $\mathrm{FeCp_2}$ or $\mathrm{NiCp_2}$. Since these differences in IP are relatively small, metal switching (reaction 1) may be seen as competitive with charge exchange. Interestingly, the ionization potential of ground-state Rh (IP = 7.46 eV)[11] is greater than that of the two metallocenes, yet behavior similar to that of the $\mathrm{Ti^+}$ reactions is observed. Since no charge exchange is observed between either $\mathrm{TiCp_2^+}$ or $\mathrm{RhCp_2^+}$ with $\mathrm{NiCp_2}$, the upper limit for the ionization potentials of both $\mathrm{TiCp_2}$ and $\mathrm{RhCp_2}$ can be set at the ionization potential of $\mathrm{NiCp_2}$, 6.8 eV.[11] This value is also consistent with not observing any $\mathrm{Fe^+}$ or $\mathrm{Ni^+}$ in reaction 1.

While there is no evidence that these metallocenes have the symmetrical sandwich structures, the lack of any significant fragmentation implies that both Cp rings remain intact. Further investigations into the gas-phase chemistry of $\mathrm{TiCp_2^+}$ and $\mathrm{RhCp_2^+}$ may provide some insights as to their actual structures. Finally, these metal-switching reactions may provide a novel method for synthesizing metallocenes and other organometallic compounds. We are currently studying the generality of these reactions with metal ions above atomic number 20 and by varying the neutral metal complexes. In addition to ferrocene and nickelocene, substituted ferrocenes and nickelocenes and other organometallic compounds such as dibenzenechromium, $\mathrm{(C_6H_6)_2Cr}$, as well as phthalocyanines and other cyclic and macrocyclic metal chelates will be examined.

Acknowledgment is made to the Department of Energy (DE-AC02-80ER10689) for supporting this research and the National Science Foundation (CHE-8002685) for providing funds to purchase the FTMS. In addition, G.D.B. thanks Chevron for providing Fellowship support.

Registry No. Titanocene cation, 54873-35-7; rhodocene cation, 37205-11-1; $\mathrm{FeCp_2}$, 102-54-5; $\mathrm{NiCp_2}$, 1271-28-9.

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[10] For a general discussion of laser/surface interactions see: Ready, J. F. "Effects of High Power Laser Radiation"; Academic Press: New York, 1971.

[11] Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, supplement no. 1.

Cyclization of Vinyl Radicals: A New Versatile Method for the Construction of Five- and Six-Membered Rings

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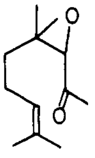
We report a new method of ring formation that we believe has considerable potential in synthesis. We previously made the suggestion that the cyclizations observed when certain unsaturated acyloxiranes react with hydrazine (cf. **1** → **2**) might involve an intermediate vinyl radical.[1] Regardless of the merit of this suggestion, it seemed to us that the possibility of forming rings by intramolecular addition of a vinyl radical to a double bond deserved to be explored. This appeared particularly true because such a process would result in the formation of a ring that would have a double bond at a predictable position (cf. **3** → **4** and **5** → **6**). This could then serve as the site of further synthetic operations.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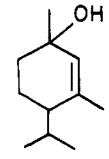
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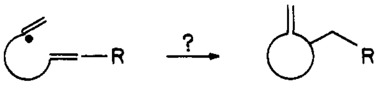
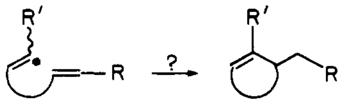


3 4



5 6

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[1] Stork, G.; Willard, P. G. *J. Am. Chem. Soc.* **1977**, *99*, 7067.

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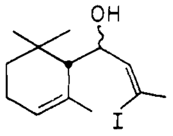
In contrast, intramolecular addition of an alkyl, rather than a vinyl, radical to an olefin results in the loss of functionality with formation of a saturated ring as shown in **7** → **8**. This is presumably why this type of reaction has seen infrequent application in synthesis,[2,3] although it has been subjected to intense mechanistic scrutiny.[4]



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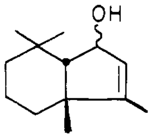
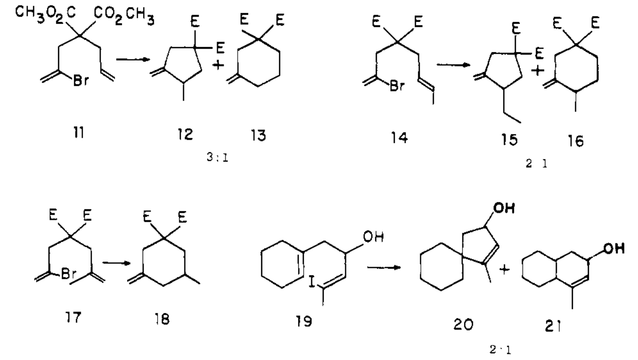


10

The vinyl radical cyclizations that we report here were all initiated with tributylstannane[5] by reaction with a vinyl bromide or a vinyl iodide. We were concerned that the relative instability of the vinyl radical[6] would increase the rate of hydrogen abstraction from the stannane and result in simple replacement of the halogen by hydrogen, without cyclization. Since, however, one is only concerned with the ratio of the rates k_c/k_H (of cyclization to abstraction from stannane) the lower stability of the vinyl radical might not affect partition between simple reduction and cyclization.[7] Actually, the k_H mentioned above is really the sum of $k_H(R_3SnH)$ and k_H(internal), the latter process representing the transformation of the vinyl radical into a more stable one.[8] The relevant rate data are not available at present, but fortunately, the examples about to be given show that the formation of five- or six-membered rings by the intramolecular addition of vinyl radicals to suitably placed double bonds is a rather general reaction.

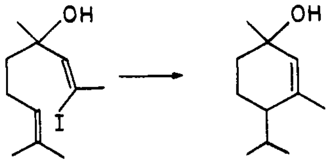
Ultraviolet irradiation of the mixture of vinyl iodide **9** and excess tri-*n*-butylstannane for 0.5–1 h under the standard conditions described later, resulted in ring closure with the formation of a cis-fused five-membered ring, thus leading to the known[9] *cis*-indenol **10**. The relation between the substitution pattern of the aceptor olefin and the size of the ring formed was investigated. Cyclization, in the usual way of the substituted malonic esters **11**, **14**, and **17**[10] gave (75–95% yield) a mixture of five- and six-membered ring products (e.g., **12**, **13**) in ratios that were determined by ^{1}H NMR and VPC analysis of the initial mixtures and of the five- and six-membered ring ketones[11] resulting from ozonolysis. In the case of the cyclization (71% yield) of **19**, infrared spectroscopy served to define the structures of the separated ketones[12] obtained by oxidation of the initial cyclization products **20** and **21**.

Scheme I



The results in Scheme I suggest that the regiochemical preference in the cyclization of vinyl radicals is qualitatively similar to that observed for the alkyl analogues: the observed 5/6 ring preference is clearly the consequence of the geometric factors that have been noted previously in the cyclization of the 5-hexenyl radical.[13] It can, however, be reversed by proper substitution of the acceptor double bond (cf. **17** → **18**).

Intramolecular vinyl radical cyclization occurs especially well when cyclization could formally result either in a six- or seven-membered ring. Only the former is found.[14] Thus, treatment of vinyl iodide **22** under the standard conditions resulted in cyclization (72% yield) to a 1:1 mixture of the diastereomeric cyclohexenols **23**.[15]



We comment at this point on the synthesis of the vinyl halide starting materials. Three different routes have been used in our work and should be generally useful: (a) introduction, e.g., by alkylation, of a substituent already containing the necessary vinyl halide function. This is especially useful with the readily available 2,3-dibromopropene (cf. malonic esters in Scheme I); (b) the Corey reductive halogenation of ethynyl carbinols[16] (cf. **9**, **22**); (c) addition of hydrogen bromide to a terminal acetylene.[17]

It is synthetically convenient, in connection with synthesis of systems such as **24**, that *either* isomer of the required vinyl halide precursor is satisfactory. This would be expected since the rate of inversion of most vinyl radicals is considerably greater (3 ×

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(2) For a specially imaginative case see Büchi, G.; Wuest, H. *J. Org. Chem.* **1979**, *44*, 546.

(3) Cyclization involving stabilized saturated radicals to form polycyclic systems have been extensively studied, especially by M. Julia. For a review, see: Julia, M. *Acc. Chem. Res.* **1971**, *4*, 386. See also: Breslow, R.; Olin, S. S.; Graves, T. J. *Tetrahedron Lett.* **1968**, 1837. Beckwith, A. L. J.; Phillipou, G.; Serelis, A. K. *Ibid.* **1981**, *22*, 2811.

(4) For excellent general reviews see: Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073. Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States"; de Mayo, Paul, Ed.; Academic Press: New York, 1980; Vol. 42-1, pp 180–181, 180–220.

(5) Kuivila, H. G. *Acc. Chem. Res.* **1968**, *1*, 299. Whitesides, G. M.; Casey, C. P.; Krieger, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 1379.

(6) Bond dissociation energies suggest that the vinyl radical is ~10 kcal mol^{-1} less stable than the ethyl radical (cf. Golden D. M.; Benson, S. W. *Chem. Rev.* **1969**, *69*, 125).

(7) See: Walling, C.; Cooley, J. H.; Ponaras, A. A.; Racah, E. J. *J. Am. Chem. Soc.* **1966**, *88*, 5361.

(8) See: Dixon, W. T.; Foxall, J.; Williams, G. H.; Edge, D. J.; Gilbert, B. C.; Kazarians-Moghaddam, H.; Norman, R. O. C. *J. Chem. Soc. Perkin Trans. 2* **1977**, 827.

(9) Ohloff, G.; Uhde, G. *Helv. Chim. Acta* **1970**, *53*, 531.

(10) Prepared in the standard manner by the alkylation (NaH–THF) of dimethyl-2-bromopropenyl malonate, itself made from dimethyl malonate and 2,3-dibromopropene (sodium methoxide–MeOH); cf.: Norris, J. F.; Tucker, H. F. *J. Am. Chem. Soc.* **1933**, *55*, 4697.

(11) In this and subsequent cases, ^{1}H NMR spectra were taken at 90 MHz. Mass and IR spectra were all compatible with the structures described here. Significant ^{1}H NMR resonances were as follows: ketone from **12**, 3.73 (6 H, s), 1.11 (3 H, d, $J = 6$ Hz); ketone from **15**, 3.7 (6 H, s), 0.9 (3 H, t, $J = 7.5$ Hz); ketone from **16**, 3.7 (6 H, d, $J = 1.2$ Hz), 1.05 (3 H, d, $J = 6.1$ Hz).

(12) The following IR spectra were taken on thin films. Enone from **20**: IR, 1670 (s), 1630 (m) cm^{-1}; ^{1},h NMR, 5.83 (1 H, s), 1.95 (3 H, d, $J = 1$ Hz). Enone from **21**: IR, 1700 (s), 1620 (s) cm^{-1}. ^{1}H NMR, 5.8 (1 H, q, $J = 1$ Hz), 2.26 (2 H, s), 2.02 (3 H, d, $J = 1$ Hz).

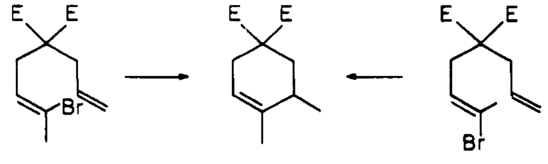
(13) See: Beckwith, A. L. J.; Easton, D. J.; Serelis, A. K. *J. Chem. Soc., Chem. Commun.* **1980**, 482. See also: Hoyland, J. R. *Theor. Chim. Acta* **1971**, *22*, 229. Fujimoto, H.; Yamabe, S.; Minato, T.; Fukui, K. *J. Am. Chem. Soc.* **1972**, *94*, 2905. Dewar, M. J. S.; Olivella, S. *Ibid.* **1978**, *100*, 5290.

(14) For the saturated radical case, see: Surzur, J. M.; Torri, F. *Bull. Soc. Chim. Fr.* **1970**, 3070.

(15) Epimer **23a**: 5.49 (1 H, bs), 1.62 (3 H, bs), 1.21 (3 H, s), 0.98 (3 H, d, $J = 7$ Hz), 0.72 (3 H, d, $J = 7$ Hz). Epimer **23b**: 5.40 (1 H, bs), 1.60 (3 H, bs), 1.20 (3 H, s), 0.94 (3 H, d, $J = 7$ Hz), 0.79 (3 H, d, $J = 7$ Hz).

(16) Corey, E. J.; Katzenellenbogen, J. A.; Posner, G. H. *J. Am. Chem. Soc.* **1967**, *89*, 4245.

(17) Cousseau, J. *Synthesis* **1980**, 805.

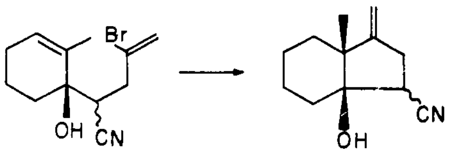


24 **26** **25**

10^7 to 3×10^9 s^{-1})[18] than the anticipated[7] rate of cyclization. From pure **24** or **25**,[19] the cyclic product **26**[20] was indeed obtained in the same yield (75%) in either case.

The general procedure for the vinyl radical cyclization is given in detail below: A solution of 200 mg of bromide **11** in 34 mL of dry benzene containing 2 mg of azobis(isobutyronitrile) and 1.1 equiv of tributylstannane was irradiated with a GE 275-W sunlamp, with aluminum foil to prevent scattering of the light. Heat from the sunlamp was used to keep the solution at reflux for 0.5–1 h (vinyl iodides) or 3–4 h (vinyl bromides). The residue after removal of benzene was stirred rapidly for 1 h with 5 mL of diethyl ether and 5 mL of saturated aqueous potassium fluoride solution. Filtration, extraction with ether, drying (sodium sulfate), and concentration, followed by purification by flash chromatography[21] (5% ethyl acetate in 30–60 °C petroleum ether), gave a mixture (3:1) of **12** and **13** in 87% yield, in addition to ~13% recovered starting material.

We conclude with an example that emphasizes the unique features that make vinyl radical cyclization so promising: Cyclization under the standard conditions of the (bromobutenyl)cyclohexenol **27**[22] gave, in 70% yield, the methyleneindanol **28**.[23]



27 **28**

This illustrates that (1) a new carbon–carbon bond is formed in good yield even though, in this particular case, it produces a quaternary center and (2) the double bond in the newly formed ring is at a predefined position, ready for further elaboration.[24]

Studies of the cyclization process with substituents other than alkyl on the radical center and of other means of generating the required vinyl radicals are in progress.

Acknowledgment. We thank the National Institutes of Health and the National Science Foundation for their support of this work.

Registry No. **9**, 81230-93-5; **10**, 42741-51-5; **11**, 81230-94-6; **12**, 81230-95-7; **13**, 81230-96-8; (*E*)-**14**, 81230-97-9; **15**, 81230-98-0; **16**, 81230-99-1; **17**, 81231-00-7; (*Z*)-**19**, 81231-01-8; **20**, 81231-02-9; **21**, 81231-03-0; (*Z*)-**22**, 81231-04-1; *cis*-**23**, 81231-05-2; (*Z*)-**24**, 81231-06-3; (*E*)-**25**, 81231-07-4; **26**, 81231-08-5; **27**, 81231-09-6; **28**, 81231-10-9; *trans*-**23**, 81231-11-0.

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[18] Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147. See: Kampmeier, J. A.; Fantazier, R. M. *J. Am. Chem. Soc.* **1966**, *88*, 1959.

[19] These were made by alkylation with (*Z*)- or with (*E*)-1,3-dibromo-2-butene, themselves synthesized from pure (*E*)- or pure (*Z*)-3-bromo-2-butenoic acid: Le Noble, W. J. *J. Am. Chem. Soc.* **1961**, *83*, 3897.

[20] ^{1}H NMR: 5.33 (1 H, m), 3.7 (6 H, s), 1.6 (3 H, bs), 1.0 (3 H, d, J = 6.8 Hz).

[21] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

[22] Prepared by addition of the anion of 4-bromo-4-pentenenitrile (LDA–THF, –78 °C) to 2-methyl-2-cyclohexenone. The bromonitrile was made by starting with 3-bromo-3-buten-1-ol.

[23] ^{1}H NMR: 5.87 (2 H, m), 3.35 (1 H, dd, J = 11, 4 Hz), 0.96 (3 H, s). IR (thin film) 3490 (s), 3100 (w), 2960 (s), 2885 (s), 2240 (m), 1660 (m), 1450 (s), 1380 (m), 1060 (m), 900 (m), 885 (m) cm^{-1}. Mass spectrum, (C.I., isobutane) 192 (m + 1), 154 (m – H 20). One of the cyano epimers crystallized: mp 94–94.5 °C; Anal. C, 75.35; H, 8.96; N, 7.32.

[24] The cis ring junction is simply the result of the required geometry of approach of the vinyl radical to the ring double bond.

Metal Effect on Aldol-Type Stereoselection. Erythro-Selective Condensations with Aldehydes via α-Mercurio Ketones

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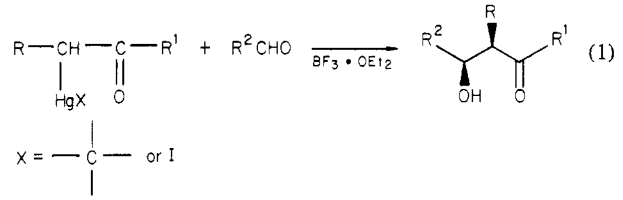
Received December 2, 1981

Development of crossed aldol and related reactions as a basic synthetic strategy to acyclic stereoselection has seen rapid growth in recent years. With the intention of predicting and explaining the stereoselection, both cyclic[1-5] and acyclic[6-8] mechanisms have been proposed. The cyclic mechanism has been proposed for metal enolates in which the metal can chelate the two oxygen atoms, i.e., for M = Li,[1] Mg,[2] Zn,[2] B,[3] Al,[4] and Ti.[5] With the cyclic mechanism, kinetic aldol product stereochemistry depends upon the enolate geometry. Trans enolates afford threo aldols predominantly, and cis enolates give erythro derivatives preferentially. An acyclic mechanism has been proposed for both TAS enolates[6] and the BF_3-mediated addition of crotyltins to aldehydes.[7] In these reactions, kinetic erythro-selective condensations are observed irrespective of the geometry of the starting enolates or the crotyl unit. For TAS enolates, erythro selectivity is ascribed to the absence of a cationic species to make the metal-linked six-membered transition state. For the crotyltin reactions, erythro selectivity is attributed to the coordination of BF_3 to the oxygen atom of aldehydes, which then prevents the coordination of the Sn atom. We now wish to report yet a third possibility of producing erythro selectivity based on the fact that α-mercurio ketones react with aldehydes in the presence of $BF_3 \cdot OEt_2$ to give kinetic erythro aldols, either predominantly or exclusively (eq 1). This result provides not only a synthetically useful method but also a new conceptual model for the metal effect on aldol stereochemistry.



$$R{-}\underset{HgX}{CH}{-}\underset{O}{\overset{}{C}}{-}R^1 + R^2CHO \xrightarrow{BF_3 \cdot OEt_2} \qquad (1)$$

$$X = {-}\overset{|}{\underset{|}{C}}{-} \text{ or } I$$

We recently reported that triphenyltin enolates generated in situ undergo a rapid aldol condensation with aldehydes to give erythro aldols predominantly regardless of the geometry of the starting enolates.[9] Furthermore, Evans[10] and we[11] independently observed similar erythro-selective condensations via zirconium enolates. As to the origin of this erythro stereoselection, Evans speculated that steric factors originated from the sterically demanding cyclopentadienyl ligands and that their interactions with the enolate substituents determined the structure of the pericyclic

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[1] For example: Dubois, J. E.; Fellmann, P. *Tetrahedron Lett.* **1975**, 1225. Kleschick, W. A.; Buse, C. T.; Heatcock, C. H. *J. Am. Chem. Soc.* **1977**, *99*, 247. Meyers, A. I.; Reider, P. J. *Ibid.* **1979**, 101, 2501.

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[7] Yamamoto, Y.; Yatagai, H.; Naruta, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 7107.

[8] Mulzer, J.; Brüntrup, G.; Finke, J.; Zippel, M. *J. Am. Chem. Soc.* **1979**, *101*, 7723. For the addition of the carboxylic acid dianions to aldehydes, the metal chelation is of no importance, and the threo stereoselection is explained by merely the HOMO–LUMO interactions.

[9] Yamamoto, Y.; Yatagai, H.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1981**, 162.

[10] Evans, D. A.; McGee, L. R. *Tetrahedron Lett.* **1980**, 3975.

[11] Yamamoto, Y.; Maruyama, K. *Tetrahedron Lett.* **1980**, 4607.

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