63.021(10), $\beta = 82.579(14)$, $\gamma = 89.386(14)^\circ$, $V = 1301.7(5)$ Å^3, $Z = 1$, $\rho_{\text{calcd}} = 1.438\,\text{g cm}^{-3}$, $F(000) = 582$, $\lambda = 0.71073$ Å, $T = 293(2)$ K, $\mu(\text{Mo}_{\text{K}\alpha}) = 0.840\,\text{mm}^{-1}$. Data were collected on a Siemens-Stoe AED2 diffractometer on an orange crystal ($0.26 \times 0.25 \times 0.04$ mm). Of the 7336 reflections collected by $\omega/2\theta$ scans ($4 \leq 2\theta \leq 50^\circ$), 4586 were unique ($R_{\text{int}} = 0.0320$) and 4270 observed with $I \geq 2\sigma(I)$. Data were corrected for absorption (Gaussian face-indexed method) with min./max. transmission factors of 0.8113/0.9672. Structure solution and refinement were as described for **4b**. Final agreement factors were $R_1 = 0.0362$ (observed reflections) and $wR_2 = 0.0760$ (all data) for 296 parameters; GOF 1.024; largest peak and hole in the final difference map 0.737 and $-0.440\,\text{e Å}^{-3}$, respectively; b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-139639 (**4a**) and CCDC-139640 (**4b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[10] a) G. Aullón, P. Alemany, S. Alvarez, *J. Organomet. Chem.* **1994**, *478*, 75; b) S. Alvarez, A. A. Palacios, G. Aullón, *Coord. Chem. Rev.* **1999**, *185–186*, 431.

Synthesis of Chiral, Enantiopure Zirconocene Imido Complexes: Highly Selective Kinetic Resolution and Stereoinversion of Allenes, and Evidence for a Stepwise Cycloaddition/Retrocycloaddition Reaction Mechanism**

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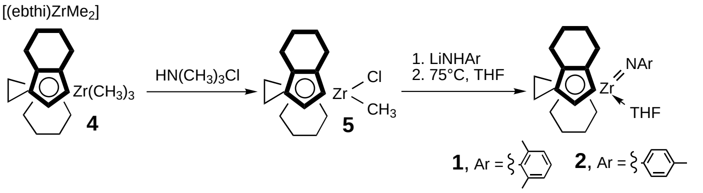
Certain metal–carbon multiple bonds exhibit substantial reactivity toward organic compounds and are important intermediates in many catalytic processes.[1] The analogous reactivity of metal–heteroatom multiple bonds, such as those in metal–imido complexes, has been known for a much shorter time and has only relatively recently been utilized in synthetic applications.[2]

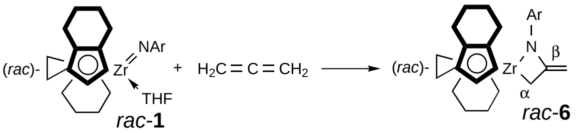
We wish to report a series of highly enantioselective reactions using isolable imido complexes with reactive metal–nitrogen double bonds.[3–9] These involve the reactions of enantiopure (ebthi)(L)Zr=NR complexes with 1,3-disubstituted allenes (L = tetrahydrofuran; ebthi = bis(tetrahydroindenyl)ethane). Our observations a) demonstrate the operation of a general and highly selective kinetic resolution, b) provide the first example of a reaction that can be used to selectively invert the absolute configuration of one (symmetrically or unsymmetrically 1,3-disubstituted) allene enantiomer within a racemic mixture, and c) provide strong mechanistic evidence for the stepwise nature of an organometallic cycloaddition reaction.

Previous work in our laboratories has shown that zirconocene–imido complexes undergo cycloaddition reactions with a wide range of unsaturated organic molecules including alkynes,[10] imines,[11] and certain alkenes.[12] Several of these reactions are important steps in catalytic transformations (for example, hydroamination or imine metathesis) mediated by the imido compounds. To extend this chemistry to systems capable of enantioselective reactions, we decided to examine the reactions of chiral disubstituted allenes with zirconium imido complexes bearing the C_2-symmetric ebthi ligand developed by Brintzinger.[13] The chiral imido complexes were synthesized in two steps from the known dimethyl complex **4**, as shown in [Eq. (1)].[14]



(1)

In order to investigate the products and diastereoselectivity of the chiral zirconocene–allene reactions, we first examined the stoichiometric reactions of racemic ebthi complexes **1** and **2** with achiral allenes and racemic chiral 1,3-disubstituted allenes. The purple metallacycle *rac*-**6** was formed rapidly upon condensation of allene onto a benzene solution of *rac*-**1** [Eq. (2)]. Production of an azametallacycle with the exocyclic methylene group in the β (as opposed to the α) position was indicated by its ^{1}H, ^{1}H NOESY spectrum, which featured a strong NOE between one of the exocyclic methylene protons and the methyl groups on the phenyl ring.



(2)

The reaction of *rac*-**1** with 1 equiv of racemic 1,3-diphenylallene, 3,4-heptadiene, 4,5-nonadiene, or 1,2-cyclononadiene at 23 °C provided a single diastereomeric product in each case, as determined by ^{1}H and ^{13}C NMR spectra ([Eq. (3)]). A bulky imido substituent is required for the selectivity in these transformations, as an 85:15 mixture of diastereomers was formed from the reaction of the *p*-tolylimido complex *rac*-**2** with diphenylallene. These results were encouraging because they suggested that the reactions are stereospecific: (*S*,*S*)-**1**

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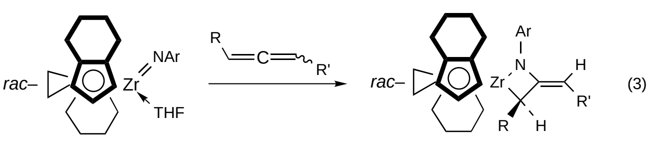


rac-**1**

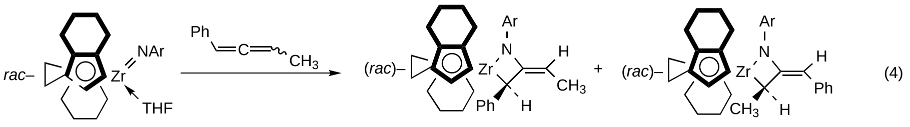
(3)

	R	R'
rac-**7**	Ph	Ph
rac-**8**	C_2H_5	C_2H_5
rac-**9**	C_3H_7	C_3H_7
rac-**10**	–$(CH_2)_6$–	

reacts preferentially with the (*S*) allene, and (*R*,*R*)-**1** with the (*R*) allene, in order to give the diastereoselectivity observed. As the data summarized below shows, the actual situation is more complicated.

Reactions of **1** with the unsymmetrically substituted allenes 1-phenyl-1,2-butadiene and 1-phenyl-1,2-pentadiene can potentially produce a mixture of diastereo- and regioisomers. However, addition of 1 equiv of 1-phenyl-1,2-butadiene to a solution of *rac*-**1** produced only the regioisomers *rac*-**11** and *rac*-**12** (1:1 ratio determined by ^1H NMR [Eq. (4)]). Therefore, even though the reaction is not regioselective, it is still highly diastereoselective. Similar results were obtained in the reaction of *rac*-**1** with 1-phenyl-1,2-pentadiene.

Deeper insight into the actual course of these reactions was provided by examining the stereochemistry of the allene cycloaddition reactions with enantiopure **1**. First, the reaction of enantiopure (*S*,*S*)-**1** with the racemic allenes used in excess provided an effective kinetic resolution even at room temperature. Addition of 1.8 equiv of racemic 1,3-diphenylallene to a benzene solution of (*S*,*S*)-**1** at 23 °C resulted in consumption of approximately 50% of the allene.[15, 16] The unreacted 1,3-diphenylallene was highly enriched in the (*R*) enantiomer (>98% *ee*). The results of enantioselective capture experiments, in which (*S*,*S*)-**1** was treated with other chiral allenes, are shown in Table 1. Notably, the cycloaddition reaction is selective for both symmetrically and unsymmetrically 1,3-disubstituted allenes with high *ee* values in most cases.[17, 18]



rac-**1** *rac*-**11** *rac*-**12**

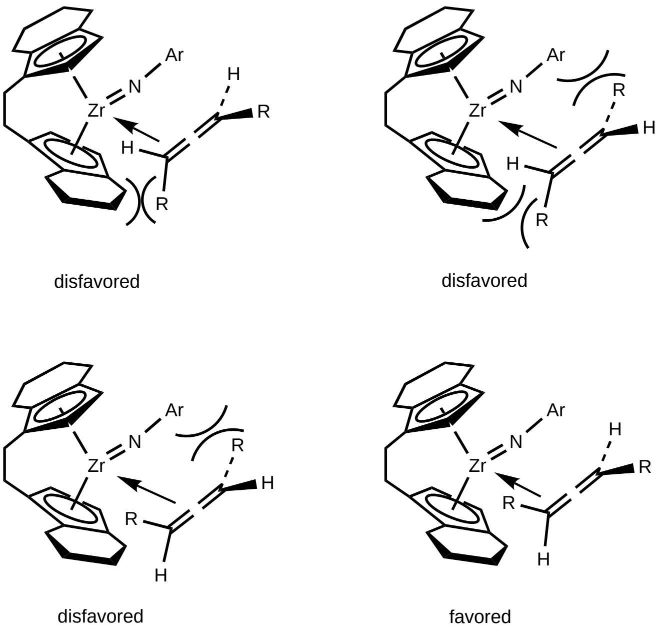
(4)

We propose that the selectivity observed in these cycloadditions is the result of mutually reinforcing stereocontrol imposed by the combination of the ebthi ligand and the bulky imido substitutent. The ebthi ligand allows the imido complex to add preferentially onto one face of the reacting π bond,[19] while the N–Ar group favors reaction of the allene enantiomer in which one olefin substituent is oriented away from the imido ligand in the cycloaddition transition state (Scheme 1).

Table 1. Enantioselective capture reactions of $(R_1)HC{=}C{=}CH(R_2)$ with (*S*,*S*)-**1**.

Entry	R_1	R_2	Allene consumed [%]	*ee*[a] [%]	Configuration of unreacted allene
1	*cyclo*-$(CH_2)_6$		54	78	(*R*)
2	C_3H_5	C_3H_5	59	>98	(*R*)
3	Ph	Me	61	94	(*R*)
4	Ph	Et	53	>98	(*R*)
5	Ph	Ph	50	>98	(*R*)

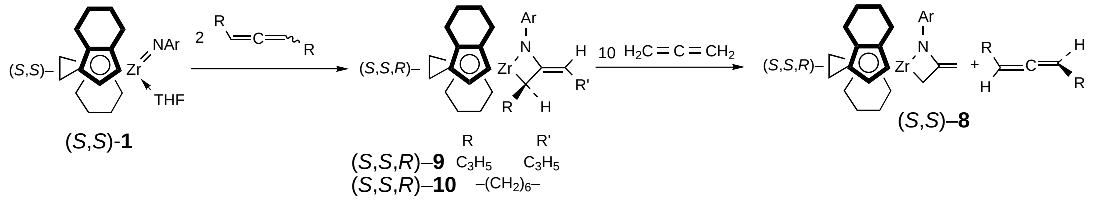
[a] Enantiomeric excess of the unreacted allene. See ref. [16] for the method of *ee* determination.



Scheme 1. Alternative structures of the π complexes formed by interaction of (*S*,*S*)-(ebthi)Zr=NAr with the two enantiomers of a 1,3-disubstituted allene.

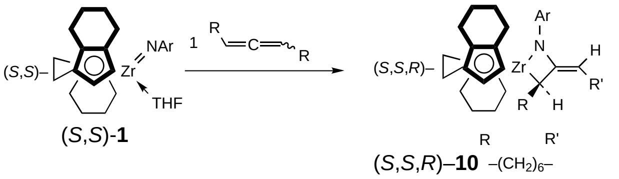
This model is supported by the observation that the reactions of **2**, which contains a smaller imido substituent, appear to be substantially less selective than the reactions of **1**. The proposal is also consistent with the absolute configuration observed in the enantioselective cycloaddition reactions.

A single metallacycle diastereomer is, by NMR spectroscopy, observed to be the major organometallic product in the enantioselective capture reactions. In separate experiments, (*S*,*S*,*R*)-**9** and (*S*,*S*,*R*)-**10** could be isolated by treatment of (*S*,*S*)-**1** with slightly more than 2 equiv of either 4,5-nonadiene or 1,2-cyclononadiene followed by removal of the excess allene in vacuo [Eq. (5)]. The faster reacting allene enantiomer was then regenerated from the metallacycle by treating it with the parent allene, 1,2-propadiene (C_3H_4). Thus, when (*S*,*S*,*R*)-**9** was treated with 1,2-propadiene, retrocycloaddition occurred slowly at 23 °C to produce (*S*,*S*)-**8** and (*S*)-4,5-nonadiene that was highly enantioenriched (93% *ee*, >95% recovery). Similarly, (*S*)-1,2-cyclononadiene (85% *ee*, >95% recovery) was produced from the reaction of 1,2-propadiene with (*S*,*S*,*R*)-**10**. By this method, it is possible to obtain good separation of allene racemates: The slower reacting allene enantiomer is recovered from the initial cycloaddition and the faster reacting allene enantiomer is recovered by displacement from the product metallacycle.



(5)

As the allene cycloaddition reactions appeared to be stereospecific, we expected that the reaction of the enantiopure imido complex with only 1 equiv of a racemic disubstituted allene (for example, 1,2-cyclononadiene) would allow reaction of the imido complex with the slower reacting allene enantiomer, once the faster reacting enantiomer had been consumed. This might then lead to a mixture of metallacycle diastereomers. We were therefore surprised to find that (*S*,*S*,*R*)-**10** was the only detectable product of the reaction between 1 equiv of racemic 1,2-cyclononadiene and (*S*,*S*)-**1** [Eq. (6)]. No intermediates were observed when this reaction was followed by ^{1}H NMR spectroscopy. Following treatment of the product mixture with 1,2-propadiene, (*S*)-1,2-cyclononadiene (84% *ee*, 93% yield) evolved.



(6)

The only way we are able to rationalize this result is to assume that when the slower reacting (*R*) allene reacts with (*S*,*S*)-**1**, its absolute configuration is inverted. To further test this conclusion, we treated (*S*,*S*)-**1** with 1,2-cyclononadiene enriched in the (*R*) enantiomer (67% *ee*). This again led to (*S*,*S*,*R*)-**10**, and condensation of 1,2-propadiene into the solution regenerated (*S*)-1,2-cyclononadiene (85% *ee*). Therefore, we suggest that: a) the faster reacting (*S*) enantiomer of 1,2-cyclononadiene forms a metallacycle, which is then regenerated in the retrocycloaddition with *retention* of its absolute configuration, but b) the slower reacting (*R*) enantiomer reacts to produce the same metallacycle as that formed for the (*S*) enantiomer, which is regenerated with overall *inversion* of its absolute configuration. The allene cycloaddition is therefore highly stereoselective but not stereospecific.[20] This system allows quantitative (rather than just 50%, as would be possible in a conventional kinetic resolution) conversion of racemic allene into material that is highly enriched in the (*R*) enantiomer. Similarly, the (*R*,*R*) imido complex can be used to convert racemic allene quantitatively into material that is highly enriched in the (*S*) enantiomer. Interconversion of (*R*) and (*S*) allenes is very slow under these conditions.

Other reactions of (*S*,*S*)-**1** with racemic chiral allenes behave analogously. The reaction of (*S*,*S*)-**1** with 1 equiv of racemic 1-phenyl-1,2-butadiene at 23 °C produced (*S*,*S*,*R*)-**11**, (*S*,*S*,*R*)-**12**, and a third, unidentified metallacycle diastereomer in a 1.0:1.0:0.5 ratio, respectively (^{1}H NMR). After 1 h, all of the disubstituted allene was consumed in the reaction. Treatment of this product mixture with 1,2-propadiene at 75 °C quantitatively converted it to (*S*,*S*)-**8** and free 1-phenyl-1,2-butadiene. Chiral GC analysis indicated that the released disubstituted allene was enantioenriched ((*S*) 43% *ee*, 90% recovery). Enantioenriched 1-phenyl-1,2-pentadiene ((*S*) 33% *ee*, >95% recovery) was also obtained by consecutive treatment of racemic 1-phenyl-1,2-pentadiene with (*S*,*S*)-**1** and 1,2-propadiene.

Previous experimental work has suggested that such organometallic cycloaddition reactions are concerted and stereospecific,[21] and several theoretical studies support this postulate.[22] However, we see no *economical* way to explain our unusual observations by assuming that the imido–allene cycloadditions are concerted processes. We therefore offer the stepwise mechanism illustrated in Figure 1 for (*S*,*S*)-**1** and 1,2-cyclononadiene, which proceeds through the diradical intermediate **C**,[23] as a working explanation for our results. The left-hand side of the diagram accounts for the kinetic resolution. It assumes that when the (*S*,*S*)-imido complex approaches the allene, perhaps to form the initial π complexes **A** and **B**, coordination of the (*S*) enantiomer of the allene gives the lower energy complex **A** because the two allene substituents can lie away from the N–Ar group and in the open quadrant of the metal coordination sphere. In complex **B**, however, the requirement that the external allene substituent lies away from the N–Ar moiety forces the internal allene substituent into the more sterically congested quadrant of the metal coordination sphere, to result in a higher energy complex. Subsequent formation of the C–N bond with rotation about one of the C–C bonds of the developing allyl radical results in the formation of intermediate **C**. However, the transition states **A**$^{\neq}$ and **B**$^{\neq}$, which lead to **C** and are not planar about the three carbon atom fragment, must still retain some of the energetics associated with the initial π complexes.[24] This accounts for the observation that one allene enantiomer reacts more quickly than the other. Once **C** has been reached, the chirality of the allene has been destroyed. Therefore a second enantioselective step is required to explain the observed stereochemistry of the metallacycle and the recovered less reactive. To account for this, we assume that ring closure in intermediate **C** can take place by rotation of the internal R group "up" into the open quadrant of the coordination sphere—which is favored—but not "down" into the more hindered quadrant.[25] Thus the same metallacycle (*S*,*S*,*R*)-**10** is formed from both allene enantiomers and the (*R*) allene enantiomer is always regenerated from this metallacycle.[26]

According to this mechanism, the selectivities of both the enantioselective capture and the retrocycloaddition reactions

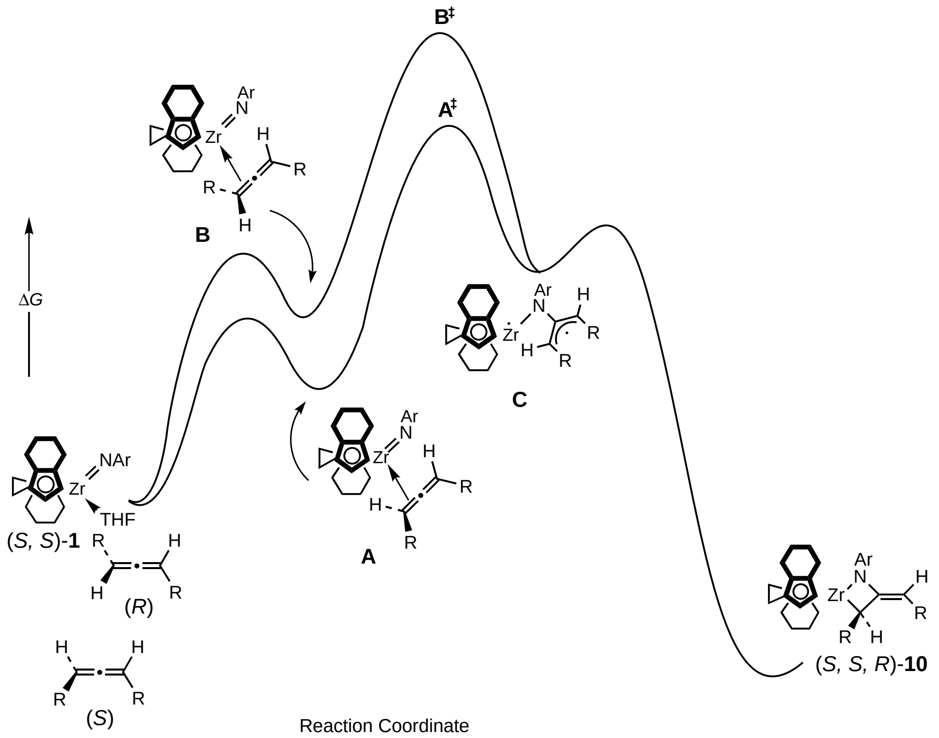


Figure 1. Reaction coordinate diagram illustrating the proposed mechanism of the reaction of imido complex (*S*,*S*)-**1** with both enantiomers of 1,2-cyclononadiene.

are a function of the free energy difference ($\Delta G^{\neq}{}_{A^{\neq}} - \Delta G^{\neq}{}_{B^{\neq}}$) for transition states $A^{\neq}$ and $B^{\neq}$. Therefore, if this model is correct, the selectivities of the enantioselective capture and retrocycloaddition reactions should be identical. Analysis of the cyclononadiene cycloaddition and retrocycloaddition reactions confirms that this is indeed the case. The selectivity of the enantioselective capture reaction in which (*S*,*S*)-**1** is treated with excess 1,2-cyclononadiene can be estimated using [Eq. (7)], where *s* is the selectivity of the reaction, *C* is the

$$s = \frac{\ln[(1-C)(1-ee)]}{\ln[(1-C)(1+ee)]} \qquad (7)$$

percentage of allene consumed in the reaction, and *ee* is the enantiomeric excess of the remaining allene.[27] Using the values in Table 1, a selectivity of 12.0 is calculated. This corresponds to a difference in the activation energies ($\Delta\Delta G^{\neq}$) of the reaction of the slower and faster reacting enantiomers of 1.5 kcal mol^{-1} at 298 K. A selectivity of 11.5 ($\Delta\Delta G^{\neq}$ = 1.4 kcal mol^{-1}, 298 K) for release of the chiral allene can be calculated directly from the enantiomeric ratio (92:8) of the cyclononadiene enantiomers following the retrocycloaddition reaction. The similarity of these values strongly supports the postulate that the formation and fragmentation of these metallacycles occur via the same pathway.

In summary, **1** undergoes highly enantioselective cycloaddition reactions and, in certain cases, this system allows conversion of an allene racemate into a mixture enriched in one enantiomer. The absolute sense of stereochemistry of these reactions appears to be so predictable that we believe they can be used to assign the absolute configurations of new, optically active allenes.

Experimental Section

(*rac*-**1**): A solution of *n*BuLi (0.50 mL of 1.6 M solution in Et_2O) was added dropwise to a stirred solution of 2,6-dimethylaniline (98 mg, 0.80 mmol) in Et_2O (5 mL) at RT to form a yellow solution. After 10 min, the yellow solution was added dropwise to a stirred suspension of *rac*-**5** (327 mg, 0.80 mmol) in THF (8 mL). This mixture was stirred overnight and the volatile materials were removed in vacuo to give a yellow residue. The yellow residue was dissolved in Et_2O and filtered. The volatile materials were removed in vacuo and the yellow solid was dissolved in THF (5 mL) and heated to 75 °C overnight in a sealed ampoule. The resulting orange solution was cooled to −30 °C overnight to precipitate 265 mg of *rac*-**1** (65 %) as orange crystals.

(*S*,*S*)-**1**: Solid $LiNH(2,6\text{-}CH_3\text{-}C_6H_3)$ was added to a solution of (*S*,*S*)-**5** (299 mg, 0.73 mmol) in benzene. The resulting yellow solution was stirred for 1 h, the volatile materials were removed in vacuo, and the remaining solid was dissolved in pentane and filtered. The volatile materials were removed in vacuo and the yellow solid was dissolved in THF (7 mL) and heated to 75 °C overnight in a sealed ampoule. The volume of the resulting orange solution was reduced in vacuo and crystallization from THF/Et_2O at −30 °C provided (*S*,*S*)-**1** (210 mg, 53 %). ^1H NMR (C_6D_6): δ = 7.23 (d, J = 7.3 Hz, 2H), 6.75 (t, J = 7.3 Hz, 1H), 6.37 (d, J = 2.7 Hz, 1H), 5.78 (d, J = 2.7 Hz, 1H), 5.35 (d, J = 2.4 Hz, 1H), 5.30 (d, J = 2.4 Hz, 1H), 3.63 (m, 2H), 3.38 (m, 2H), 3.05 (m, 1H), 2.83 (m, 1H), 2.67 (m, 3H), 2.51 (m, 11H), 2.21 (m, 2H), 1.72 (m, 1H), 1.46 (m, 6H), 1.15 (m, 5H). $^{13}C\{^1H\}$ NMR ([D_8]THF; assignments made by DEPT spectrum): quaternary: δ = 157.2, 133.1, 130.1, 128.3, 127.5, 117.9, 115.7; methine: δ = 127.7, 115.0, 109.6, 108.2, 103.7, 100.5; α-methylene in coordinated THF: δ = 68.4; methyl: δ = 26.55; aliphatic CH_2: δ = 28.9, 28.2, 26.4, 25.8, 25.4, 25.3, 24.9, 24.8, 24.7, 24.0. IR (Nujol): $\tilde{\nu}$ = 3061, 2881, 1582, 1315, 1005, 844, 761 cm^{-1}. Elemental analysis: calcd for $C_{32}H_{41}NOZr$: C 70.28, H 7.56, N 2.56; found: C 70.07, H 7.83, N 2.50. M.p. (*rac*)-**1**: 145–158 °C; (*S*,*S*)-**1**: 170–185 °C. $[\alpha]^{25}_{D}$ = −665.5° (c = 5.27 mg mL^{-1}, C_6D_6).

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[1] a) B. Cornils, W. A. Herrmann, *Applied Homogeneous Catalysis with Organometallic Compounds, Vols. 1 & 2*, VCH, Weinheim **1996**, pp. 318 ff, 557 ff, 1150 ff.; b) M. P. Doyle, D. C. Forbes, *Chem. Rev.* **1998**, *98*, 911; c) K. H. Dötz, P. Tomuschat, *Chem. Soc. Rev.* **1999**, *28*, 187; d) R. H. Grubbs, S. Chang, *Tetrahedron* **1998**, *54*, 4413; e) M. Schuster, S. Blechert, *Angew. Chem.* **1997**, *109*, 2124; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2037; f) J. Feldman, R. R. Schrock in *Prog. Inorg. Chem.*, *Vol. 39* (Ed.: S. J. Lippard), Wiley, New York, **1991**, 1.

[2] a) W. A. Nugent, J. M. Meyer, *Metal–Ligand Multiple Bonds*, Wiley, New York, **1988**; b) D. E. Wigley in *Prog. Inorg. Chem.*, *Vol. 42* (Ed.: K. D. Karlin), Wiley, New York, **1994**; c) R. Taube in *Homogeneous Catalysis with Organometallic Compounds* (Eds.: B. Cornils, W. A. Herrmann), VCH, Weinheim, **1996**, Chap. 2.7.

[3] S. Minakata, T. Ando, M. Nishimura, I. Ryu, M. Komatsu, *Angew. Chem.* **1998**, *110*, 3596; *Angew. Chem. Int. Ed.* **1998**, *37*, 3392.

[4] Z. Li, R. W. Quan, E. N. Jacobsen, *J. Am. Chem. Soc.* **1995**, *117*, 5889.

[5] D. A. Evans, M. M. Faul, M. T. Bilodeau, *J. Am. Chem. Soc.* **1994**, *116*, 2742.

[6] E. A. Kretzschmar, J. Kipke, J. Sundermeyer, *Chem. Commun.* **1999**, 2381.

[7] X.-G. Zhou, X.-Q. Yu, J.-S. Huang, C.-M. Che, *Chem. Commun.* **1999**, 2377.

[8] P. O'Brien, *Angew. Chem.* **1999**, *111*, 339; *Angew. Chem. Int. Ed.* **1999**, *38*, 326.

[9] A. E. Rubin, K. B. Sharpless, *Angew. Chem.* **1997**, *109*, 2751; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2637.

[10] A. M. Baranger, P. J. Walsh, R. G. Bergman, *J. Am. Chem. Soc.* **1993**, *115*, 2753.

[11] S. W. Krska, R. L. Zuckerman, R. G. Bergman, *J. Am. Chem. Soc.* **1998**, *120*, 11828, and references therein.

[12] P. J. Walsh, F. J. Hollander, R. G. Bergman, *Organometallics* **1993**, *12*, 3705.

[13] F. R. W. P. Wild, M. Wasiucionek, G. Huttner, H. H. Brintzinger, *J. Organomet. Chem.* **1985**, *288*, 63.

[14] Enantioresolved complexes **1** and **5** were confirmed to be enantiopure by NMR analysis of the products formed by treating the zirconium complexes with enantiopure (*R*)-mandelic acid, as described by earlier workers: a) A. Schafer, L. Zsolnai, G. Huttner, H. H. Brintzinger, *J. Organomet. Chem.* **1987**, *328*, 87; b) R. B. Grossman, W. M. Davis, S. L. Buchwald, *J. Am. Chem. Soc.* **1991**, *113*, 2321; c) B. Chin, S. L. Buchwald, *J. Org. Chem.* **1997**, *62*, 2267.

[15] The reaction was stopped 10 min after addition of the allene.

[16] Enantioenrichments of the allenes were determined by chiral vapor-phase chromatography, in which the resolution is calibrated using racemic mixtures.

[17] Y. Noguchi, H. Takiyama, T. Katsuki, *Synlett* **1998**, 543.

[18] The configuration of cyclononadiene was assigned by comparison with material prepared in partially enantioenriched form by resolution with $[(-)\text{-(isopinylcampheyl)}_2BH]_2$. Resolution using this reagent is known to provide cyclononadiene enriched in the *S* enantiomer. See: a) R. D. Bach, J. W. Holubka, C. L. Willis, *J. Am. Chem. Soc.* **1982**, *104*, 3980; b) W. R. Moore, H. W. Anderson, S. D. Clark, *J. Am. Chem. Soc.* **1973**, *95*, 835.

[19] A. H. Hoveyda, J. P. Morken, *Angew. Chem.* **1996**, *108*, 1378; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1263.

[20] E. L. Eliel, S. H. Wilen, L. N. Mander, *Stereochemistry of Organic Compounds*, John Wiley and Sons, Inc., New York, **1994**, p. 837.

[21] B. R. Bender, D. L. Ramage, J. R. Norton, D. C. Wiser, A. K. Rappe, *J. Am. Chem. Soc.* **1997**, *119*, 5628.

[22] a) T. H. Upton, A. K. Rappe, *J. Am. Chem. Soc.* **1985**, *107*, 1206; b) E. Folga, T. Ziegler, *Organometallics* **1993**, *12*, 325.

[23] We postulate a diradical structure for the intermediate because the thermal dimerization of allenes is known to proceed via this type of species. For leading references, see: a) D. J. Pasto, *Tetrahedron*, **1984**, *40*, 2805; b) *The Chemistry of the Allenes* (Ed.: S. R. Landor), Academic Press, London, **1982**. However, with our presently available data, we cannot distinguish between a diradical and the corresponding zwitterion (presumably with a positive charge on Zr and a negative charge on the allyl moiety) or a π-allyl complex in which the C3 fragment in intermediate **C** is coordinated to the Zr center. Evidence has been proposed for diradical intermediates in several organometallic reactions; for examples, see: c) S. L. Buchwald, E. V. Anslyn, R. H. Grubbs, *J. Am. Chem. Soc.* **1985**, *107*, 1766; d) L. Cavallo; H. Jacobsen, *Angew. Chem.* **2000**, *112*, 602; *Angew. Chem. Int. Ed.* **2000**, *39*, 589, and references therein.

[24] The assumption of initial π-complex formation is convenient but not required to explain the enantioselective behavior of this system; the initial interaction between imido complex **1** and the allenes could lead directly to the transition states A^+ and B^+.

[25] There is, of course, a higher energy path leading from intermediate **C** to the more sterically congested isomer of the metallacycle. Because we do not observe detectable amounts of this product, we have omitted this pathway and product from the diagram for the sake of clarity.

[26] One can always postulate more complicated mechanisms that will also account for a particular set of experimental results. Therefore, as noted by two referees, we cannot rule out alternative scenarios in which the faster reacting allene enantiomer reacts by a concerted mechanism and the slower reacting allene reacts by a stepwise process proceeding through intermediate **C** or through a less stable diastereoisomer of (*S*,*S*,*R*)-**10**. Experiments are under way aimed at distinguishing these possibilities.

[27] H. B. Kagan, J. C. Fiaud, *Top. Stereochem.* **1988**, *18*, 249.

Oxygenation of Hydrocarbons Mediated by Mixed-Valent Basic Iron Trifluoroacetate and Valence-Separated Component Species under Gif-Type Conditions Involves Carbon- and Oxygen-Centered Radicals[**]

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A remarkable series of iron-based systems for oxidizing hydrocarbons—such as the century-old Fenton reagent,[1] the biologically relevant Udenfriend system,[2] and the more recently developed Gif systems[3]—have received detailed attention, but the nature of the active oxidants involved (free $HO^\bullet/RO^\bullet$ radicals or metal-bound $Fe^{IV/V}{=}O/Fe^{II/III}{-}OO(H)$ units) and their mode of action (radical or concerted) are topics of current debate.[4, 5] Recent advances towards elucidating the functional behavior of high-valent Fe=O units, presumed to operate in biological monooxygenases (P-450,[6] sMMO[7]), have cast suspicion as to whether similar metal-centered oxidants participate in oxygenated Fenton,[4, 8] Gif,[9] and other allegedly biomimetic systems.[10] There is now consensus[11] that at least *t*BuOOH-dependent versions of these systems involve $t\text{BuO}^\bullet/t\text{BuOO}^\bullet$ and substrate-centered radicals ($RO^\bullet/ROO^\bullet$). The recognition that *t*BuOOH-supported shunt pathways of P-450-type mimics[12] frequently generate $t\text{BuO}^\bullet/t\text{BuOO}^\bullet$ radicals limits the usefulness of these systems in probing mechanistic distinctions. Evidence to support a radical mechanism[13] for mainstream H_2O_2- or O_2/Zn-dependent Gif-type systems is currently resting on insufficient experimental basis.[14] Reported in the present study is a persuasive case of a typical Gif reagent which performs oxidation of substrates with H_2O_2 in pyridine/trifluoroacetic acid (py/TFA) by radical pathways.

The reaction of $[Fe_3O(O_2CCH_3)_6(H_2O)_3]$ with excess TFA is known[15] to yield $[Fe_3O(O_2CCF_3)_6(H_2O)_3]\cdot 3.5\,H_2O$. In our hands, samples prepared in TFA/H_2O (4/1 v/v) afford red crystals of $[Fe_3O(O_2CCF_3)_6(H_2O)_3]\cdot 2.5\,H_2O\cdot CF_3COOH$ (**1**, see Scheme 1). The structure of **1** at 133 K (see the Supporting Information) indicates a valence-trapped state within the triangular Fe_3O core (av $Fe^{III}{-}O$ 1.864(8), $Fe^{II}{-}O$ 2.034(3) Å). In dimethyl sulfoxide (DMSO), **1** affords red $[Fe_3O(O_2CCF_3)_6(DMSO)_3]$ (**2**), whose structure at 213 K (see the Supporting Information) reveals partial valence trapping, as there is only a 0.065 Å difference between the longer and shorter Fe–O distances.

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