Effective Uses of Dirhodium(II) Tetrakis[methyl 2-oxopyrrolidine-5(*R* or *S*)-carboxylate] for Highly Enantioselective Intermolecular Cyclopropenation Reactions

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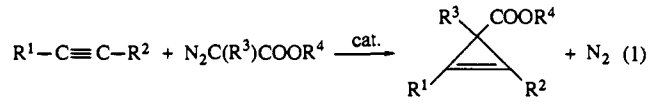
Received April 28, 1994®

Abstract: The title compounds are effective catalysts for intermolecular cyclopropenation reactions of 1-alkynes with diazo esters and diazo amides. Diastereoselectivities achieved from the appropriate match with *d*- or *l*-menthyl diazoacetate are 77 to ≥94% de. Enantioselectivities up to ≥94% ee with 3-methoxy-1-propyne and 3,3-diethoxy-1-propyne have been obtained. Variations in these values for metal carbene additions to alkynes are associated with electronic and/or steric influences from the alkyne or carbene substituents. *N,N*-Dimethyldiazoacetamide provides a higher level of enantiocontrol than do diazo esters. The absolute configurations of the cyclopropene products have been established; dirhodium(II) tetrakis[methyl 2-oxopyrrolidine-5(*S*)-carboxylate], $Rh_2(5S\text{-MEPY})_4$, produces 2-substituted-2-cyclopropene-1-carboxylates having the (*S*)-configuration whereas use of $Rh_2(5R\text{-MEPY})_4$ provides these cyclopropene products in the (*R*)-configuration. Diimide reduction of these cyclopropenecarboxylates produces the *cis*-disubstituted cyclopropane products exclusively.

Expanding interest in cyclopropenes as synthetic intermediates has prompted increased attention to their synthesis and their reactivities.[1-3] Their uses in cycloaddition and sigmatropic reactions,[4,5] suitability for functionalization by X–Y addition,[1,2,6,7] and rearrangements to vinylcarbenes catalyzed by transition metal compounds[8-11] have brought new importance to these previously obscure strained compounds. Furthermore, an increasing number of biomolecules that possess a cyclpropene ring, including fatty acids and sterols,[12,13] has been isolated and characterized.

The synthesis of cyclopropenes by copper- or rhodium-catalyzed reactions of diazocarbonyl compounds with alkynes (eq 1)[2,3,9,14-17] is a simple and convenient methodology. Although intramolecular



cyclopropenation reactions often result in extensive rearrangements primarily due to the instability of the intermediate cyclopropene,[8,10,11] intermolecular reactions form stable cyclopropenes when mild reaction conditions are employed.[9,14-18] Of the catalysts that have been employed for cyclopropenation, those of rhodium(II) have been the most generally effective.

We have previously reported that the chiral dirhodium(II) catalysts, dirhodium(II) tetrakis[methyl 2-oxopyrrolidine-5(*S*)-carboxylate], $Rh_2(5S\text{-MEPY})_4$, and its enantiomeric counterpart, $Rh_2(5R\text{-MEPY})_4$, are exceptionally effective for highly enantioselective intermolecular cyclopropenation reactions of alkyl diazoacetates.[19] With *l*-(−)- or *d*-(+)-menthyl diazoacetate, for example, diastereoselectivities as high as ≥94% de were achieved with propargyl methyl ether and propargyl acetate. An alternative chiral semicorrin copper catalyst[20] was relatively ineffective for these same reactions.[19] We now wish to report the scope of these enantioselective cyclopropenation reactions, factors that enhance enantiocontrol, and the absolute stereochemistry of the cyclopropene products.

Results

Diastereoselectivity. Diazo decomposition of *d*- or *l*-menthyl diazoacetate with $Rh_2(MEPY)_4$ catalysts in the presence of select

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• Abstract published in *Advance ACS Abstracts*, September 1, 1994.

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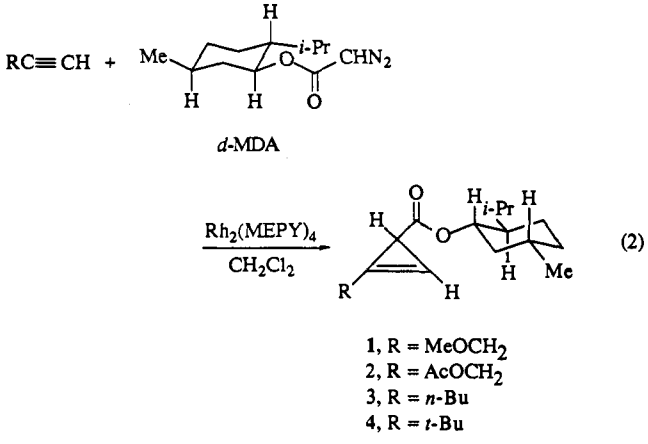
Table 1. Diastereoselective Cyclopropenation of Representative 1-Alkynes by Menthyl Diazoacetates Catalyzed by $Rh_2(5R\text{-MEPY})_4$ and $Rh_2(5S\text{-MEPY})_4$

catalyst	diazoacetate,[a] R′ =	1-alkyne, R =	cyclopropene[b]	yield, %[c]	de, %[d]	absolute config[e]
$Rh_2(5R\text{-MEPY})_4$	*d*-menthyl	$MeOCH_2$	**1*Rd***	43	≥94	*R*
$Rh_2(5R\text{-MEPY})_4$	*l*-menthyl	$MeOCH_2$	**1*Rl***	45	43	*R*
$Rh_2(5S\text{-MEPY})_4$	*d*-menthyl	$MeOCH_2$	**1*Sd***	30	40	*S*
$Rh_2(5S\text{-MEPY})_4$	*l*-menthyl	$MeOCH_2$	**1*Sl***	20	≥94	*S*
$Rh_2(5S\text{-MEPY})_4$	*l*-menthyl	$AcOCH_2$	**2*Sl***	30	≥94	*S*
$Rh_2(5R\text{-MEPY})_4$	*d*-menthyl	*n*-Bu	**3*Rd***	46	86	*R*
$Rh_2(5R\text{-MEPY})_4$	*l*-menthyl	*n*-Bu	**3*Rl***	46	20	*R*
$Rh_2(5S\text{-MEPY})_4$	*d*-menthyl	*n*-Bu	**3*Sd***	24	14	*S*
$Rh_2(5S\text{-MEPY})_4$	*l*-menthyl	*n*-Bu	**3*Sl***	45	84	*S*
$Rh_2(5R\text{-MEPY})_4$	*d*-menthyl	*t*-Bu	**4*Rd***	51	77	*R*
$Rh_2(5R\text{-MEPY})_4$	*l*-menthyl	*t*-Bu	**4*Rl***	50	56	*R*

[a] *l*-Menthyl = (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl; *d*-menthyl = (1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl. [b] *R* or *S* is catalyst configuration; *d* or *l* is configuration of menthyl. [c] Yield of chromatographically purified cyclopropene. [d] From ^1H NMR analyses, ±3%; with those at ≥94%, minimum value is given. Results confirmed with duplicate runs. [e] For assignment see section on absolute configurations of cyclopropenes.

1-alkynes forms cyclopropene derivatives (eq 2) in moderate yield



(2)

1, R = $MeOCH_2$
2, R = $AcOCH_2$
3, R = *n*-Bu
4, R = *t*-Bu

but, with the match of *d*-menthyl diazoacetate (*d*-MDA) with $Rh_2(5R\text{-MEPY})_4$ or *l*-menthyl diazoacetate (*l*-MDA) with $Rh_2(5S\text{-MEPY})_4$, high diastereocontrol (Table 1). Product yields are those of the purified cyclopropenes, isolated by chromatography, and are not optimized. Diastereomeric excesses (% de) are from direct ^1H NMR analyses (±3%) of the cyclopropene vinyl hydrogen near δ 6.3. Use of $Rh_2(5R\text{-MEPY})_4$ provides substantial enhancement of % de for cyclopropene products formed by reactions of *d*-menthyl diazoacetate with 1-alkynes over that from reactions with *l*-menthyl diazoacetate. Likewise, $Rh_2(5S\text{-MEPY})_4$ provides a mirror image enhancement of % de for cyclopropene products formed by reactions with *l*-menthyl diazoacetate. Polar ether or acetate substituents, from methyl propargyl ether or propargyl acetate, respectively, gave enhanced diastereocontrol over that found with aliphatic substituents. Use of the neopentyl ester derivative of $Rh_2(5S\text{-MEPY})_4$, $Rh_2(5S\text{-NEPY})_4$,[21] gave the same results with methyl propargyl ether/*l*-menthyl diazoacetate as those reported in Table 1 for $Rh_2(5S\text{-MEPY})_4$.

Selective cyclopropenation of enynes has been reported for $Rh_2(OAc)_4$-catalyzed reactions of methyl diazoacetate.[22] However, the vinylcyclopropene products derived from these metal carbene reactions are unstable and undergo [2 + 2] cycloaddition.

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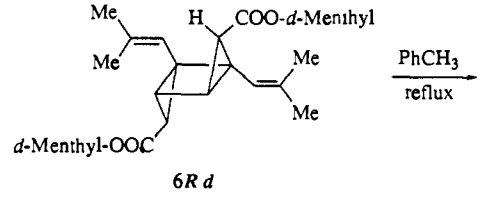
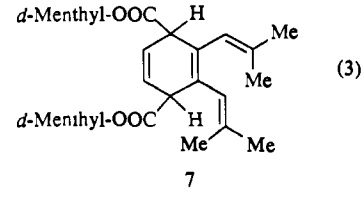
Diazo decomposition of *d*-menthyl diazoacetate in the presence of 4-methylpent-3-en-1-yne catalyzed by $Rh_2(5R\text{-MEPY})_4$ produced the cycloaddition product **6*Rd*** in 75% yield following chromatography and in 70% de (Scheme 1). With *l*-MDA and 4-methylpent-3-ene-1-yne catalyzed by $Rh_2(5S\text{-MEPY})_4$, the analogous product **6*Sl*** was produced in 68% de (55% yield), but the use of *d*-MDA with $Rh_2(5S\text{-MEPY})_4$ catalysis gave **6*Sd*** in only 30% de (53% yield). The major byproduct from these transformations was the water insertion products of the menthyl diazoacetates.

Product analyses were performed by mass spectroscopy and by ^1H NMR spectroscopy which showed characeristic absorptions for **6** at δ 2.5 and 5.3. Two isomers were observed in each case, and they were assigned to the diastereomeric forms of **6** that possess the 1,2-divinyl arrangement and exo,exo-dicarboxylate configuration. The *anti*-divinyl isomers were not observed, which is consistent with prior observations of methyl ester derivatives[22] and of the "head-to-head" [2 + 2]-cyclodimerization of 1-vinylcyclopropene.[24] Thermal decomposition of **6*Rd*** in refluxing toluene yielded **7** quantitatively (eq 3) and with the same % de as the reactant.

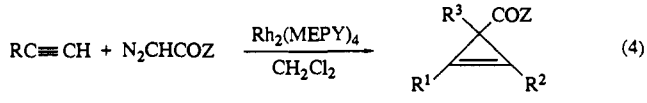




(3)

Diazodecomposition of *d*-menthyl diazoacetate by dirhodium(II) tetrakis[4(*R*)-benzyl-2-oxazolidinone], $Rh_2(4R\text{-BNOX})_4$[25] in the presence of 4-methylpent-3-en-1-yne produced **6*Rd*** in 79% yield but with only 8% de. The sterically restrictive catalyst, dirhodium(II) tetrakis[4(*S*)-phenyloxazolidinone], $Rh_2(4S\text{-PHOX})_4$,[26] was unreactive towards diazodecomposition under the same reaction conditions.

Enantioselectivity. The high level of diastereocontrol in cyclopropenation reactions with menthyl diazoacetates and the divergence in selectivity with the use of their *d*- and *l*-enantiomers prompted us to examine the influence of diazo esters and diazoamides on enantiocontrol. Increasing the size of the ester alkyl group of diazoacetates and the use of diazoacetamides have been previously shown to increase stereocontrol in intermolecular cyclopropanation reactions.[27] The results from a series of these cyclopropenation transformations catalyzed by $Rh_2(5S\text{-MEPY})_4$ and $Rh_2(5R\text{-MPEY})_4$ (eq 4) are reported in Table 2.



(4)

8, R = $CH(OEt)_2$ a, Z = OMe
9, R = CH_2OMe b, Z = OEt
10, R = *n*-Bu c, Z = O-*t*-Bu
11, R = *t*-Bu d, Z = NMe_2
12, R = *n*-Pent

As is evident from the data, enantioselectivities are moderate to high, reaching ≥94% with propargyl methyl ether/*N*,*N*-dimethyldiazoacetamide and ≥98% with the diethyl acetal of

Scheme 1

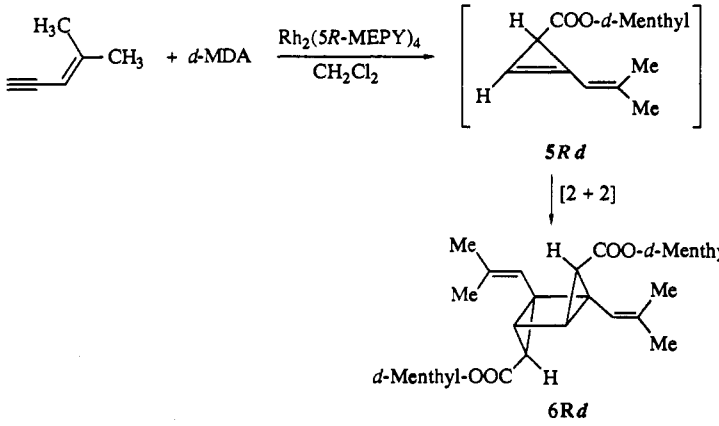


Table 2. Enantioselective Cyclopropenation of Representative 1-Alkynes by Diazoacetate Esters and *N,N*-Dimethyldiazoacetamide Catalyzed by $Rh_2(5S\text{-MEPY})_4$ and $Rh_2(5R\text{-MEPY})_4$

catalyst	N_2CHCOZ, Z =	R	cyclopropene[a]	yield, %[b]	ee, %[c]	absolute config[d]
$Rh_2(5S\text{-MEPY})_4$	OMe	$CH(OEt)_2$	**8a*S***	42	≥98	*S*
$Rh_2(5S\text{-MEPY})_4$	O-*t*-Bu	CH_2OMe	**9c*S***	52	78	*S*
$Rh_2(5R\text{-MEPY})_4$	OEt	CH_2OMe	**9b*R***	73	69	*R*
$Rh_2(5R\text{-MEPY})_4$	O-*t*-Bu	CH_2OMe	**9c*R***	56	78	*R*
$Rh_2(5R\text{-MEPY})_4$	NMe_2	CH_2OMe	**9d*R***	22	≥94	*R*
$Rh_2(5R\text{-MEPY})_4$	OEt	*n*-Bu	**10b*R***	70	54	*R*
$Rh_2(5R\text{-MEPY})_4$	O-*t*-Bu	*n*-Bu	**10c*R***	69	53	*R*
$Rh_2(5R\text{-MEPY})_4$	NMe_2	*n*-Bu	**10d*R***	49	78	*R*
$Rh_2(5S\text{-MEPY})_4$	OEt	*n*-Bu	**10b*S***	60	51	*S*
$Rh_2(5R\text{-MEPY})_4$	OEt	*t*-Bu	**11b*R***	85	57	*R*
$Rh_2(5R\text{-MEPY})_4$	O-*t*-Bu	*t*-Bu	**11c*R***	57	70	*R*
$Rh_2(5R\text{-MEPY})_4$	NMe_2	*t*-Bu	**11d*R***	47	89	*R*
$Rh_2(5S\text{-MEPY})_4$	OMe	*n*-pentyl	**12a*S***	83	48	*S*

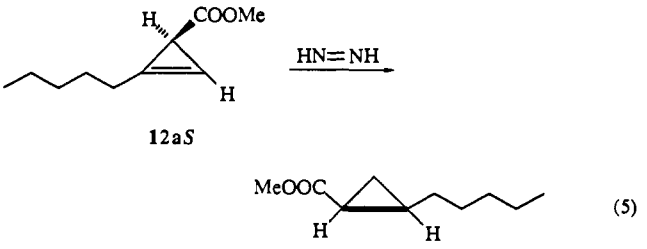
[a] *R* or *S* is the catalyst configuration. [b] Yield of the chromatographically purified cyclopropene. [c] From GC or ^1H NMR analyses. Results confirmed with duplicate runs. [d] For assignment see section on absolute configurations of cyclopropenes.

propynal. *tert*-Butyl diazoacetate generally provides a higher degree of enantiocontrol than does methyl or ethyl diazoacetate, but *N,N*-dimethyldiazoacetamide elicits the highest level of selectivity among the diazo compounds employed for this investigation. Product yields are generally higher in reactions with methyl, ethyl, and *tert*-butyl diazoacetate esters than with menthyl diazoacetates, but yields from reactions with the diazoacetamide are low to moderate.

The major competing reaction in $Rh_2(MEPY)_4$-catalyzed transformations is carbene dimer formation; but, in general, cyclopropene formation is a relatively clean process, and products can be purified without undue difficulties. However, in reactions between propargyl methyl ether and *N,N*-dimethyldiazoacetamide multiple products were formed whose identities were not determined. The use of alternative dirhodium(II) catalysts for cyclopropenation did not provide any advantage. For example, enantiomeric excesses were only 5% [$Rh_2(4S\text{-BNOX})_4$], 6% [$Rh_2(4S\text{-IPOX})_4$][28] and 22% [$Rh_2(5S\text{-NEPY})_4$] for reactions between 1-hexyne and ethyl diazoacetate, relative to 54% with $Rh_2(5R\text{-MEPY})_4$, and competing dimer formation was more important with these catalysts. Similarly, **12a*S*** was produced by $Rh_2(4S\text{-PHOX})_4$ catalysis with 38% ee but in only 19% yield. With the use of $Rh_2(4S\text{-MEOX})_4$ enantiomeric excesses were only 14% for **10c*S*** and 57% for **9b*S***. As was previously reported,[19] a chiral(semicorrinato)-copper(II) catalyst, bis{(1*S*,9*S*)-1,9-bis-[(*tert*-butyldimethylsilyl)oxy]methyl]-5-cyanosemicorrinato}-copper(II), was not effective for enantioselective cyclopropenation reactions; both % ee values and product yields were low.

The use of disubstituted acetylenes gave unsatisfying results. With 1-phenylpropyne, cyclopropenation with ethyl diazoacetate catalyzed by $Rh_2(5S\text{-MEPY})_4$ produced the corresponding cyclopropene product in 39% yield with only 16% ee, and similar results (26% yield and 20% ee) were found for reactions performed with methyl diazoacetate. Even lower selectivities (<2% ee) were found for cyclopropenation of 1-(trimethylsilyl)-1-hexyne.

Absolute Configurations of Cyclopropenes. Cyclopropene **12a*S*** having an enantiomeric excess of 48% was reduced to the cis-disubstituted cyclopropane **13** (eq 5) by diimide reduction. The



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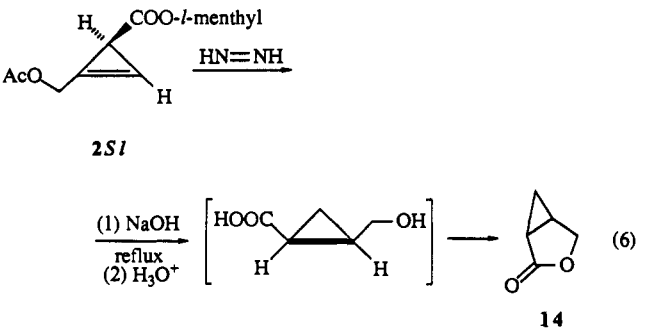
sign of its optical rotation, which is positive, was compared to that of the cis stereoisomer of methyl 2-(*n*-pentyl)cyclopropane-1-carboxylate (**13**),[20b] and the configuration of **12a*S*** was assigned (*S*). Cyclopropene **2*Sl*** was reduced by diimide and then hydrolyzed with base. After extraction of the liberated *l*-menthol, the solution was acidified, and the resulting hydroxy acid was cyclized to produce bicyclic lactone **14** (eq 6), the absolute configuration of which has been assigned as (1*S*,5*R*) based on



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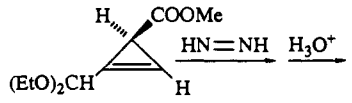
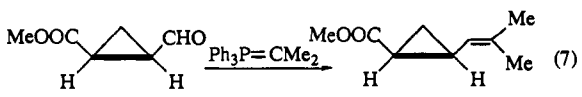
(28) Dirhodium(II) tetrakis[4(*S*)-isopropyl-2-oxazolidinone] is $Rh_2(4S\text{-IPOX})_4$.

the sector rule,[29] by correlation with dictyopterene C of known absolute configuration,[30] and by comparison with the same product formed by intramolecular cyclopropanation of allyl diazoacetate.[31] Finally, diethyl acetal **8a*S*** was also reduced by diimide, and then the acetal was selectivity hydrolyzed to aldehyde **15** which underwent the Wittig reaction to furnish **16** of known configuration (1*S*,2*R*) (eq 7).[20b]



8a*S*



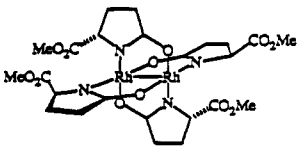
(7)

15 **16**

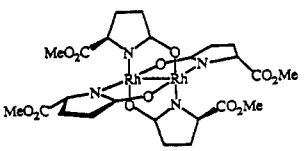
By inference from these results, catalysis by Rh_2(5*S*-MEPY)$_4$ resulted in the production of (*S*)-cyclopropenes in enantiomeric excess, and catalysis by Rh_2(5*R*-MEPY)$_4$ forms the (*R*)-cyclopropene enantiomers predominantly. Gas chromatographic separations on chiral cyclodextrin columns correlate precisely with these assignments, as do chemical shifts of the menthyl esters. Absolute configurations of cyclopropenecarboxylates formed with other dirhodium(II) catalysts correlate predictably with the configuration of the catalyst ligands.

Discussion

Dirhodium(II) catalysts that possess chiral 2-pyrrolidone-5-carboxylate ester ligands are the most effective among those of dirhodium or copper for highly diastereoselective and enantioselective intermolecular cyclopropenation reactions between 1-alkynes and diazoesters. Product yields are moderate, and enantiomeric excesses (Table 2) range from 40% to greater than 98%. Furthermore, the absolute configurations of the major enantiomer/diastereoisomer is predictable from the catalyst that is employed: Rh_2(5*S*-MEPY)$_4$ (**17S**) produced cyclopropenecarboxylates in the (*S*)-configuration, and Rh_2(5*R*-MEPY)$_4$ (**17*R***) forms the (*R*)-enantiomer predominantly.

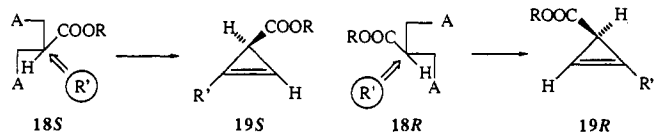


17S

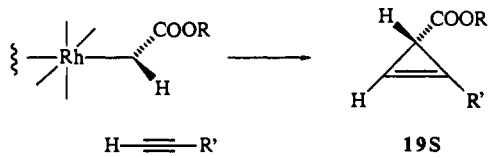


17R

The absolute configuration of cyclopropene products is predictable from analysis of the reactive conformation of the intermediate metal carbene. Looking down the rhodium–rhodium bond axes of **17*S*** and **17*R***, the carboxylate attachments (A) are oriented counterclockwise in Rh_2(5*S*-MEPY)$_4$ and clockwise in Rh_2(5*R*-MEPY)$_4$. The carbene is bound to rhodium with minimum energy conformations that have previously been modeled for cyclopropanation reactions[25] and are depicted by **18*S*** and **18*R***. Approach by the terminal alkyne, depicted by R′ projected out of a circle, to the carbene center occurs such that the alkyne is perpendicular to the catalyst face (e.g., **20**), in accordance with the principle of least motion and in order to maximize overlap in the transition state. In this way, Rh_2(5*S*-MEPY)$_4$ produces **19*S***, and Rh_2(5*R*-MEPY)$_4$ forms **19*R***. Approach of the alkyne to the carbene so that the alkyne is perpendicular to the catalyst face also explains the failure of internal alkynes to undergo efficient cyclopropenation reactions and give even moderate enantiomeric excesses; steric restrictions from the catalyst face prevent close approach of the alkyne π-bond to the carbene center in **18** and, with Rh_2(5*S*-MEPY)$_4$ for example, allow enhanced competition from metal carbene conformation **21**. The influences of increasing the size of R in the carbene and of the steric and/or electronic nature of R′ are more subtle, and they are likely to result, at least in part, from interactions between carbene substituents and the alkyne substituent.



18*S* **19*S*** **18*R*** **19*R***



20 **19S**

21 **19*R***

Diimide reduction of these cyclopropene isomers produces the corresponding *cis*-disubstituted cyclopropane esters exclusively with the moderate to high enantiomeric/diastereoisomeric excesses achieved by cyclopropenation; alternative attempts to produce the *cis*-disubstituted cyclopropane compounds directly by enantioselective intermolecular olefin cyclopropanation[32] have not been comparatively successful. Overall, as is demonstrated by results in eq 5–7, cyclopropenation–reduction (with diimide) is a viable methodology for the clean and efficient formation of enantiomerically-enriched *cis*-disubstituted cyclopropane compounds.

Experimental Station

General Methods: Dirhodium(II) tetraacetate was obtained commercially or prepared from rhodium(III) chloride hydrate.[33] Rh_2(5*S*-MEPY)$_4$, Rh_2(5*R*-MEPY)$_4$, Rh_2(4*S*-BNOX)$_4$, Rh_2(4*S*-IPOX)$_4$, and Rh_2(4*S*-PHOX)$_4$ were synthesized from $Rh_2(OAc)_4$ as previously described.[25,26] *d*-(+)-Menthyl diazoacetate and *l*-(−)-menthyl diazoacetate[20b] were prepared from their corresponding diazoacetoacetate esters[34] by deacylation in aqueous acetonitrile using 3.0 equiv of lithium hydroxide monohydrate. Dichloromethane was distilled from calcium hydride prior to use. Microanalyses were performed at Texas Analytical Laboratories, Inc.

Cyclopropenation of 1-Alkynes with Diazoacetate Esters. To a light blue solution of 1-alkyne (10.0 mmol) and chiral Rh_2(MEPY)$_4$(0.010 mmol) in 10 mL of anhydrous CH_2Cl_2 at room temperature and under nitrogen was added the diazoester (1.00 mmol) in 5 mL of CH_2Cl_2 through a syring pump at a rate of 1.0 mL/h. The blue color for the solution generally remained until near the end of the addition at which time the

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reaction solution became red. After addition was complete, the reaction mixture was filtered through a 1-cm silica plug to separate the catalyst, and the plug was eluted with 70 mL of CH_2Cl_2. The dichloromethane solution was then evaporated under reduced pressure. Cycloprop-2-ene-1-carboxylate esters were purified by column chromatography on silica gel with hexane–ethyl acetate as the eluent. Diastereomeric excesses for **1–4** were obtained by direct NMR analysis of the vinylic proton (±3%); in all cases the *Rd* and *Sl* diastereoisomers had the higher chemical shift. Enantiomeric excesses of **9–11** were determined with the use of chiral NMR shift reagent Eu(tfc)$_3$ on the vinylic proton[35] and for **9–11b** and **9–11c** by chromatographic separation on a Chiraldex γ-cyclodextrin trifluoroacetate (G-TA) column with correspondence to within ±2%. 2-Cyclopropenes formed from 1-phenylpropyne[35] and 1-trimethylsilyl-1-hexyne[36] have been previously reported. 2-Cyclopropene-1-carboxylates formed in reactions catalyzed by Rh$_2$(5*R*-MEPY)$_4$ were spectroscopically identical with those from Rh$_2$(5*S*-MEPY)$_4$-catalyzed reactions.

(1*R*,2*S*,5*R*)-Menthyl 2-(Methoxymethyl)cycloprop-2-ene-1-carboxylate (1*Rd*). Mass spectrum, *m/e* (rel abundance): 266 (0.6, M), 138 (19), 128 (18), 111 (17), 97 (12), 96 (33), 95 (40), 83 (100), 81 (35), 69 (24), 67 (30), 55 (64), 53 (32). IR (neat): 3138, 1800 (C=C), 1729 (C=O) cm^{-1}. Anal. Calcd for $C_{16}H_{26}O_3$: C, 72.14; H, 9.84. Found: C, 72.20; H, 9.87. **Major diastereoisomer.** ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.67 (q, *J* = 1.5 Hz, 1H), 4.69 (dt, *J* = 10.8, 4.4 Hz, 1H), 4.47 (dd, *J* = 17.5, 1.8 Hz, 1H), 4.41 (dd, *J* = 17.5, 1.9 Hz, 1H), 3.43 (s, 3H), 2.28 (d, *J* = 1.5 Hz, 1H), 2.02–1.86 (m, 1H), 1.86–1.80 (m, 1H), 1.73–1.62 (m, 2H), 1.56–1.24 (m, 3H), 1.14–0.80 (m, 2H), 0.89 (d, *J* = 6.8 Hz, 6H), 0.76 (d, *J* = 7.0 Hz, 3H). **Minor diastereoisomer.** ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.66 (q, *J* = 1.5 Hz, 1H), 4.69 (dt, *J* = 10.8, 4.4 Hz, 1H), 4.47 (dd, *J* = 17.5, 1.8 Hz, 1H), 4.41 (dd, *J* = 17.5, 1.9 Hz, 1H), 3.42 (s, 3H), 2.27 (d, *J* = 1.5 Hz, 1H), 2.02–1.86 (m, 1H), 1.86–1.80 (m, 1H), 1.73–1.62 (m, 2H), 1.56–1.24 (m, 3H), 1.14–0.80 (m, 2H), 0.89 (d, *J* = 6.7 Hz, 6H), 0.77 (d, *J* = 6.9 Hz, 3H).

(1*S*,2*R*,5*S*)-Menthyl 2-(Acetoxymethyl)cycloprop-2-ene-1-carboxylate (2*Sl*). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.70 (q, *J* = 1.5 Hz, 1H), 5.02 (d, *J* = 1.4 Hz, 2H) 4.70 (dt, *J* = 10.7, 4.3 Hz, 1H), 2.30 (d, *J* = 1.5 Hz, 1H), 2.03 (s, 3H), 2.00–0.70 (m, 18H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 174.6 (s), 170.3 (s), 111.1 (s), 98.6 (d), 74.3 (d), 58.0 (d), 47.1 (d), 45.4 (d) 41.0 (t), 34.4 (t), 31.4 (d), 29.7 (t), 26.5 (d), 23.5 (t), 22.0 (q), 20.8 (q), 20.7 (q), 16.4 (q). Mass spectrum, *m/e* (rel abundance): 294 (M$^+$, absent), 155 (10), 138 (20), 111 (100), 83 (50). A de of 98% determined by ^{1}H NMR (400 MHz) from q at 6.70 and 6.69 ppm: $[\alpha]^{20}_D$ = –70° ($CHCl_3$, *c* = 6.7). Product was purified by column chromatography on silica (hexane:ethyl acetate = 5:1).

(1*R*,2*S*,5*R*)-Menthyl 2-(*n*-Butyl)cycloprop-2-ene-1-carboxylate (3*Rd*). Mass spectrum, *m/e* (rel abundance): 278 (0.2, M), 140 (18), 123 (12), 97 (27), 95 (100), 83 (55), 81 (31), 69 (28), 67 (22), 55 (64), 53 (23). Anal. Calcd for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86. Found: C, 77.54; H, 10.92. **Major diastereoisomer.** ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.34 (q, *J* = 1.5 Hz, 1H), 4.68 (dt, *J* = 10.9, 4.4 Hz, 1H), 2.49 (dt, *J* = 7.1, 1.4 Hz, 2H), 2.11 (d, *J* = 1.5 Hz, 1H), 2.00–1.93 (m, 1H), 1.93–1.80 (m, 1H), 1.72–1.61 (m, 2H), 1.61–1.31 (m, 7H), 1.14–0.80 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 6H), and 0.75 (d, *J* = 7.0 Hz, 3H). IR (neat): 3140, 1803 (C=C), 1729 (C=O) cm^{-1}. **Minor diastereoisomer.** ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.32 (q, *J* = 1.4 Hz, 1H), 4.69 (dt, *J* = 10.8, 4.4 Hz, 1H), 2.50 (dt, *J* = 7.2, 1.3 H, 2H), 2.10 (d, *J* = 1.4 Hz, 1H), 2.00–1.93 (m, 1H), 1.93–1.80 (m, 1H), 1.72–1.61 (m, 2H), 1.61–1.31 (m, 7H), 1.14–0.80 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.89 (d, *J* = 7.1 Hz, 6H), 0.76 (d, *J* = 7.0 Hz, 3H).

(1*R*,2*S*,5*R*)-Menthyl 2-(*tert*-Butyl)cycloprop-2-ene-1-carboxylate (4*Rd*). IR (neat): 3140, 1798 (C=C), 1730 (C=O) cm^{-1}. Anal. Calcd for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86. Found: C, 77.57; H, 10.91. **Major diastereoisomer.** ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.20 (d, *J* = 1.5 Hz, 1H), 4.69 (dt, *J* = 10.8, 4.3 Hz, 1H), 2.15 (d, *J* = 1.5 Hz, 1H), 2.01–1.91 (m, 1H), 1.91–1.81 (m, 1H), 1.72–1.61 (m, 2H), 1.57–1.31 (m, 3H), 1.17 (s, 9H), 1.14–0.80 (m, 2H), 0.89 (d, *J* = 7.2 Hz, 6H), 0.75 (d, *J* = 6.9 Hz, 3H). Mass spectrum, *m/e* (rel abundance): 263 (0.2, M – 15), 140 (17), 125 (44), 123 (12), 95 (100), 83 (24), 81 (13), 69 (15), 67 (37), 55 (48), 53 (11). **Minor diastereoisomer.** ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.23 (d, *J* = 1.6 Hz, 1H), 4.70 (dt, *J* = 10.9, 4.4 Hz, 1H), 2.17 (d, *J* = 1.6 Hz, 1H), 2.01–1.91 (m, 1H), 1.91–1.81 9m, 1H), 1.72–1.61 (m, 2H), 1.57–1.31 (m, 3H), 1.18 (s, 9H), 1.14–0.80 (m, 2H), 0.89 (d, *J* = 7.2 Hz, 6H), and 0.75 (d, *J* = 6.9 Hz, 3H). Mass spectrum, *m/e* (rel abundance): 263 (0.2, M – 15), 140 (14), 125 (36), 123 (10), 95 (100), 83 (21), 81 (10), 69 (12), 67 (29), 55 (38), 53 (8).

Methyl 2-(Diethoxymethyl)cycloprop-2-ene-1-carboxylate (8a*S*). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.79–6.78 (m, 1H), 5.48 (d, *J* = 1.1 Hz, 1H), 3.67 (s, 3H), 3.75–3.45 (m, 4H), 2.37 (d, *J* = 1.4 Hz, 1H), 1.25–1.17 (dt, 6H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 175.4 (s), 112.7 (s), 100.3 (d), 96.0 (d), 61.6 (t), 51.6 (q), 20.6 (d), 15.1 (q), 15.05 (q). Mass spectrum, *m/e* (rel abundance): 200 (M$^+$, absent), 169 (2), 155 (25), 141 (8), 127 (74), 103 (74), 75 (56), 59 (31), 47 (100). IR ($CHCl_3$): 1723 cm^{-1}. $[\alpha]^{20}_D$ = +29.5° ($CHCl_3$, *c* = 2.61) for >98% ee (GC on Lipodex E column from reaction catalyzed by Rh$_2$(5*S*-MEPY)$_4$). 42% Yield after preparative TLC (SiO_2, hexane:ethyl acetate = 3:1).

Ethyl 2-(Methoxymethyl)cycloprop-2-ene-1-carboxylate (9b*R*). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.67 (q, *J* = 1.6 Hz, 1H), 4.46 (AB, 2H), 4.14 (dq, *J* = 6.7, 2.6 Hz, 2H), 3.43 (s, 3H), 2.29 (d, *J* = 1.6 Hz), 1.26 (t, *J* = 6.7 Hz, 3H). IR (neat): 3143, 1802 (C=C), 1728 (C=O) cm^{-1}. $[\alpha]^{23}_D$ = –64.5° ($CHCl_3$, *c* = 1.55) for 69% ee from reaction catalyzed by Rh$_2$(5*R*-MEPY)$_4$. Anal. Calcd for $C_8H_{12}O_3$: C, 61.54: H, 7.69. Found: C, 61.32; H, 7.84.

***tert*-Butyl 2-(Methoxymethyl)cycloprop-2-ene-1-carboxylate (9c*R*).** ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.64 (q, *J* = 1.4 Hz, 1H),, 4.53 (s, 2H), 3.43 (s, 3H), 2.20 (d, *J* = 1.4 Hz, 1H), 1.45 (s, 9H). IR (neat): 3148, 1801 (C=C), 1724 (C=O) cm^{-1}. Mass spectrum, *m/e* (rel abundance): 169 (0.2, M – 15), 141 (0.5), 128 (3.6, M – C_4H_8), 96 (13), 83 (100), 68 (21), 57 (72), 55 (57), 53 (70). $[\alpha]^{23}_D$ = –58.8° ($CHCl_3$, *c* = 2.50) for 78% ee from reaction catalyzed by Rh$_2$(5*R*-MEPY)$_4$. On the Chiraldex G-TA column (105 °C) the R-enantiomer eluded at 22.7 min and the S-enantiomer eluted at 23.8 min.

Ethyl 2-(*n*-Butyl)cycloprop-2-ene-1-carboxylate (10b*R*). ^{1}H NMR ($CDCl_3$ 300 MHz): δ 6.34 (q, *J* = 1.4 Hz, 1H), 4.14 (dq *J* = 7.1, 3.1 Hz, 2H), 2.51 (dt *J* = 7.1, 1.4 Hz, 2H), 2.14 (d, *J* = 15 Hz, 1H) 1.58 (quin, J = 7.1 Hz, 2H), 1.40 (sex, J = 7.0 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), and 0.93 (t, *J* = 7.2 Hz, 3H). IR (neat): 3142, 1807 (C=C), and 1732 (C=O) cm^{-1}. Mass spectrum, *m/e* (rel abundance): 168 (1.2), 139 (5), 125 (10), 97 (80), 95 (100), 67 (30), 55 (40), 53 (61). $[\alpha]^{23}_D$ = –34.1° ($CHCl_3$, *c* = 0.82) for 54% ee from reaction catalyzed by Rh$_2$(5*R*-MEPY)$_4$. This compound has been previously prepared.[16,37]

***tert*-Butyl 2-(*n*-Butyl)cycloprop-2-ene-1-carboxylate (10c*R*).** ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.30 (q, *J* = 1.5 Hz, 1H), 2.49 (tt, *J* = 7.2, 1.2 Hz, 2H), 2.03 (d, *J* = 1.5 Hz, 1H), 1.57 (quin, *J* = 7.2 Hz, 2H), 1.44 (s, 9H), 1.39 (sex, *J* = 7.2 Hz, 2H), 0.92 (t, *J* = 7.2 Hz, 3H). IR (neat): 3140, 1802 (C=C), 1725 (C=O) cm^{-1}. Mass spectrum, *m/e* (rel abundance): 181 (0.1, M – 15), 140 (7.6), 111 (2), 97 (32), 95 (100), 57 (52), 55 (14), 53 (26). $[\alpha]^{23}_D$ = –34.8°, $[\alpha]^{23}_{436}$ = –70.4°, $[\alpha]^{23}_{365}$ = –115° ($CHCl_3$, *c* = 0.54) for 53% ee from reaction catalyzed by Rh$_2$(5*R*-MEPY)$_4$. On the Chiraldex G-TA column (100 °C for 2 min, then 0.5 °C/min to 120 °C), the R-enantiomer eluted at 22.1 min and the S-enantiomer eluted at 23.1 min. Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.22; H, 10.19.

Ethyl 2-(*tert*-Butyl)cycloprop-2-ene-1-carboxylate (11b*R*). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.21 (d, *J* = 1.5 Hz, 1H), 4.22–4.04 (m, 2H), 2.17 (d, *J* = 1.5 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.18 (s, 9H). IR (neat): 3019, 1793 (C=C), 1707 (C=O) cm^{-1}. $[\alpha]^{23}_D$ = –53.2° ($CHCl_3$, *c* = 1.40) for 57% ee from reaction catalyzed by Rh$_2$(5*R*-MEPY)$_4$. This compound has been previously prepared.[16,37]

***tert*-Butyl 2-(*tert*-Butyl)cycloprop-2-ene-1-carboxylate (11c*R*).** ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.18 (d, *J* = 1.6 Hz, 1H), 2.08 (d, *J* = 1.6 Hz 1H), 1.43 (s, 9H), and 1.18 (s, 9H). IR (neat): 3146, 1795 (C=C), 1730 (C=O) cm^{-1}. Mass spectrum, *m/e* (rel abundance): 181 (0.1, M – 15), 140 (5.9, M – C_4H_8), 125 (47), 95 (100), 79 (18), 67 (51), 57 (54), 55 (36). $[\alpha]^{23}_D$ = –34.8°, $[\alpha]^{23}_{576}$ = –41.5°, $[\alpha]^{23}_{435}$ = –71.0° ($CHCl_3$, *c* = 1.81) for 70% ee from reaction catalyzed by Rh$_2$(5*R*-MEPY)$_4$. On the Chiraldex G-TA column (100 °C), the *R*-enantiomer eluted at 14.2 min and the *S*-enantiomer eluted at 14.8 min. Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.48; H, 10.23.

Methyl 2-(*n*-Pentyl)cycloprop-2-ene-1-carboxylate (12a*S*).[26] ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.32–6.20 (m, 1H), 3.66 (s, 3H), 2.53–2.42 (m, 2H), 2.12 (d, *J* = 1.6 Hz, 1H), 1.65–1.21 (m, 6H), 0.96–0.88 (t, 3H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 177.0 (s), 115.5 (s), 93.8 (d), 51.4 (q), 31.2 (t), 26.2 (t) 24.8 (t), 22.2 (t), 19.4 (t), 13.8 (q). IR ($CHCl_3$): 3025, 1713 cm^{-1}. $[\alpha]^{20}_D$ = +32° ($CHCl_3$, *c* = 1.9) for 48% ee from reaction catalyzed by Rh$_2$(5*S*-MEPY)$_4$.

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Dirhodium(II)-Catalyzed Diazodecomposition of Menthyl Diazoacetate in the Presence of 3-Methylpent-3-en-1-yne. To a rapidly stirred solution of dirhodium(II) catalyst (4.1×10^{-3} mmol) and enyne (0.422 g, 5.28 mmol) in 4.0 mL of anhydrous CH_2Cl_2 was added by syringe pump 4.0 mL of a dichloromethane solution of menthyl diazoacetate (0.308 g, 1.97 mmol) over 8 h at a rate of 0.5 mL/h. The additon was performed at room temperature during which the original lilac solution color changed to green and then tan. After addition was complete, the solvent and excess enyne were evaporated to leave 0.376 g of a residue whose ^1H NMR spectrum was obtained; the residue was then purified by column chromatography on silica gel (hexane:ethyl acetate = 95:5) which yielded ***6Rd*** and menthyl glycolate. The spectral characteristics of *6Rd* were virtually identical with those of dimethyl ester.[22]

Di-(1*R*,2*S*,5*R*)-menthyl 1,2-Bis(2-Methylprop-1-enyl)tricyclo[3.1.0.0^{2,4}]-hexane-*exo*-3,*exo*-6-dicarboxylate (*6Rd*). ^1H NMR ($CDCl_3$, 300 MHz): δ 5.25–5.20 (m, C*H*=), 4.52 (dt, J = 10.9, 4.4 Hz, C*H*O), 2.57 (d, J = 1.1 Hz, 2H), 2.08–2.05 (m, 2H), 1.95–1.70 (m, 4H), 1.68–1.55 (m, 4H), 1.63 (d, J = 1.4 Hz, 6H), 1.61 (d, J = 1.3 Hz, 6H), 1.50–1.10 (m, 4H), 1.10–0.70 (m, 6H), 0.82 (d, J = 5.8 Hz, 6H), 0.80 (d, J = 5.8 Hz, 6H), 0.66 (d, J = 6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.8 (C=O), 139.8 (=CMe_2), 116.9 (d), 74.2 (d), 47.1 (d), 43.5 (d), 41.1 (t), 40.8 (s), 34.4 (t), 31.4 (d) 28.5 (d), 26.2 (d) 25.7 (q), 23.5 (t), 22.0 (q), 20.9 (q), 19.3 (q), 16.3 (q). Mass spectrum, m/e (rel abundance): 554 (M^+, 0.1), 552 (M – 2, 0.4), 414 (0.9), 369 (1.5), 276 (15), 232 (14), 231 (37), 189 (13), 175 (35), 171 (11), 143 (10), 97 (18), 83 (100), 69 (37), 57 (35), 55 (50). FAB spectroscopy identified the molecular ion, 552 (M – 2) and major fragmentations at m/e 414, 276, 138.

Di-(1*R*,2*S*,5*R*)-menthyl 1,2-Bis(2-Methylprop-1-enyl)tricyclo[3.1.0.0^{2,4}]-hexane-*exo*-3,*exo*-6-dicarboxylate (*6Sd*). ^1H NMR ($CDCl_3$, 300 MHz): δ 5.15–5.10 (m, C*H*=), 4.58 (dt, J = 10.9, 4.4 Hz, C*H*O), 2.52 (d, J = 1.1 Hz, 2H), 2.12–2.09 (m, 2H), 1.95–1.70 (m, 4H), 1.68–1.55 (m, 4H), 1.65 (d, J = 1.4 Hz, 6H), 1.60 (d, J = 1.3 Hz, 6H), 1.50–1.10 (m, 4H), 1.10–0.70 (m, 6H), 0.81 (d, J = 5.8 Hz, 6H), 0.77 (d, J = 5.8 Hz, 6H), 0.64 (d, J = 6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.8 (C=O), 138.2 (=CMe_2), 117.1 (d), 74.1 (d), 47.2 (d), 43.7 (d), 41.0 (t), 40.9 (s), 34.4 (t), 31.4 (d), 28.9 (d), 26.4 (d), 25.7 (q), 23.4 (t), 22.0 (q), 20.9 (q), 18.8 (q), 16.2 (q). Mass spectrum, m/e (rel abundance): 554 (M^+, absent), 552 (M – 2, 0.2), 414 (0.7), 369 (0.9), 276 (14), 232 (9), 231 (27), 189 (14), 175 (40), 171 (8), 143 (8), 97 (16), 83 (100), 69 (39), 57 (37), 55 (50). FAB spectroscopy identified the molecular ion, 552 (M – 2), and major fragmentations at m/e 414, 276, 230, 138.

Thermal Decomposition of *6Rd*. A solution of *6Rd* (0.302 g, 0.725 mmol, 70% de) in 5.0 mL of dry toluene was refluxed for 3.5 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel to yield 0.300 g of a viscous oil whose isomeric composition determined by ^1H NMR spectroscopy (68 ± 3% de) was the same as the reactant.

Di-(1*R*,2*S*,5*R*)-menthyl 1,2-Bis(2-methylprop-1-enyl)cyclohexa-1,4-diene-*trans*-3,6-dicarboxylate (*7Rd*). ^1H NMR ($CDCl_3$, 300 MHz): δ 5.82–5.77 (m, C*H*=), 5.47–5.42 (m, =C*H*), 4.63–4.58 (m, 2H), 3.80 (d, J = 1.5 Hz, 2H), 1.90–1.70 (M, 4H), 1.70–1.50 (m, 4H), 1.63 (d, J = 1.4 Hz, 6H), 1.48 (d, J = 1.3 Hz, 6H), 1.50–1.20 (m, 4H), 1.10–0.70 (m, 6H), 0.84 (d, J = 6.5 Hz, 6H), 0.81 (d, J = 6.5 Hz, 6H), 0.69 (d, J = 6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 171.9 (C=O), 135.1 (=CMe_2), 128.8 (s), 124.8 (d), 123.6 (d), 74.7 (d), 48.2 (d), 47.0 (d), 40.8 (t), 34.3 (t), 31.4 (d), 26.1 (d), 25.7 (q), 23.3 (t), 22.0 (q), 20.8 (q), 19.7 (q), 16.1 (q). Mass spectrum, m/e (rel abundance): 554 (M^+, absent), 550 (M – 4, 0.5), 427 (2.8), 412 (2.0), 342 (1.5), 275 (17), 274 (91), 259 (48), 241 (11), 232 (47), 218 (42), 97 (16), 95 (19), 83 (100), 69 (48), 57 (39), 55 (73). FAB spectroscopy identified 552 (M – 2), 550 (M – 4), and major fragmentations at m/e 428, 410, 290, 272, 138, 136, 134.

Di-(1*R*,2*S*,5*R*)-menthyl 1,2-Bis(2-methylprop-1-enyl)cyclohexa-1,4-diene-*trans*-3,6-dicarboxylate (*7Sd*). ^1H NMR $CDCl_3$, 300 MHz): δ 5.79–5.74 (m, CH=), 5.44–5.40 (m, =CH), 4.58–4.53 (m, 2H), 3.76 (d, J = 1.6 Hz, 2H), 1.90–1.70 (m, 4H), 1.70–1.50 (m, 4H), 1.72 (d, J = 1.4 Hz, 6H), 1.30 (d, J = 1.3 Hz, 6H), 1.50–1.20 (m, 2H), 1.10–0.70 (m, 6H), 0.88 (d, J = 6.0 Hz, 6H), 0.86 (d, J = 6.0 Hz, 6H), 0.72 (d, J = 7.0 Hz, 6H).

Dirhodium(II)-Catalyzed Diazodecomposition of *N,N*-Diazoacetamide in the Presence of 1-Alkynes. To a blue solution of the dirhodium(II) catalyst (0.030 mmol) and 1-alkyne (6.7 mmol) in 3.0 mL of anhydrous dichloromethane, heated at reflux, was added *N,N*-dimethyldiazoacetamide (1.0 mmol) in 5.0 mL of dichloromethane through a syringe pump at a rate of 1.0 mL/h. After addition was complete the red-brown solution was filtered through a 3-cm plug of silica to separate the catalyst, and the plug was eluted with an additional 20 mL of CH_2Cl_2. The combined solvent and alkyne were evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel with hexane–ethyl acetate as the eluent. Enantiomeric excesses were determined with the vinylic proton using the chiral NMR shift reagent $Eu(tfc)_3$.

***N,N*-Dimethyl-2-(methoxymethyl)cycloprop-2-ene-1-carboxamide (*9dR*).** ^1H NMR ($CDCl_3$, 300 MHz): δ 6.64 (q, J = 1.5 Hz, 1H), 4.49 (d, J = 1.4 Hz, 1H), 4.48 (d, J = 1.7 Hz, 1H), 3.35 (s, 3H), 3.13 (s, 3H), 2.89 (s 3H), and 2.47 (d, J = 1.5 Hz, 1H). IR (neat): 1792 (C=C), 1644 (C=O) cm^{-1}. Mass spectrum, m/e (rel abundance): 155 (M^+, 4.9), 154 (M – 1, 1.6), 140 (12), 125 (30), 124 (57), 111 (37), 96 (20), 83 (72), 72 (40), 68 (26), 55 (63), 53 (100). This compound defied purification by distillation or column chromatography.

***N,N*-Dimethyl-2-(*n*-butyl)cyclopropene-1-carboxamide (*10dR*).** ^1H NMR ($CDCl_3$, 300 MHz): δ 6.32 (d, J = 1.4 Hz, 1H), 3.3–2.9 (broad, 6H), 2.60–2.42 (m, 2H), 2.36 (d, J = 1.4 Hz, 1H), 1.63–1.53 (m, 2H), 1.38 (sextet, J = 7.1 Hz, 2H), 0.92 (t, J = 7.3 Hz, 3H). IR (neat): 1790 (C=C), 1631 (C=O) cm^{-1}. Anal. Calcd for $C_{10}H_{17}ON$: C, 71.80; H, 10.25; N, 8.38. Found: C, 71.94; H, 10.22; N, 8.31. $[\alpha]^{23}_D$ = –28.2° ($CHCl_3$, c = 1.7) for ee of 78% from reaction catalyzed by Rh_2(5*R*-MEPY)$_4$.

***N,N*-Dimethyl-2-*tert*-butylcyclopropene-1-carboxamide (*11dR*).** ^1H NMR ($CDCl_3$, 300 MHz): δ 6.24 (d, J = 1.4 Hz, 1H), 3.22 (s, 3H), 2.96 (s, 3H), 2.40 (d, J = 1.4 Hz, 1H), 1.18 (s, 9H). IR (neat): 1783 (C=C), 1637 (C=O) cm^{-1}. Anal. Calcd for $C_{10}H_{17}ON$: C, 71.80; H, 10.25; N, 8.38. Found: C, 71.58; H, 10.23; N, 8.31. $[\alpha]^{23}_D$ = –25.7° ($CHCl_3$, c = 1.4) for ee of 88% from reaction catalyzed by Rh_2(5*R*-MEPY)$_4$.

Methyl *cis*-2-(*n*-Pentyl)cyclopropane-1-carboxylate (13). To dipotassium azodicarboxylate,[38] prepared from azodicarboxamide (2.32 g, 20 mmol) in dry THF, was added 1.0 mmol of ***12aS*** in THF. Acetic acid was added in portions of 2.5 mL over a period of 15 min, and the resulting mixture was stirred overnight at 25 °C. After dilution with water, the mixture was washed three times with 100-mL portions of CH_2Cl_2. The combined dichloromethane solution was washed with water until the aqueous extract was neutral, dried over anhydrous $MgSO_4$, and concentrated. The residue was purified by bulb-tube distillation (20 °C/0.2 Torr) to provide **13** in 35% yield. $[\alpha]_D$ = +32° ($CHCl_3$, c = 2.0) for 46% ee from reaction performed with Rh_2(5*S*-MEPY)$_4$; lit[20b] $[\alpha]_D$ = +51° ($CHCl_3$, c = 0.2) for 93% ee (1*S*,2*R*)-**13**. ^1H NMR ($CDCl_3$, 200 MHz): δ 3.66 (s, 3H), 1.73–1.61 (m, 1H), 1.54–1.15 (m, 9H), 1.05–0.83 (m, 5H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 173.5 (s), 51.4 (t), 31.4 (t), 29.2 (t), 26.9 (t), 21.9 (d), 17.9 (d), 13.9 (q), 13.4 (t). IR ($CHCl_3$): 1722 cm^{-1}.

3-Oxabicyclo[3.1.0]hexan-2-one (14). Compound ***2Sl*** was subjected to diimide reduction as described for **13**, and (1*S*,2*R*,5*S*)-menthyl *cis*-2-(acetoxymethyl)cyclopropane-1-carboxylate was isolated in 85–91% yield as a colorless oil, bp 80–100 °C/0.2 Torr (bulb-tube distillation). $[\alpha]_D$ = –27° ($CHCl_3$, c = 6.6). This product (102 mg, 0.35 mmol) was treated with 2.2 mL of 25% aqueous sodium hydroxide in 10 mL of methanol and heated at reflux for 17 h. The resulting solution was cooled, diluted with water and extracted with ether to remove the liberated *l*-menthol. To the aqueous solution was added 10 mL of dioxane and 3.0 mL of 5% aqueous H_2SO_4, and the mixture was heated at reflux for 8 h. After cooling, the mixture was diluted with water and extracted with dichloromethane. After drying the solution over anhydrous $MgSO_4$ and evaporation of the solvent, the crude product was purified by bulb-tube distillation (bp 50 °C/0.2 Torr) to afford 20 mg (15% yield) of lactone **14**, $[\alpha]_D$ = –58.2° ($CHCl_3$, c = 6.6); lit.[30] $[\alpha]^{20}_D$ = –69.5° ($CHCl_3$, c = 6.8) for (1*S*,5*R*)-**14** with 100% ee, and lit.[29] $[\alpha]_D$ = –61.8° ($CHCl_3$, c = 8) for (1*S*,5*R*)-**14** with 100% ee.

Methyl *cis*-2-(2-Methylpropen-1-yl)cyclopropane-1-carboxylate (16). To dipotassium azodicarboxylate,[38] prepared from azodicarboxamide (2.32 g, 20 mmol), was added ***8aS*** (1.0 mmol) in 5.0 mL of THF. Acetic acid (15 mL) was added in 2.5 mL portions over 15 min during which time a white precipitate formed. The solution was stirred overnight at 25 °C after which it was diluted with water and extracted three times with 100-mL portions of dichloromethane. The organic phase was washed with water and dried over anhydrous $MgSO_4$. After evaporation of the solvent under reduced pressure, the residue was purified by bulb-tube distillation at 50–60 °C/0.2 Torr to yield methyl *cis*-2-(diethoxymethyl)-cyclopropane-1-carboxylate in 59% yield, $[\alpha]_D$ = +42.4° ($CHCl_3$, c = 2.6) for >98% ee from reaction catalyzed by Rh_2(5*S*-MEPY)$_4$. ^1H NMR

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($CDCl_3$, 200 MHz): δ 4.44 (d, J = 7.8 Hz, 1H), 3.71–3.40 (m, 4H), 1.87–1.76 (m, 1H), 1.71–1.54 (m, 1H), 1.22 (t, J = 7.1 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 172.8 (s), 101.5 (d), 61.7 (t), 61.7 (t) 51.8 (q), 23.8 (d), 16.8 (d), 15.4 (q), 15.2 (q), 11.6 (t). Mass spectrum, m/e (rel abundance): 202 (M^+, absent), 157 (85), 97 (100); HRMS: 158.0974, calcd for $C_8H_{14}O_3^+$ 158.0942.

Methyl *cis*-2-(diethoxymethyl)cyclopropane-1-carboxylate (101 mg, 0.50 mmol) was hydrolyzed with 2.0 mL of 3N $HClO_4$ in 5.0 mL of THF during 3 h at 0 °C with vigorous stirring under nitrogen. After neutralization with saturated aqueous sodium bicarbonate, the solution was extracted with dichloromethane, and the organic solution was dried over anhydrous $MgSO_4$. The solvent was evaporated, and the residue was distilled by bulb-tube distillation (20 °C/0.2 Torr) to afford **15** in 72% yield, which was used without further purification. ^1H NMR ($CDCl_3$, 200 MHz): δ 9.33 (d, J = 6.3 Hz, 1H), 3.72 (s, 3H), 2.30–2.18 (m, 1H), 2.09–1.87 (m, 2H), 1.59–1.51 (m, 1H).

Isopropylidenetriphenylphosphorane, prepared from isopropyltriphenylphosphonium bromide (180 mg, 0.47 mmol) and *n*-butyllithium,[39] was added to aldehyde **15** (60 mg, 0.47 mmol) in 5.0 mL of dry ether under N_2 at room temperature. After 1 h of stirring, water was added, and the mixture was extracted with dichloromethane. The organic solution was washed until neutral and dried over anhydrous $MgSO_4$, and the solvent was evaporated. The residue was purified by bulb-tube distillation (20 °C/0.2 Torr) followed by preparative TLC (silica gel/CH_2Cl_2) to yield 20 mg (26% yield) of a mixture containing 86% *cis*-**16**, 7% of its trans isomer and 7% of an unknown impurity that could not be separated: $[\alpha]_D$ = +101.9° (CH_2Cl_2, c = 2.61); lit. $[\alpha]_D$ = +231° (CH_2Cl_2, c = 0.75) for the (1*S*,2*R*)-**16** enantiomer.

Acknowledgment. Financial support for this research from the National Science Foundation, the National Institutes of Health (Grant No. GM 46503), and The Robert A. Welch Foundation to M.P.D. and from the Swiss National Science Foundation (Grant No. 20-32, 117.91 and 21-36,707.92) to P.M. is gratefully acknowledged. We wish to thank Susan Weintraub for mass spectral analyses of ***6Rd***, ***6Sd***, and ***7Rd***.

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