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Substrate *versus* Catalyst Control of Stereoselectivity in the Cyclopropanation of a Carbon-Carbon Double Bond Linked to the Reactant Diazoacetate through a Chiral Linker

Thomas M. Weathers Jr.,[a] Michael P. Doyle,[a,*] Michael D. Carducci[b]

[a] Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland, 20742, USA
Fax: (+1)-301-314-2779, e-mail: mdoyle3@umd.edu
[b] Department of Chemistry, University of Arizona, Tucson, AZ 85721-0041, USA
Fax: (+1)-1-520-621-8407

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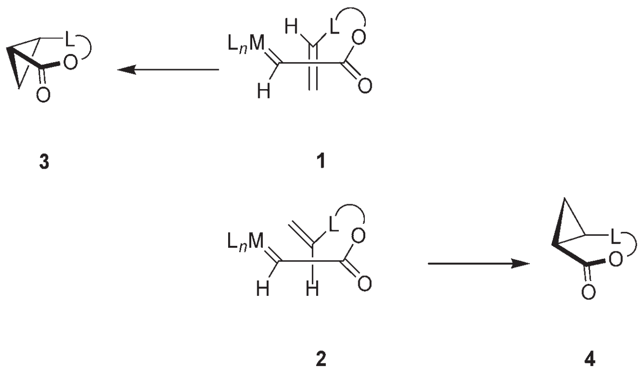
Abstract: The trajectory of a carbon-carbon double bond onto a metal carbene for cyclopropane formation is dependent on the the configurations of the catalyst and the reacting substrate. Diazoacetates prepared from the butane-2,3-diacetals (BDA) of (L)- and (D)-threitol were employed to examine the influence of a remote conformational bias on diastereoselectivity in cyclopropanation. Diastereoselectivities in the dirhodium(II) carboxamidate-catalyzed diazo decomposition reactions are as high as a 91:9 with match/mismatch selectivites, dependent on catalyst configuration, and are favored in the order: $Rh_2(MEPY)_4 > Rh_2(MEOX)_4 > Rh_2(MEAZ)_4 > Rh_2(MPPIM)_4$. The reactions catalyzed by the $Cu(CH_3CN)_4PF_6$/(*S,S*)-*t*-Bu-BOX produce as major isomers those in which the relative stereochemistry of the cyclopropane products is the same, regardless of which diazoacetate enantiomer is employed.

Keywords: addition; carboxamidates; configurational bias; copper(I); diastereoselectivity; dirhodium(II); macrocyclization

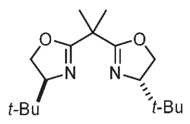
Introduction

Dirhodium(II)-catalyzed diazo decomposition of diazoacetates is known to form cyclopropanes through carbene addition to alkenes in both intermolecular and intramolecular reactions,[1] and since 1995[2] dirhodium(II) catalysts have also been reported to promote cyclopropanation to afford medium and large rings.[3] Enantioselective intramolecular cyclopropanation forming 10- to 15-membered rings with modest to high enantioselectivity has been described using dirhodium(II) carboxamidate catalysts, and copper(I) catalysts having chiral bis-oxazoline ligands produce even larger ring compounds with higher enantioselectivity.[3,4] Based on results from these studies a cyclopropanation mechanism focused on olefin trajectories for addition was proposed for both dirhodium(II) and copper(I) catalysts.[5] A prediction from this mechanism (Scheme 1) was that a chiral linker between the reactant metal carbene and carbon-carbon double bond would influence selectivities quite differently, showing match/mismatch effects with rhodium(II) carboxamidate catalysts (**1**→**3**)[6] but exhibiting an inverse (or mirror image) influence on selectivity with dominant effect by the ligand in chiral bis-oxazolidine ligated copper(I) catalysis (**2**→**4**).[7] Based on this prediction, we have synthesized a diazoacetate linked to an allyl ether through a stereochemically well-defined tether that imposes a remote conformational bias, and we now report how the configuration imposed by the tether influences reaction selectivity when using dirhodium(II) and copper(I) catalysts.

Prior research determined that the $[Cu(CH_3CN)_4]$-PF_6/(bis-oxazoline **5**) complex favors the same clockwise rotation of the tethered olefin (L = linker) about the metal carbene as metal carbene intermediates

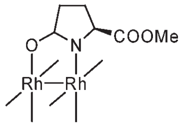


Scheme 1. Configurational dependence on olefin trajectory.



(S,S)-t-Bu-BOX

5



Rh_2(5S-MEPY)$_4$

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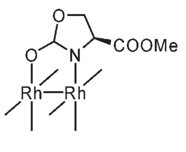

Rh_2(4S-MEOX)$_4$

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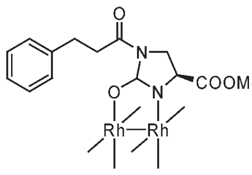

Rh_2(4S-MPPIM)$_4$

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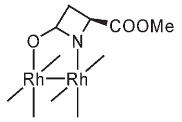

Rh_2(4S-MEAZ)$_4$

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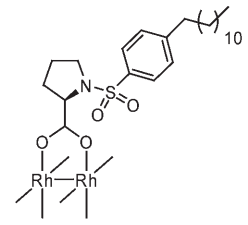


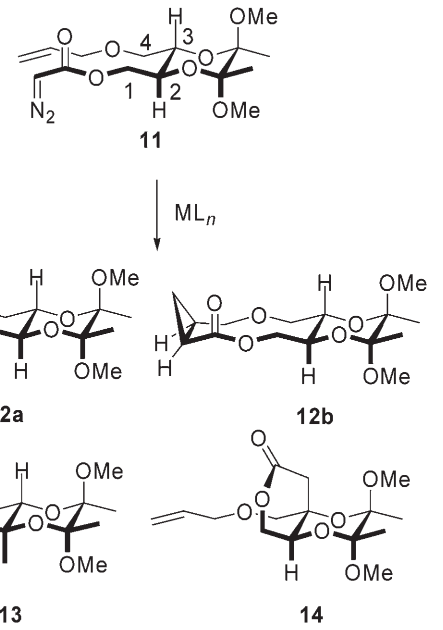
Rh_2(4S-DOSP)$_4$

10

formed from [*cis*-2,2]-(*S*)-dirhodium(II) carboxamidates (**6**–**9**),[8] but that a different olefin trajectory in copper-catalyzed cyclopropanation (**2**) is required for its approach to the metal carbene intermediate.[5] The result of the change in olefin orientation from **1** to **2** is the formation of **4**, the enantiomer of the cyclopropane product **3** that is formed using chiral dirhodium(II) *S*-carboxamidate catalysts. A remote linker between the allyl group and the diazoacetate provides a conformational bias that will influence the trajectory of the olefin to the metal carbene. As dirhodium(II) carboxamidates and bis-oxazoline-ligated copper(I) catalysts prefer different olefin trajectories, the impact of a remote conformational bias on reaction selectivity is not expected to be the same.

Results and Discussion

Ley and co-workers reported that a highly crystalline, conformationally rigid butane-2,3-diacetal (BDA) of threitol could be obtained from (L)-tartaric acid in good yields.[9] This BDA provided a scaffold with a fixed dihedral angle between carbon 1 and carbon 4 of threitol (as numbered on diazoacetate **11**) that we utilized to create diazoacetate **11** (Scheme 2). Diazo decomposition of **11**, catalyzed by dirhodium(II) carboxamidates **6**–**9**, [$Cu(CH_3CN)_4$]PF_6/(bis-oxazoline **5**), and other rhodium(II) and copper(I) catalysts for comparison, afforded two cyclopropane diastereoisomers (**12a** and **12b**) from carbene addition to the allylic carbon-carbon double bond (Table 1).



Scheme 2. Products from diazo decomposition of **11**.

Analysis of **12a** and **12b** by ^1H NMR showed that both were *cis*-disubstituted cyclopropane compounds,[10] and the configurational relationships of **12a** were verified from its X-ray structure (Figure 1).[9] Evidence was obtained for the water insertion product **13** and for a δ-lactone product presumed to be **14** (from C–H insertion), but they were generally minor components of the reaction mixture.

The dirhodium(II) tetraacetate-catalyzed diazo decomposition of **11** shows preferential formation of **12a** over **12b** in a ratio of 70:30 due to the conformational bias that exists in the metal carbene derived from **11**. Decomposition reactions using the *R*-enantiomers of dirhodium(II) carboxamidate catalysts **6**–**9** show a **12a**:**12b** ratio averaging 87:13, with the highest being 91:9, and using the *S*-enantiomers of each catalyst a virtually constant 63:37 ratio (**12a**:**12b**) is obtained with generally lower yields. Decomposition of **11** catalyzed by copper(I) hexafluorophosphate gives similar diastereoselectivity and chemoselectivity to that seen in the dirhodium(II) tetraacetate-catalyzed decomposition of **11**, while the chiral [$Cu(CH_3CN)_4$]PF_6/**5** complex enhances diastereoselectivity to 81:19.

To further investigate this double diastereoselectivity, ***ent*-11** was also prepared from D-tartaric acid. Diazo decomposition of ***ent*-11** catalyzed by dirhodium(II) tetraacetate (Scheme 3) yielded cyclopropane diastereoisomers ***ent*-12a** and ***ent*-12b** in the ratio of 70:30 (Table 2) with nearly identical chemoselectivity to that seen in the dirhodium(II) tetraacetate catalyzed diazo decomposition of **11** (Table 1). The subtle differences in chemoselectivity seen in diazo decomposition of **11** and ***ent*-11** were concluded to be due to experimental error.[12]

Table 1. Diastereoselectivities in intramolecular cyclopropanation reactions of **11** catalyzed by dirhodium(II) and copper(I) catalysts.[a]

Catalyst	**12a**[b]	**12b**[b]	**13**[b]	**14**[b]	dr (**12a**:**12b**)[b]	Yield (**12a**+**12b**) [%][c]
$Rh_2(OAc)_4$	64	29	3	4	70:30	72
(*R*-**6**)	85	8	3	4	91:9	77
(*S*-**6**)	43	26	6	25	63:37	47
(*R*-**7**)	67	11	12	10	86:14	59
(*S*-**7**)	40	24	13	23	63:37	45
(*R*-**8**)[d]	74	15	5	6	83:17	75
(*S*-**8**)[d]	55	30	8	7	64:36	62
(*R*-**9**)	85	11	3	1	88:12	69
(*S*-**9**)	60	35	3	2	63:37	70
(*S*-**10**)	62	35	2	1	64:36	62
Rh_2(5S-NEPY)$_4$[e]	40	23	21	16	64:36	39
$[Cu(CH_3CN)_4](PF_6)$	63	35	1	1	64:36	57
$[Cu(CH_3CN)_4]PF_6$/**5**[f]	67	15	2	16	81:19	69

[a] Diazoacetate **11** was added over 2 h to a refluxing catalyst/DCM solution.

[b] Product ratios were obtained by GC analysis on a 30-m SPB-5 column.

[c] Yields determined by crude mass and ^1H NMR integration.

[d] Product ratios are the average of results from three separate reactions with variance of ±4% in the relative yields of **12a** and **12b**.

[e] This catalyst is the neopentyl ester analogue of *S*-**6**.

[f] Compound **5** is (*S,S*)-*t*-Bu-BOX.

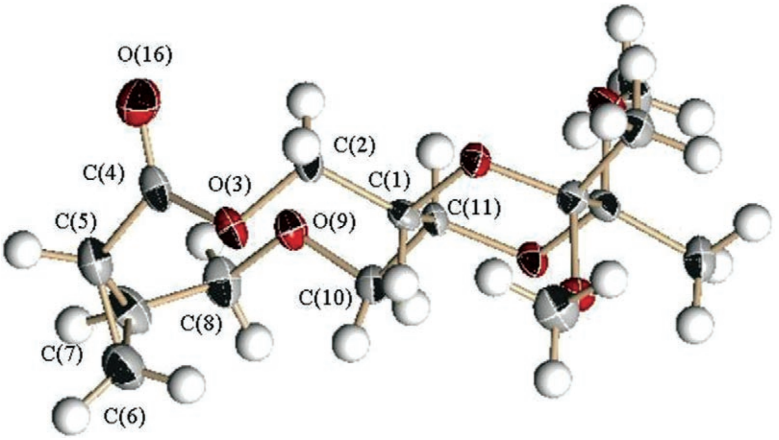
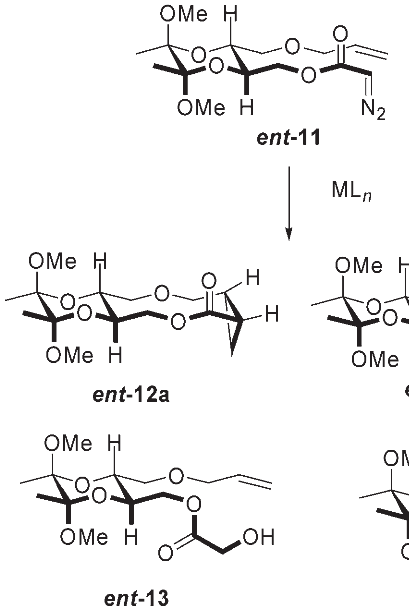


Figure 1. ORTEP Diagram of **12a** with hydrogen atoms. Selected bond lengths [Å] and angles [°]: C(4)–O(16) 1.200(4), C(5)–C(6) 1.483(5), C(5)–C(7) 1.524(5), C(6)–C(7) 1.464(4); C(6)–C(5)–C(7) 58.3(2), C(6)–C(7)–C(5) 59.5(2), C(7)–C(6)–C(5) 62.3(2), O(3)–C(4)–C(5)–C(7) –78.0(3), C(6)–C(7)–C(8)–O(9) –55.2(4), C(2)–C(1)–C(11)–C(10) –69.4(3).

Results from diazo decomposition of ***ent*-11** by Rh_2(5*R*-MEPY)$_4$ in Table 2 matched those in Table 1 for Rh_2(5*S*-MEPY)$_4$, and the same outcome was found with $Rh_2(MEOX)_4$, $Rh_2(MEAZ)_4$, and $Rh_2(MPPIM)_4$ catalysts. A comparison of diastereoselectivity in the diazo decomposition of **11** and ***ent*-8** by Rh_2(5*S*-NEPY)$_4$ also shows the expected outcome. However, results from catalytic diazo decomposition of **11** and ***ent*-11** by Rh_2(4*S*-DOSP)$_4$ do not exhibit differences in either diastereoselectivity or chemoselectivity. As expected, the same diastereoselectivity and chemoselectivity ratios were obtained from the matched pair of **11** and Rh_2(5*R*-MEPY)$_4$ and the enantiomer of each (***ent*-11** and Rh_2(5*S*-MEPY)$_4$). Diasteroselectivity in the dirhodium(II) carboxamidate-catalyzed diazo decomposition of **11** and ***ent*-11** is favored in the order of: $Rh_2(MEPY)_4 > Rh_2(MEOX)_4 > Rh_2(MEAZ)_4 > Rh_2(MPPIM)_4$.

The difference in diastereoselectivity seen in dirhodium(II) carboxamidate-catalyzed reactions between matched and mismatched pairs was not observed in the $[Cu(CH_3CN)_4]PF_6$/**5** catalyzed diazo decomposition of **11** and ***ent*-11**. Rather, complete reversal of the diastereoisomer ratio was observed. The cyclopropane stereochemistry of the major isomer (**12a** and ***ent*-12b**) formed from diazo decomposition of both **11** and



Scheme 3. Products from diazo decomposition of ***ent*-11**.

***ent*-11** is identical (Figure 2). The remote conformational bias of the diazoacetate does not yield an enhancement or reduction of diastereoisomer ratios in $[Cu(CH_3CN)_4]PF_6$/**5**-catalyzed diazo decomposition of **11** and ***ent*-11**, and match and mismatch pairs cannot be assigned based on diastereoselectivity, though the relative ratios of other detected compounds varies.

Conclusion

The conformational bias in diazoacetates **11** and ***ent*-11** affords cyclopropane diastereoisomers from diazo decomposition by dirhodium(II) tetraacetate and copper(I) hexafluorophosphate whose modest diastereoisomer ratios are indicative of dominant substrate control of stereoselection. With chiral dirhodium(II) carboxamidate catalysts, however, the influence of chiral ligands forms stereochemically matched and mismatched pairs between diazoacetate and catalyst yielding enhancement and diminution, respectively, of stereocontrol. In contrast, diazo decomposition of **11** catalyzed by a $Cu(CH_3CN)_4PF_6$/**5** complex yields cyclopropanes **12a** and **12b** in a 81:19 ratio, and decomposition of ***ent*-11** catalyzed by the $[Cu(CH_3CN)_4]PF_6$/**5** complex yields ***ent*-12a** and ***ent*-12b** in a 19:81 ratio. Whereas $Rh_2(5R\text{-MEPY})_4$ affords as the major isomers cyclopropanation products having the same *relative* stereochemistry (**12a** from **11** and ***ent*-12a** from ***ent*-11**), the $Cu(CH_3CN)_4PF_6$/**5**-catalyzed reaction affords major isomers in which the relative stereochemistry is not the same (**12a** from **11** and ***ent*-12b** from ***ent*-11**). The conformational bias inherent in the reactant diazoacetate appears to have minimal influence on diastereoselectivity when interacting with the $Cu(CH_3CN)_4PF_6$/**5** catalyst. These results are consistent with the mechanism of addition described by Doyle and Hu,[5] further illustrating the differences between chiral copper(I) and dirhodium(II) carboxamidate catalysts.

Using Scheme 1 as the model template, the 1,4-dioxane linker in **15** (Scheme 4) is represented as being repelled from the face of the dirhodium(II) catalyst, ori-

Table 2. Diastereoselectivities in intramolecular cyclopropanation reactions of ***ent*-11** catalyzed by dirhodium(II) and copper(I) catalysts.[a]

Catalyst	***ent*-12a**	***ent*-12b**	**13**	**14**	dr (***ent*-12a**:**ent-*12b***)	Yield (***ent*-12a** + ***ent*-12b**) [%]
$Rh_2(OAc)_4$	67	29	2	2	70:30	66
(*R*-**6**)	48	23	4	25	67:33	54
(*S*-**6**)	85	9	2	4	90:10	67
(*R*-**7**)	52	32	4	12	62:38	50
(*S*-**7**)	81	10	4	5	89:11	73
(*R*-**8**)[d]	42	28	8	22	60:40	60
(*S*-**8**)[d]	73	14	5	8	84:16	69
(*R*-**9**)	60	35	2	3	63:37	74
(*S*-**9**)	86	12	1	1	88:12	71
(*S*-**10**)	59	33	7	1	64:36	64
$Rh_2(5S\text{-NEPY})_4$[e]	75	13	5	7	86:14	49
$[Cu(CH_3CN)_4]PF_6$/**5**[f]	10	44	40	6	19:81	42

[a] Diazoacetate ***ent*-11** was added over 2 h to a refluxing catalyst/DCM solution.

[b] Product ratios were obtained by GC analysis on an SPB-5 column.

[c] Yields determined by crude mass and ^1H NMR integration.

[d] Product ratios are the average of results from three separate reactions with variance of ±4% in the relative yields of ***ent*-12a** and ***ent*-12b**.

[e] This catalyst is the neopentyl ester analogue of *S*-**6**.

[f] Compound **5** is (*S,S*)-*t*-Bu-BOX.

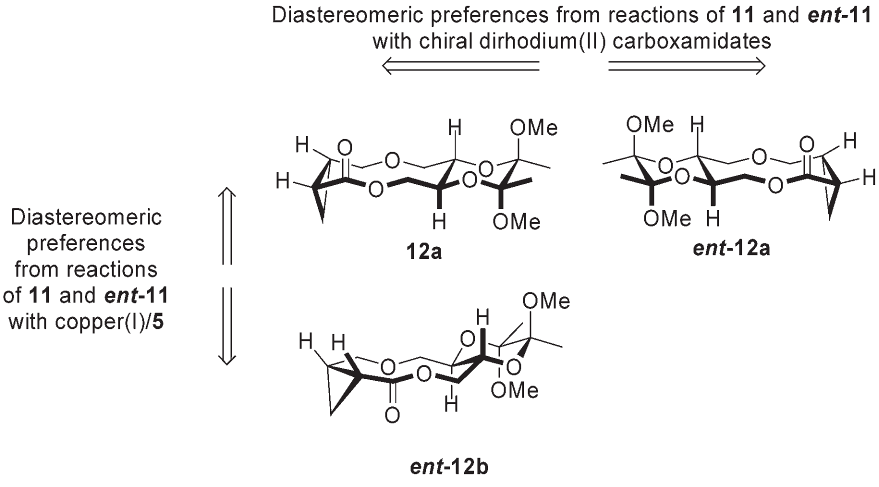
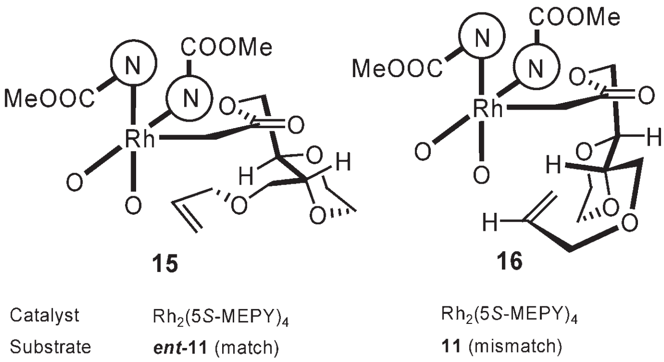


Figure 2. Diastereomeric preferences from cyclopropanation reactions of **11** and ***ent*-11** with chiral dirhodium(II) carboxamidates and copper(I)/**5**.



Scheme 4. Conformational representation of carbene intermediates from reactions of **11** and ***ent*-11** with chiral dirhodium(II) *S*-carboxamidates.

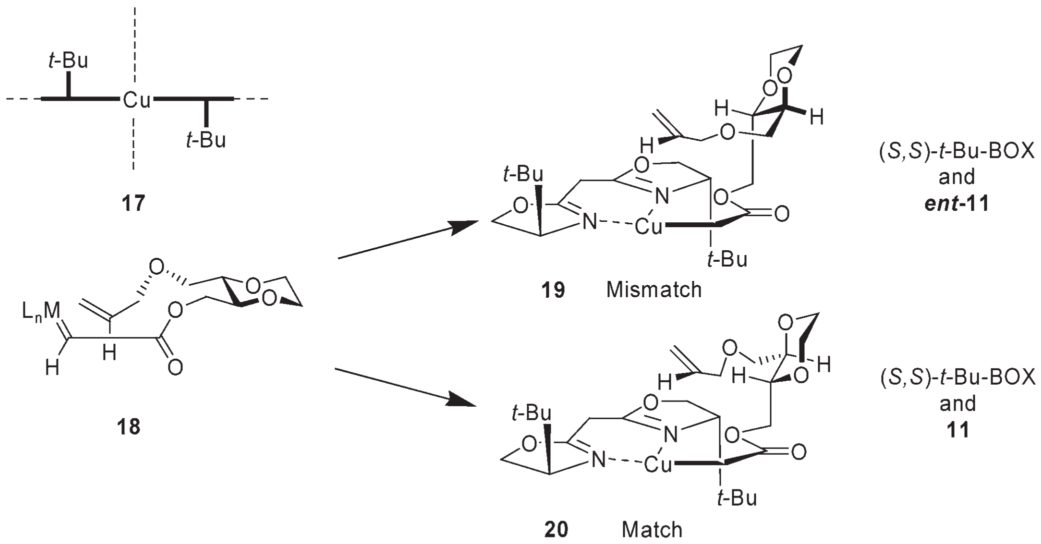
enting the substrate such that the conformational bias derived from the 1,4-dioxane ring directs the olefin toward the chiral metal center in the reaction between Rh$_2$(5*S*-MEPY)$_4$ and ***ent*-11** (note that Me and MeO groups are removed for clarity). The olefin orientation in relation to the catalyst face favors the formation of ***ent*-12a** because of the conformational bias provided by the substrate. Conversely, in the formation of metal carbene intermediate **16** from diazo decomposition of **11**, the conformational bias favors positioning the olefin away from the catalyst, reducing the facial selectivity in carbene addition to the olefin. Model structure **16** also shows that the C–H bond that must undergo insertion to form a six-membered lactone is favorably oriented in relationship to the metal carbene intermediate.

The [Cu(CH$_3$CN)$_4$]PF$_6$/**5** complex viewed in the plane of the bis-oxazoline ligand can be divided into quadrants in which bulky chiral *tert*-butyl groups occupy the upper left and lower right quadrants, while the remaining two quadrants are open. The metal-carbene intermediate **19** (Scheme 5, note that Me and MeO groups of the BDA linker are removed for clarity), formed from diazo decomposition of **11**, orients itself so that the remote conformational bias is placed in an open quadrant, allowing the trajectory of the olefin to the carbene to form the major diastereoisomer **12a** observed in this reaction. Diazo decomposition of ***ent*-11** forms a metal carbene intermediate (**20**) that also places the remote conformational bias in an open quadrant of the chiral bis-oxazoline ligand, even though the conformational bias of the substrate is reversed. The conformation of **20** also favors the trajectory of the olefin to the carbene that is illustrated in **20**. The result is that the chiral bis-oxazoline ligand plays a more significant role in diastereoselectivity than the conformational bias of diazoacetate compounds **11** and ***ent*-11**.

Experimental Section

General Remarks

^{1}H and ^{13}C spectra were obtained as solutions in CDCl$_3$. Diastereoisomer ratios (dr) were measured on a HP5890A workstation with an HP3392 integrator and an SPB-5 column (Supelco 5% diphenylsilane/95% dimethylsilane bonded, 30 m × 0.25 mm ID). Infrared spectra were obtained using a Nicolet 560 EXC or Nicolet Impact 400D spectrophotometer as films on KBr plates with absorptions recorded in wavenumbers (cm^{-1}). Anhydrous dichloromethane (DCM) was distilled over CaH$_2$ prior to use. Preparations of copper(I) hexafluorophosphate,[13] 2,2-bis{2-[4(*S*)-*tert*-butyl-1,3-oxazolinyl]}propane [(*S*,*S*)-*t*-Bu-BOX],[14] Rh$_2$(4*S*-MEPY)$_4$,[15] Rh$_2$(4*S*-MPPIM)$_4$,[16] Rh$_2$(4*S*-MEOX)$_4$,[17] and Rh$_2$(4*S*-MEAZ)$_4$,[18] and Rh$_2$(4*S*-DOSP)$_4$[19] have been previously reported. All reactions were performed under an atmosphere of argon unless otherwise noted.



Scheme 5. Conformational representation of carbene intermediates from reactions of **11** and ***ent*-11** with copper(I) with chiral ligand **5**.

General Procedure for Diazo Decomposition of 11 and *ent*-11 by Dirhodium(II) Catalysts

The procedure for diazo decomposition of **11** catalyzed by Rh_2(5*S*-MEPY)$_4$ is representative. To a refluxing solution of Rh_2(5*S*-MEPY)$_4$ (6.0 mg, 0.0070 mmol, 0.010 equiv.) in DCM (5.0 mL) was added a solution of **11** (0.24 g, 0.70 mmol, 1.0 equivs.) dissolved in DCM (5 mL) *via* syringe pump at a rate of 5 mL/h. The resulting solution was heated at reflux for an additional 1 h before filtration through a silica gel plug, which was rinsed with ethyl ether (20 mL). The resulting crude solution was concentrated under reduced pressure to afford **12a**, **12b**, **13**, and **14**. A small aliquot was then removed for GC analysis on an SPB-5 column, and the ratio of the products was determined by comparison of retention times versus previously isolated samples [retention times: (**14**) 18.4 min, (**13**) 22.9 min, (**12b**) 25.3 min, (**12a**) 25.5 min]. Isolation of **12a** and **12b** was accomplished by flash chromatography on silica gel (66:34 petroleum ether:diethyl ether). The formation of **13** was inferred from the IR absorbance at 3458 cm^{-1}, and in the peak area integration values of the ^{1}H NMR spectrum, although the compound could not be isolated. A fourth material (**14**) that is consistent with a six-membered lactone was also detected but could not be isolated.[20]

(1*S*,5*R*,7*S*,11*S*,13*R*,14*R*)-13,14-Dimethoxy-13,14-dimethyl-3,9,12,15-tetraoxatricyclo[9.4.0.0^{5,7}]pentadecan-4-one (12a): ^{1}H NMR (600 MHz): $\delta = 4.33$ (dd, $J = 11.4$, 9.7 Hz, 1H), 4.21 (dd, $J = 11.4$, 4.2 Hz, 1H), 4.12 (dt, $J = 9.7$, 4.2 Hz, 1H), 4.02 (dd, $J = 12.0$, 6.3 Hz, 1H), 3.86 (dd, $J = 10.6$, 4.2 Hz, 1H), 3.73 (dt, $J = 9.7$, 4.2 Hz, 1H), 3.55 (dd, $J = 12.0$, 6.3 Hz, 1H), 3.36 (dd, $J = 10.6$, 4.6 Hz, 1H), 3.26 (s, 3H), 3.23 (s, 3H), 1.84 (ddd, $J = 9.5$, 8.0, 6.3 Hz, 1H), 1.46 (ddq, $J = 9.5$, 8.2, 6.3 Hz, 1H), 1.28–1.21 (mult, 1H), 1.26 (s, 3H), 1.25 (s, 3H), 1.03 (dt, $J = 8.2$, 5.1 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 171.7$, 98.8, 98.4, 71.4, 70.8, 70.0, 66.3, 63.3, 48.0, 47.9, 18.8, 18.7, 17.4, 17.3, 12.1; IR (solid deposition on KBr plate): $\nu_{(C=O)} = 1727$ cm^{-1}.

(1*S*,5*S*,7*R*,11*S*,13*R*,14*R*)-13,14-Dimethoxy-13,14-dimethyl-3,9,12,15-tetraoxatricyclo[9.4.0.0^{5,7}]pentadecan-4-one (12b): ^{1}H NMR (600 MHz): $\delta = 4.56$ (dd, $J = 11.8$, 10.0 Hz, 1H), 4.08 (dd, $J = 11.8$, 5.9 Hz, 1H), 4.05–3.99 (comp, 2H), 3.77 (dd, $J = 10.7$, 4.1 Hz, 1H), 3.69 (dt, $J = 9.1$, 3.9 Hz, 1H), 3.43 (dd, $J = 10.7$, 3.9 Hz, 1H), 3.29 (s, 3H), 3.22 (s, 3H), 3.20 (dd, $J = 11.8$, 8.2 Hz, 1H), 1.88 (ddd, $J = 9.4$, 8.0, 6.1 Hz, 1H), 1.57 (dddt, $J = 9.4$, 8.2, 8.0, 6.3 Hz, 1H), 1.28 (s, 3H), 1.27 (s, 3H), 1.24 (ddd, $J = 7.7$, 6.1, 5.2 Hz, 1H), 1.03 (dt, $J = 8.0$, 5.2 Hz, 1H); ^{13}C NMR (150 MHz): $\delta = 172.5$, 99.0, 98.9, 71.3, 70.5, 69.6, 67.6, 64.1, 48.1, 48.0, 19.5, 19.1, 17.5, 17.4, 12.4; IR (solid deposition on KBr plate): $\nu_{(C=O)} = 1727$ cm^{-1}.

Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-280559. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

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References and Notes

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[8] Ligands are arranged so that there are two nitrogens and two oxygens on each rhodium and that the two nitrogens (or two oxygens) are *cis* to each other: M. P. Doyle, T. Ren, in *Progress in Inorganic Chemistry*, (Ed.: K. Karlin), Wiley, New York, **2001**, Vol. 49, pp 113–168.

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[11] Crystal data for **12a**: $C_{15}H_{24}O_7$, MW = 316.35, monoclinic, space group P2 (1), $a = 6.8596(12)$ Å, $b = 9.5668(16)$ Å, $c = 11.922(2)$ Å, $\beta = 95.413(3)°$, $V = 778.9(2)$ Å^3, $Z = 2$, $\rho_{calcd.} = 1.349$ Mg/m^3, $F(000) = 340$, $\lambda = 0.71073$ Å, $\mu_{eff.}$ (Mo-Kα) = 0.107 mm^{-1}, data for the structure were collected by the ω-scan technique on an X-ray diffractometer equipped with a CCD detector. Intensity measurements were performed on a crystal (dimensions $0.3 \times 0.15 \times 0.025$ mm) in the range $1.72 < 2\theta < 26.08°$. Of the 7693 measurements, 3025 were independent ($R_{int} = 0.0470$). The structure was solved by direct methods (Bruker AXS ShelXTL Version 6.10) and refined by full-matrix least squares on F^2. The final refinements converged at $R_1 = 0.0471$ for $I2\sigma(I)$, $wR_2 = 0.1147$ for all data. The final difference Fourier synthesis gave a min/max residual electron density of –0.204/+0.308 e Å^{-3}.

[12] Several of these reactions were repeated, including that of dirhodium(II) tetraacetate and **8**. The resulting product ratios obtained from GC analysis in these reactions showed that the peak area ratios varied by 1–3% in three runs of the same reaction.

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[20] The C=O stretching frequency for **41** is 1734 cm^{-1}, The ^{1}H NMR spectrum shows that the olefinic protons of the allyl ether have not changed in chemical shift or *J*-coupling values. In addition, the signals for each methyl group of the starting diazoacetate **8** are present in the spectrum. No signals consistent with maleate or fumarate esters (singlet at 6.9 or 6.3 ppm) are observed.