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Perspective on Dirhodium Carboxamidates as Catalysts

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Abstract

Dirhodium compounds are emerging as highly efficient catalysts for diverse reactions, and those with carboxamidate ligands have the broadest applications. The unique features of these compounds are their structural rigidity, ease of ligand exchange, open diaxial sites for coordination with Lewis bases, and their low oxidation potential. As consequences of this, dirhodium carboxamidates are efficient and effective catalysts for metal carbene reactions, Lewis acid catalyzed processes, and chemical oxidations. With chiral carboxamidate ligands these dirhodium compounds show exceptional enantiocontrol for intramolecular cyclopropanation and carbon-hydrogen insertion reactions of diazoacetates, and they are also highly efficient and selective for hetero-Diels-Alder reactions. Their limitations lie in their moderate reactivities for metal carbene generation and Lewis acid catalysis and in the cost of the precious metal rhodium.

Background

More than 20,000 kg of rhodium (about 200,000 moles) was produced in 2005, the vast majority from South Africa, and 85% of that was used for catalytic converters. Of the three dominant precious metals used for catalysis – platinum, palladium, and rhodium – rhodium is the least abundant and also the most expensive, about five-times that of platinum and more than fifteen-times that of palladium. Rhodium costs are highly variable, ranging from $30 to $100 per gram, dependent on supply and demand considerations. The value of rhodium as a catalyst must therefore be related to its supply and recovery costs, so that turnover numbers (TON) and rates, product yields, and selectivities are positioned against supply and recovery costs to achieve a suitable evaluation of value. It is with these considerations that this perspective is written.

Dirhodium(II) compounds have played an important, and often unique, role in the development of catalytic synthetic methodology in organic chemistry. Appreciation for the unique paddlewheel structure of dirhodium(II) tetraacetate, $Rh_2(OAc)_4$, with its two axial coordination sites[1] led to the discovery in the 1970's by the Teyssie group that

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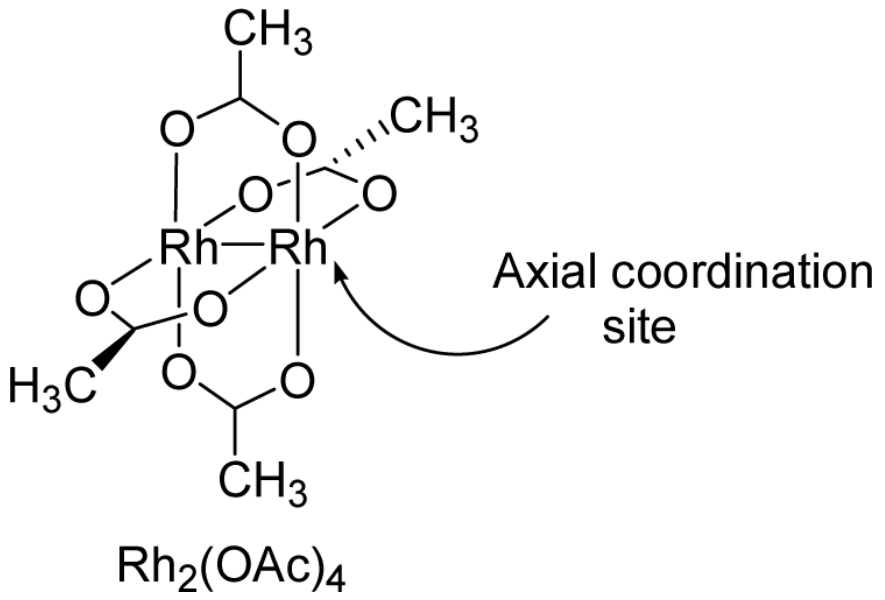


$Rh_2(OAc)_4$

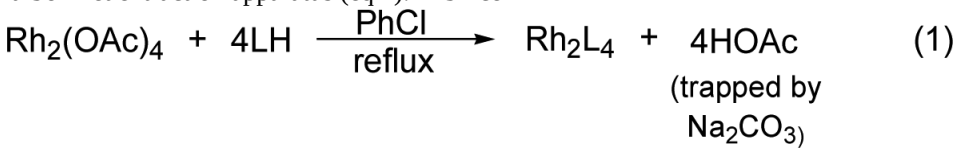
this structurally well-defined compound catalyzed the decomposition of ethyl diazoacetate.[2] Subsequent synthetic and methodological developments and mechanistic insights placed $Rh_2(OAc)_4$ in a unique position among transition metal catalysts used in reactions of diazocarbonyl compounds,[3] especially in carbon-hydrogen insertion[4] and ylide[5] transformations (Scheme 1) and for direct correlation through reactivity/selectivity determinations with known metal carbenes.[6] In addition, this dirhodium(II) compound was also reported to catalyze selected oxidation[7] and reduction[8] reactions, but the integrity of the catalyst was not maintained. Despite the relative expense of rhodium, $Rh_2(OAc)_4$ exhibited clear advantages for metal carbene transformations with diazocarbonyl compounds in turnover numbers and selectivity. Furthermore, the Merck synthesis of the antibiotic thienamycin via dirhodium(II)-catalyzed intramolecular N-H insertion of a diazoacetoacetate (Scheme 2)[9] added considerable interest. But when my research group began our excursions into rhodium catalysis in 1980 with only a small initial cohort consisting of undergraduate student Bill Buhro, postdoc Bill Tamblyn, and exchange visitor from the University of Groningen, Daan van Leusen, only the Teyssie group was actively engaged.

One further advantage of dirhodium(II) tetraacetate has been its ability to undergo ligand exchange – the replacement of acetate by another carboxylate or by an analogue (carboxamidate, phosphate, among others).[10] The viability of the exchange process made possible consideration of the placement of chiral ligands onto the dirhodium(II) framework and the development of these compounds as asymmetric catalysts. Carboxylate exchange with chiral *N*-protected amino acids was the most straightforward and, although the carboxylate ligand's chiral center is placed far away from the site of carbene formation at the axial coordination site of dirhodium, initial efforts[11,12] found that prolinate ligands[12] had unusual selectivity in reactions of diazoacetates and related substrates. This catalyst design has led to significant undertakings, especially by Davies in C-H insertion reactions with aryl- and vinyldiazoacetates.[13-15] Alternative chiral carboxylates have also provided high selectivity in C-H insertion reactions.[16] However, it has been the development of dirhodium(II) tetrakis (carboxamidates) that has afforded the greatest versatility in stereocontrol and applications.

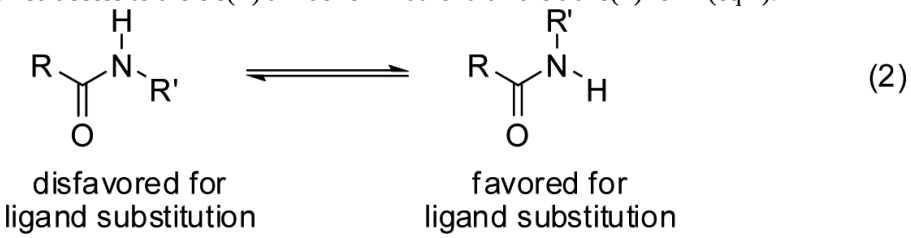
Dirhodium Carboxamidate Catalysts

The first synthesis of a dirhodium(II) carboxamidate occurred in the 1980s when dirhodium (II) tetra(acetamidate) was isolated from a melt of acetamide containing $Rh_2(OAc)_4$.[17]

Multiple isomers are possible, but the one in which two nitrogens and two oxygens are bound to each rhodium with the two nitrogens cis (the *cis*-2,2 isomer, Figure 1) is dominant.[18] In catalytic reactions with diazocarbonyl compounds the carboxamidates exhibited lower reactivity for diazo decomposition than the corresponding carboxylates, but higher selectivities.[19] Access to chiral analogues in which the asymmetric center was alpha to nitrogen, near to the site of carbene formation at the axial coordination site of dirhodium, was made possible by a procedure in which the liberated acetic acid is trapped by sodium carbonate in a Soxhlet extraction apparatus (eq 1).[20] Since



ligand exchange is negligible at room temperature, and because of the need to remove acetic acid (bp 118°C) so as to inhibit reverse exchange, these reactions are conducted in refluxing chlorobenzene (bp 130°C). Initial attempts to use a broad swath of chiral carboxamides led us to the realization that acyclic amides were not generally suitable because ligand exchange required access to the cis(*E*) amide form rather than the trans(*Z*) form (eq 2).[21]



Consequently, reported chiral carboxamidate ligands for dirhodium(II) are cyclic amides (examples in Scheme 3). These depictions are usually intended to represent only the *cis*-2,2 isomer (see Figure 2). The ester functionality, which can provide either the S or R configuration to the ligand, is essential for high enantiocontrol in catalytic reactions.[3] Ligand costs, since they are derived from relatively inexpensive amino acids, are relatively low and should not add enormously to the overall cost of the chiral dirhodium(II) carboxamidate.

Each of these compounds has a paddlewheel structure defined by four bridging carboxamidate ligands about a Rh_2^{4+} core. Because the chiral carboxamidate ligands are unsymmetrical bridges, four different geometries are possible: *cis*-(2,2), *trans*-(2,2), (3,1) and (4,0) (see Figure 1). The *cis*-(2,2) isomer is dominant or exclusive in these preparations, and the *trans*-(2,2) isomer has only recently been observed as a very minor constituent.[26] A formal single bond joins the two rhodium atoms, and with acetonitrile or benzonitrile usually coordinated in the axial positions, these air stable complexes typically crystallize as red solids. The axial ligands, that are derived from the solvent in which the complex is crystallized, can be easily removed by placing the solid under vacuum or in a poorly coordinating solvent (*e.g.* dichloromethane) yielding a blue species. However, removal of the axial ligands is not required to achieve catalytic reactivity in solution. Only recently has the complexity of the synthetic process been realized,[26] so that conflicting results from different laboratories can now be attributed to the purity of the *cis*-(2,2) isomer in the catalyst preparation. The need for careful crystallization and analysis is evident in these recent results; what is perhaps surprising is the ease with which the pure *cis*-(2,2) isomer can be obtained by crystallization or column chromatography and crystallization. Unpublished experiments in which the *cis*-(2,2) isomer is heated in refluxing dichloromethane (bp 40°C) and in 1,2-dichloroethane (bp 83°C) and monitored by HPLC for isomer formation, as well as in determinations by stereoselectivity in select reactions with

diazoacetates, show that there is no exchange in refluxing dichloromethane, even after 24 h, and exchange is slow in refluxing dichloroethane, noticeable only after several hours.

The ligands that surround the dirhodium core greatly influence the reactivities and selectivities afforded by their catalytic uses. The strain provided by four-membered azetidinone ligands in compounds such as Rh_2(4*S*-MEAZ)$_4$ lengthen the Rh-Rh bond distance and results in higher reactivities for diazo decomposition.[25] The steric bias intrinsic in the design of the Rh_2(MPPIM)$_4$ catalysts influences the conformation of attached carbenes derived from diazoacetates[27] and also provides the highest degree of enantiocontrol in Lewis acid catalyzed Hetero-Diels-Alder reactions.[28]

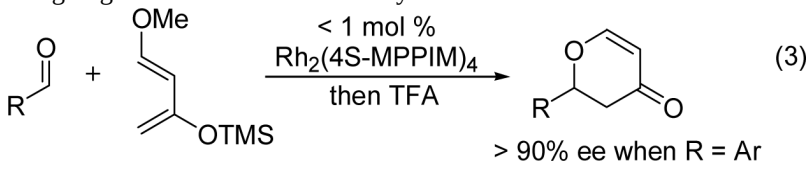
When we began to use the chiral dirhodium carboxamidates in 1989−90, our first attempts were with accessible oxazolidinones that were widely used as chiral auxiliaries, and to use menthyl diazoacetates for intermolecular cyclopropanation of styrene. With initial disappointing results,[21] we selected the methyl ester of commercially-available pyroglutamic acid as an alternative ligand for dirhodium and, with the suggestion of Paul Müller who was spending a sabbatical year with me, phenyl diazoacetate as the substrate for intramolecular cyclopropanation. The first trial was conducted by Amy Kazala, then a freshman student at Trinity University, who was instructed to heat a combination of rhodium acetate and ligand in refluxing chlorobenzene for a period of time, then take a drop or two of the resulting solution, presumably containing Rh_2(MEPY)$_4$, to add to a dichloromethane solution of prenyl diazoacetates (3-methyl-2-buten-1-yl diazoacetate); two days later she reported that the product was formed in 89% ee. Subsequent controlled reactions using the purified Rh_2(MEPY)$_4$ catalyst showed that product formation occurred with 98.6% ee with (*cis*-2,2)-Rh_2(MEPY)$_4$.[20b]

The readily accessible Rh_2(MEPY)$_4$ catalysts[20] work best in intramolecular cyclopropanation reactions of allyl diazoacetates,[22] but they generally show low diastereoselectivity in carbon-hydrogen insertion reactions of diazoacetates derived from secondary alcohols like cyclohexanol. The Rh_2(MEOX)$_4$ catalysts are more reactive than the Rh_2(MPPIM)$_4$ or Rh_2(MEPY)$_4$ catalysts, but selectivities found with their uses are generally somewhat lower. The physical properties of the chiral carboxamidate catalysts are readily modified by attachment, for example, of an octadecyl group in place of methyl to render high solubility in hydrocarbon solvents,[3] or to attach the ester to a polymer backbone which provides convenient means for recovery and reuse (Scheme 4).[29] A more clever and practical attachment, however, has been through coordination by polymer-linked pyridine to the axial coordination sites of dirhodium carboxylates.[30]

The carboxamidates of dirhodium(II) have a much lower oxidation potential than do the dirhodium(II) carboxylates,[31] and this has been both an advantage and a disadvantage. The advantage is the suitability of these catalysts, but especially dirhodium(II) caprolactamate ($E_{1/2}$ of 11 mV), as catalysts for chemical oxidations (Scheme 5).[32-35] The disadvantage is evident in the synthesis of sulfur analogues of the dirhodium compounds of Scheme 3 and the failure of the catalytic methodology for metal carbene reactions due to the oxidation of Rh(II) Rh(II) to Rh(II)Rh(III); this transformation is easily observed by a change in color from blue-green to pink-red and observation of a relatively long wavelength absorption near 1000 nm. In diazo chemistry, especially with diazoacetates, the oxidized Rh(II)Rh(III) may be reduced to Rh(II)Rh(II), giving the dirhodium(II) catalysts the characteristic of being oxidatively stable and capable of high turnover numbers in catalytic reactions.

Lewis acid catalysis is a recently discovered characteristic of chiral dirhodium(II) carboxamides.[28,36-38] Although linked to basic understandings of coordination chemistry with rhodium carboxylates,[39] the availability of the axial coordination site of dirhodium(II)

for Lewis acid catalysis has not been widely recognized. Equilibrium constants for aldehyde[28,37] and nitrile[10,18,23,40] coordination with chiral dirhodium(II) carboxamidates have values that are dependent on structure and substituents, but their values are rarely greater than 100 M^{-1}. This sensitivity to on and off rates gives dirhodium(II) carboxamidates an advantage in reactions such as the hetero-Diels-Alder reaction (eq 3) in which the cycloaddition product, being larger than the reactant carbonyl

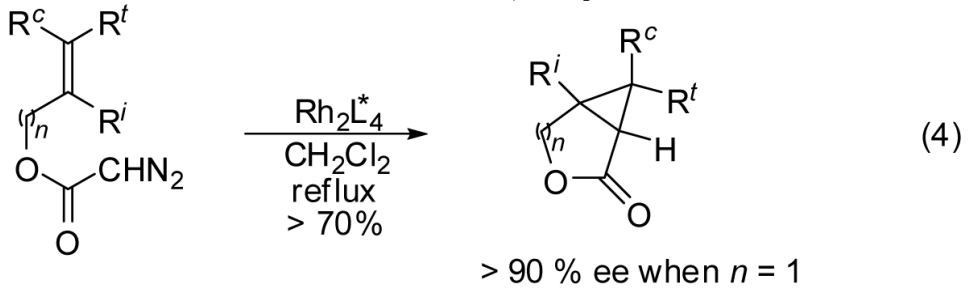


(3)

compound, has a faster off rate with consequent TON up to an amazing 10,000.[28,38] Furthermore, there is potential for selectivity in axial ligand association as a result of configurational match/mismatch[41] with chiral dirhodium(II) complexes that is as yet not fully explored. The next challenge in understanding coordination complexes with dirhodium compounds lies in the equilibrium constants and on-off rates with Rh(II)Rh(III) complexes.

Catalysts for Metal Carbene Reactions

Dirhodium catalysts are especially prominent in metal carbene transformations, and they are often the catalysts of choice.[3,10,13,14,18,42-44] Their applications are numerous, and I will only summarize here the highlights of what has been and continues to be their crowning achievements. They allay themselves in applications as catalysts for cyclopropanation (including "cycloaddition" on aromatic rings), carbon-hydrogen insertion, ylide-formation and rearrangement, and other processes. In cyclopropanation reactions, dirhodium(II) carboxamidates are the catalysts of choice for intramolecular cyclopropanation of allylic diazoacetates, resulting in the corresponding bicyclic lactones in high yield and enantiomeric excesses that routinely exceed 95% (eq 4: L* = chiral ligand, R^t = trans substituent, R^c = cis substituent, R^i = internal double bond substituent). The preferred



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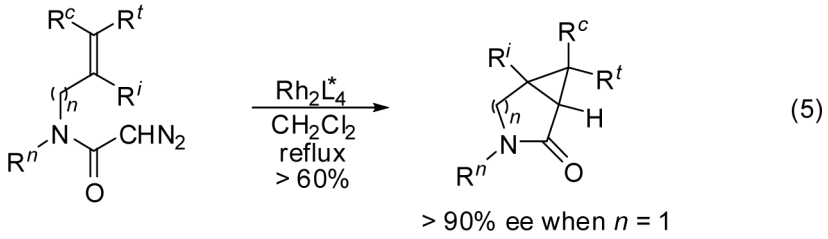
catalysts are the $Rh_2(MEPY)_4$ compounds (Scheme 3),[22] but in those cases where the $Rh_2(MEPY)_4$ catalysts result in lower enantiocontrol (*trans*-olefin geometry, <90% ee with the MEPY catalysts) the $Rh_2(MPPIM)_4$ catalysts improve enantiocontrol.[42] These reactions can be performed with 0.1 mol % of catalyst or less. Homoallylic diazoacetates show somewhat reduced enantiocontrol, but stereoselectivity in these cases is still higher than those with any alternative catalytic system.[22] Similar allylic and homoallylic diazoacetamides also give high enantiocontrol in reactions catalyzed by chiral dirhodium carboxamidates (eq 5),[43] but the amide nitrogen must have a substituent other than hydrogen in addition to the



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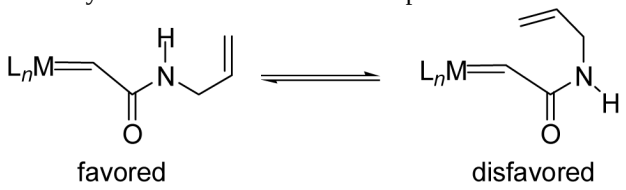
allyl or homoallyl group, presumably because the preferred conformation of the compounds with N-H places the reacting double bond away from the putative metal carbene (eq 6). Operational utility in these cases results from optimization of the



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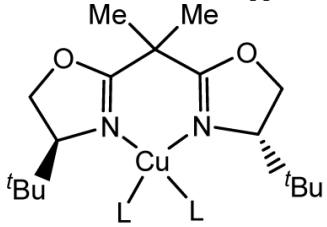
conformational placement of the reacting functional group into proximity with the carbene center. Enantioselectivities decrease to a level of 40−70% ee when *n* in eq 4 is increased beyond 2 to 8;[44] in these cases chiral copper(I) bis-oxazoline catalysts show increased stereoselectivities and become superior in enantiocontrol over chiral dirhodium(II) carboxamidates (Figure 3).[45] The mechanistic influences of this selectivity have been discussed, and a clear picture of differences between chiral dirhodium(II) carboxamidates and copper(I) with chiral bis-oxazoline ligands is emerging.[46-48]

For *intermolecular cyclopropanation reactions* of diazoacetates, chiral copper(I) bis-oxazoline catalysts (e.g., **1**) are generally preferred for enantiocontrol, but diastereoselectivities are often low. In these cases, a range of catalysts has been used to achieve a balance between high diastereoselectivity and high enantioselectivity, and these considerations have been reviewed.[3,18,49] High enantiocontrol and high trans selectivity have been achieved in select cases with chiral ruthenium(II) catalysts[50] and with chiral porphyrin- and salen-ligated cobalt(II) catalysts.[51] With diazomalonates no catalyst has been able to achieve high enantiocontrol in intermolecular cyclopropanation reactions, although the class of chiral dirhodium(II) azetidinones (Scheme 3) has been modestly effective;[25] this area represents an unmet challenge for future activity. Diazoketones are another unmet opportunity for selectivity enhancement in metal carbene reactions. In both cases the approach of the double bond to one side of the carbene is dependent on the differentiation by the catalyst, not aided or influenced by carbene substituents. With phenyldiazoacetates and styryldiazoacetates, the $Rh_2(DOSP)_4$ catalysts [e.g., **2** with Ar = $CH_3(CH_2)_{11}$] are superior to all others, and reasons for this have been discussed.[52] Critical considerations are the fit of carbene substituents on the face of the catalyst and restrictions to the approach of the alkene to the carbene center.



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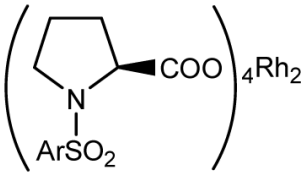

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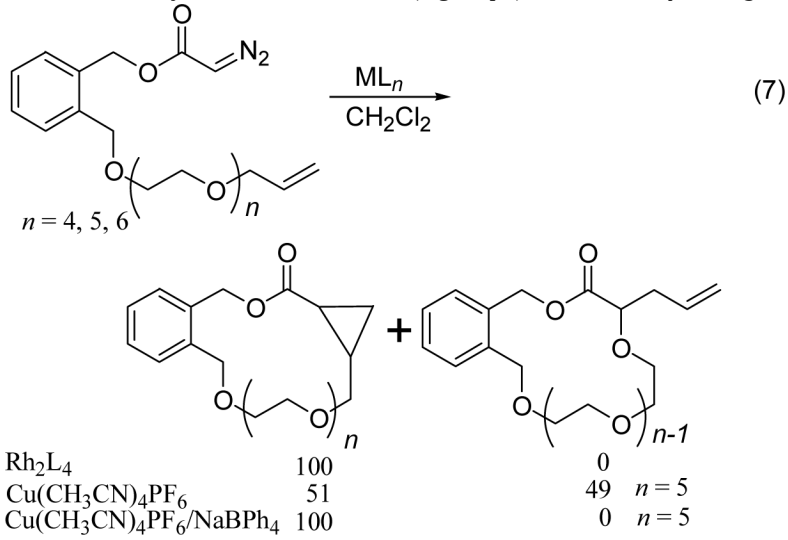
A major breakthrough in synthetic carbon-carbon bond forming reactions occurred with the realization that dirhodium(II) compounds are effective catalysts for *carbon-hydrogen insertion reactions* of diazocarbonyl compounds. Intramolecular reactions of diazoacetates effect efficient formation of γ-lactones in good yield and with high enantioselectivity (Schemes 6 and 7),[27,53] generally without competition from insertion at other carbon positions, although β-lactone formation has been reported in select cases.[54] Diazoacetamides, in contrast, show a higher propensity for β-lactam formation and require a protective group on nitrogen in order to achieve high yields;[3] this transformation has not been fully utilized for organic synthesis.

A recent exciting development in transition metal catalyzed C-H insertion has been the selective intermolecular reactions of styryl diazoacetates and phenyldiazoacetates, catalyzed by chiral dirhodium(II) prolinate catalysts, that was discovered by H. M. L. Davies and coworkers.[14] These reactions utilize the chiral $Rh_2(DOSP)_4$ catalysts that have higher reactivity for diazo decomposition and greater access by substrates to the rhodium carbene than do the dirhodium(II) carboxamidates. This opening to insertion reactions has created new vistas for synthetic design,[55] but extensions in diazo substrate structure from the original compounds are yet to be uncovered.

One of the last remaining challenges in metal carbene chemistry lies in *asymmetric ylide chemistry*, and dirhodium(II) carboxamidates have played an instrumental role in advances in this area. Not long ago there was belief that asymmetric induction based on chirality transfer in a metal-ylide complex could not be achieved. Ylide dissociation from the bound ylide was thought to be required if further reaction of the ylide was to occur. In other words, reaction could only occur from the “free” ylide, not the metal-bound ylide. This view was convincingly challenged by results described in Scheme 8 in which ylide formation is followed by [2,3]-sigmatropic rearrangement and further confirmed by asymmetric induction in reactions of ethyl diazoacetate with allyl iodide.[56] Since this report there have been several examples of enantioselective ylide transformations,[57] including one providing 90% ee in a carbonyl ylide transformation,[58] but further advances remain a formidable challenge.

Macrocyclization via metal carbene intermediates is a recent and relatively unused methodology, despite its recognized advantages in the formation of large rings in cyclopropanation reactions.[45] These reactions, which are appropriate for addition and ylide-forming reactions but, as yet, not C-H insertion (e.g., eq 7),[59] *do not require high*



(7)

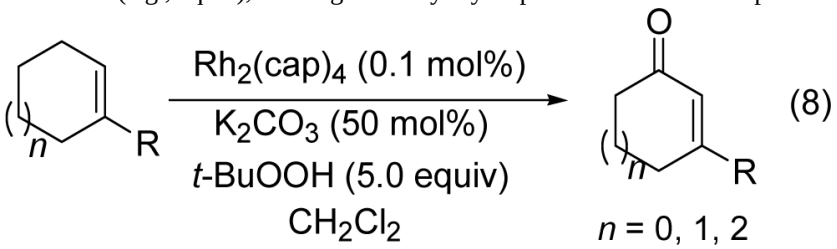
dilution or other extraordinary conditions to achieve high product yields, and enantiocontrol parallels that found in intermolecular reactions (Figure 3). Although examples exist for cyclopropanation,[60] cyclopropenation,[61] aromatic cycloaddition,[62] ylide[59] and coupling[63] reactions, their versatility has not yet been realized in synthetic applications. One of the crowning achievements of this methodology is seen in the preparation of presqualene alcohol, the synthetic investigation for which uncovered macrocyclic cyclopropanation (Scheme 9).[64]

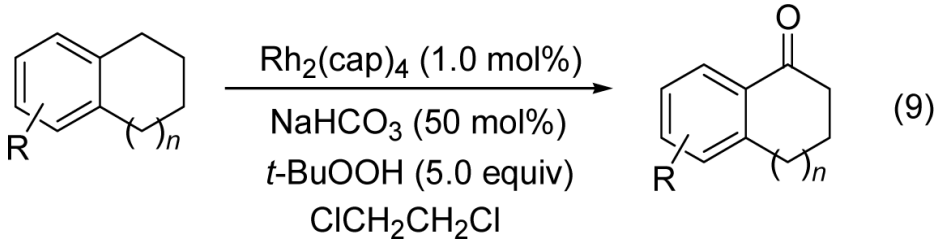
Lewis Acid Catalysts

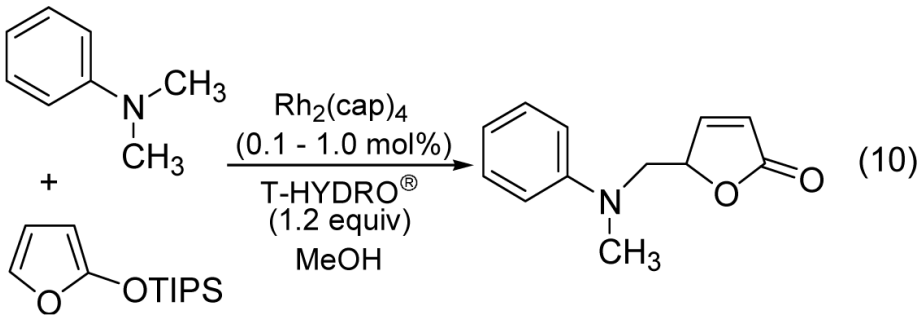
The discovery that chiral dirhodium(II) carboxamidates could effectively catalyze the hetero-Diels-Alder (HDA) reaction (eq 3) with high enantiocontrol and turnover numbers (TON) up to 10,000[28,37,65] has given Lewis acid catalyzed processes new standards for achievement.[66] The HDA reaction occurs in a concerted fashion and is amenable to rigorous physical organic chemical analysis with dirhodium(II) catalysts. As we are discovering, in addition to effective coordination of the reacting substrate to the catalyst, the major challenge in Lewis acid catalysis is high off rates for the product, which are achieved with the chiral dirhodium carboxamidate catalysts. That dirhodium carboxamidates give high selectivities and TON suggests that they may be suitable for other catalytic processes. Indeed, they have been employed for a [2+2]-cycloaddition reaction,[67] but their low equilibrium association constants currently limit their applications. However, they are weak Lewis acids that have limited effectiveness in catalyzing reactions that require stronger Lewis acidity than are inherent in dirhodium(II) carboxamidates.

Dirhodium Carboxamidates as Oxidation Catalysts

We found more than twenty years ago that dirhodium(II) carboxylates could be used as oxidation catalysts,[7] but their reactions were limited, and further investigations were not pursued. The realization that dirhodium(II) caprolactamate, $Rh_2(cap)_4$, with its low oxidation potential, was a highly effective catalyst has come only recently,[10] and examples of allylic oxidation (eq 8),[32] benzylic oxidation (eq 9),[34] and selective amine oxidations coupled with Mannich addition (e.g., eq 10),[35] using *tert*-butyl hydroperoxide have been reported.







Oxidative reactions with *N*-bromosuccinimide and *p*-toluenesulfonamide in the presence of potassium carbonate leading to aziridine products[33] have also been reported, but this reaction has not yet shown a propensity for enantiocontrol. Key to understanding these processes are the mechanism(s) of action of the dirhodium catalyst with the primary oxidants. In the allylic and benzylic oxidations, ketone products are formed in high yield without the intervention of alcohol intermediates, and in allylic oxidations epoxidation is not a competitive reaction.

The ability to access the higher oxidation states of dirhodium compounds does afford opportunities for the development of new chemistries that were not considered possible a mere thirty years ago when dirhodium tetraacetate was first introduced as a new catalyst. The possible use of Rh(II)Rh(III) compounds as Lewis acid catalysts that are more active than their Rh(II)Rh(II) counterparts is just one of several directions for which these dirhodium carboxamidates may be effective.

Conclusion

The uses of dirhodium carboxamidates have expanded significantly since their introduction as viable catalysts for metal carbene transformations approximately fifteen years ago.[19,20] They are uniquely suited for intramolecular allylic cyclopropanation[18,68,69] and intramolecular carbon-hydrogen insertion[18,69] reactions of diazoacetates that occur uniformly with exceptionally high enantiocontrol, and the list of syntheses that employ the chiral dirhodium carboxamidate catalysts is expanding.[69-71] Applications to ylide-derived, aromatic cycloaddition, and macrocyclization reactions involving metal carbene intermediates are in their infancy and provide opportunities for further development. Remarkably, synthetic applications beyond the simplest addition and insertion reactions remain relatively undeveloped. The newer developments in Lewis acid catalyzed reactions and in oxidative transformations using dirhodium carboxamidates offer a breadth of utility that point to their continued applications for unique advantages. Do these advantages justify the cost of using the rhodium catalyst in a particular application? The answer depends on the application, of course, but with their unique advantages in select applications, the case can be made for the uses of dirhodium carboxamidates beyond laboratory scale reactions.

The chiral dirhodium(II) carboxamidates were initially commercialized by Regis Chemical Company in Skokie, IL. Several of them were subsequently prepared by Johnson Matthey and sold directly.[72] Currently, commercial samples of some of the chiral dirhodium(II) carboxamidates are available from several catalog suppliers, but the most diverse supply remains with the author.

Acknowledgment

The research that is described in this article is a composite of work performed at four academic institutions at which the author resided and nine universities at which collaborators provided their data and insights. This adventure involved nearly seventy undergraduate students, including ten who came from overseas laboratories, thirty-two postdoctoral

associates, and eight graduate students, all of whom are coauthors of publications, some of which are referenced in this perspectives article. Generous support for this research has come from the National Science Foundation for excursions into dirhodium carboxamidate design and chemistries, and from the National Institute of General Medical Sciences of the National Institutes of Health for applications of these compounds as catalysts, particularly the chiral dirhodium(II) carboxamidates.

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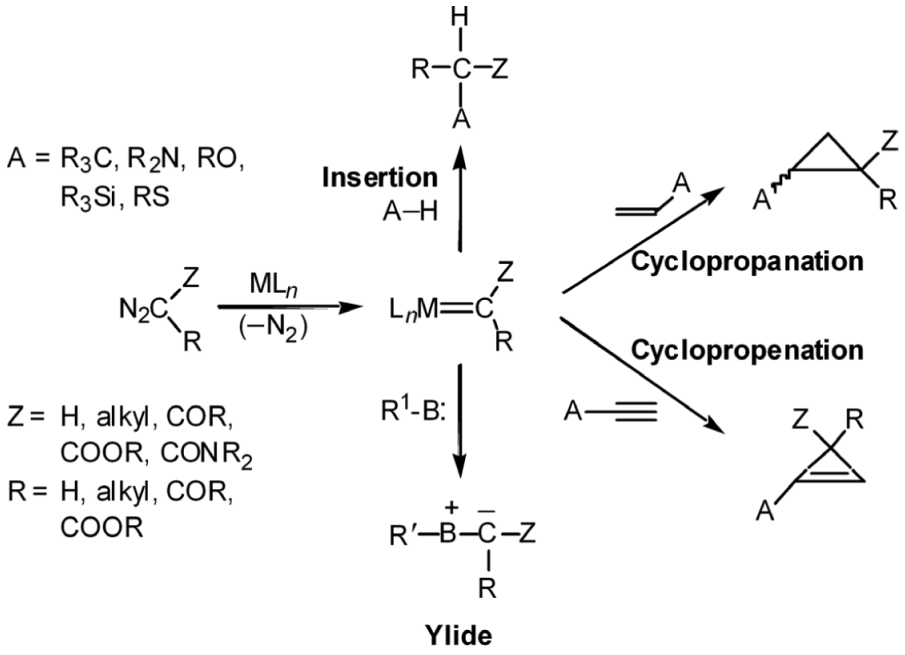
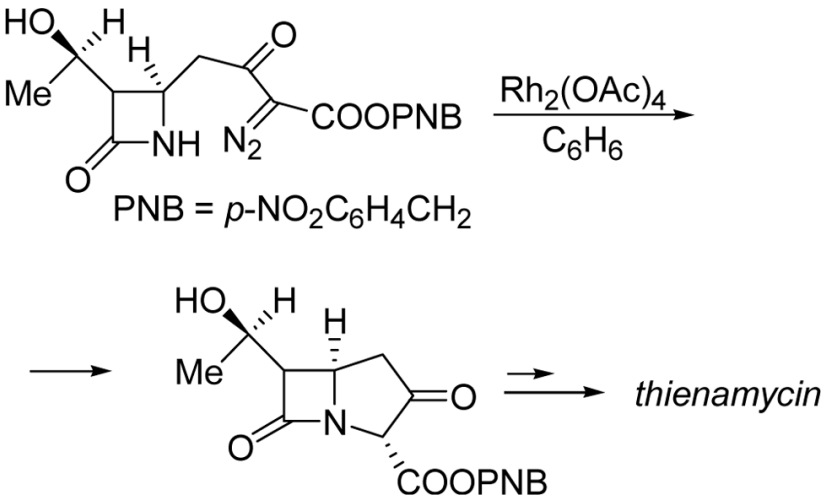


SCHEME 1.
Some metal catalyzed reactions of diazocarbonyl compounds



SCHEME 2.
Nitrogen-hydrogen insertion in the Merck synthesis of thienamycin

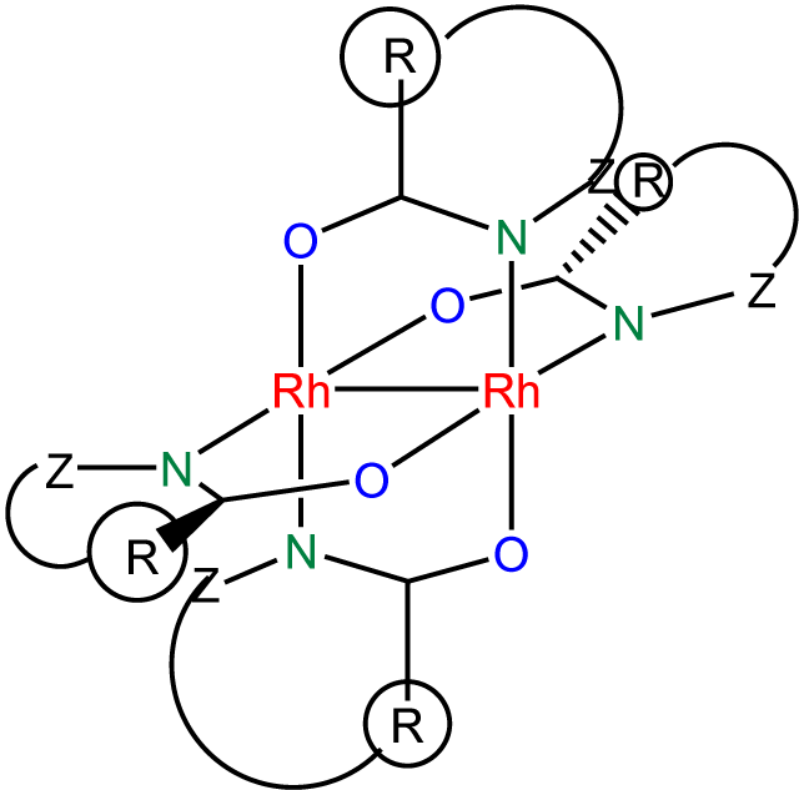
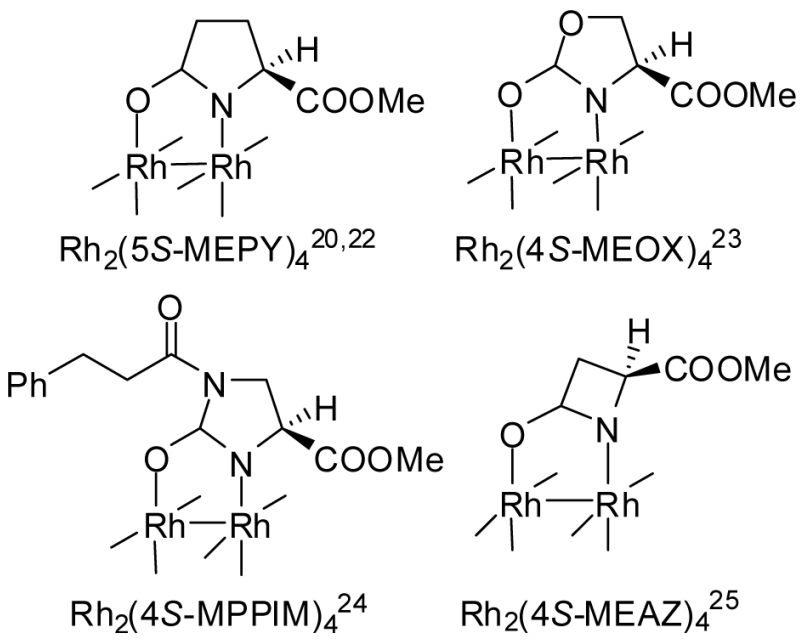


FIGURE 1.
Generalized structure for (*cis*-2,2) dirhodium carboxamidates; (*cis*-2,2) refers to the atomic distribution of N and O on rhodium.



SCHEME 3.
Chiral dirhodium(II) carboxamidate

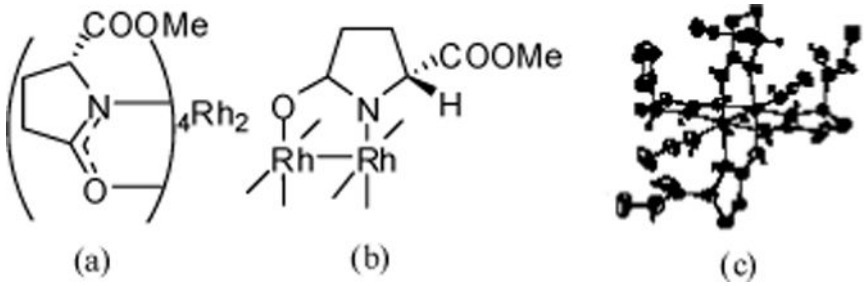
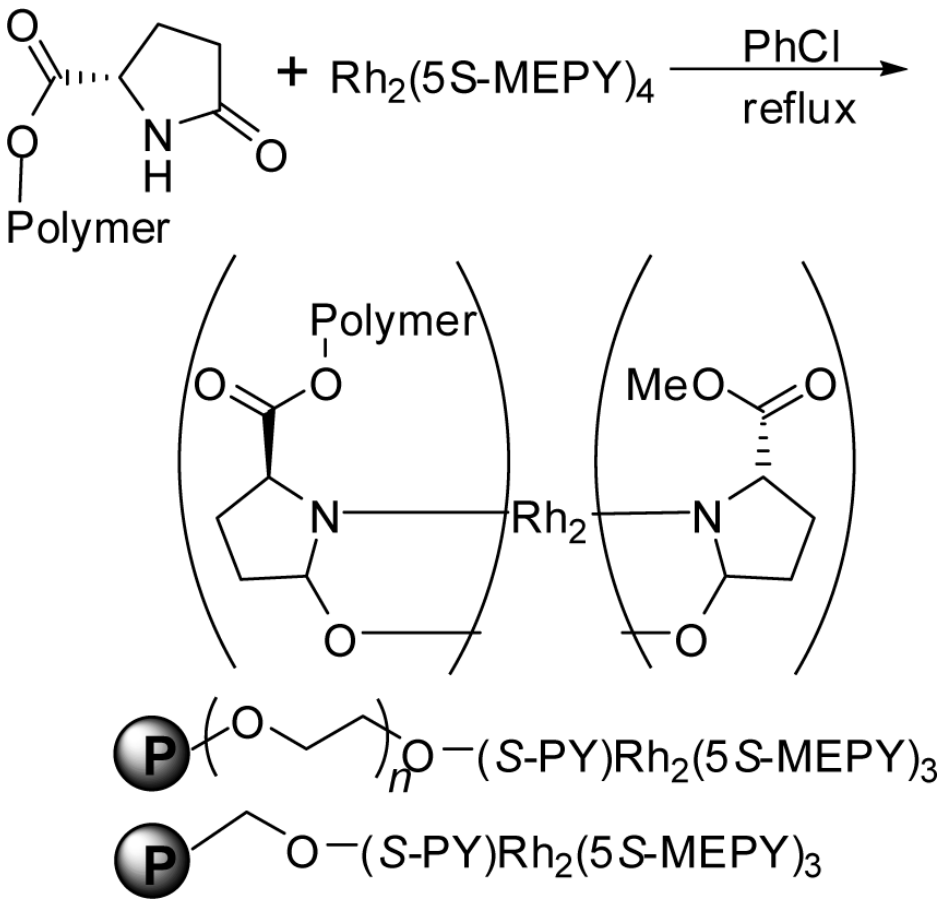
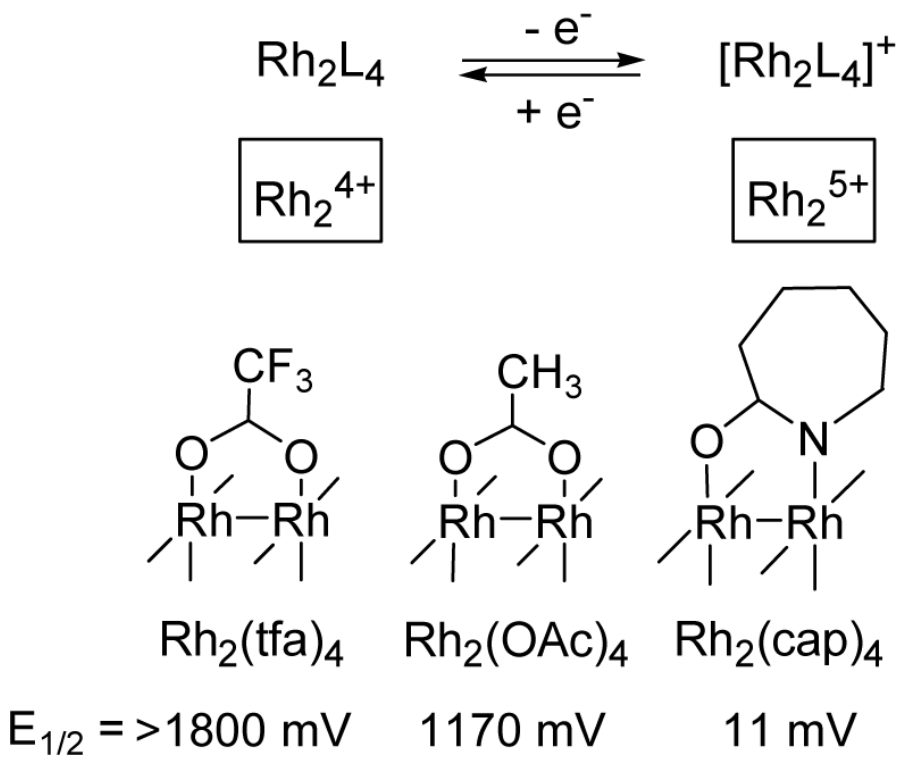


FIGURE 2.

Structure of $Rh_2(5R\text{-}MEPY)_4$, MEPY = methyl 2-oxapyrrolidine-5R-carboxylate: (a) and (b) are common representations, (c) is the x-ray structure with axially-coordinated acetonitrile molecules.



SCHEME 4.
Attachment of a dirhodium carboxamidate to a polymer backbone (polystyrene-polyethylene glycol and Merrifield resins)



SCHEME 5.
Oxidation potentials for dirhodium(II) compounds

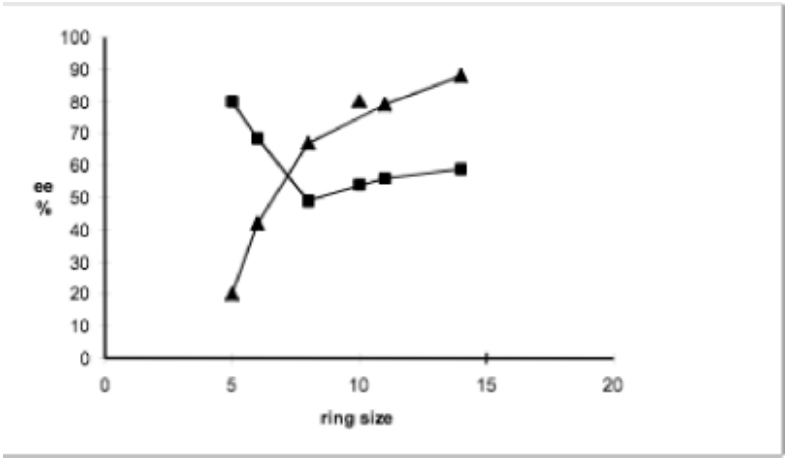
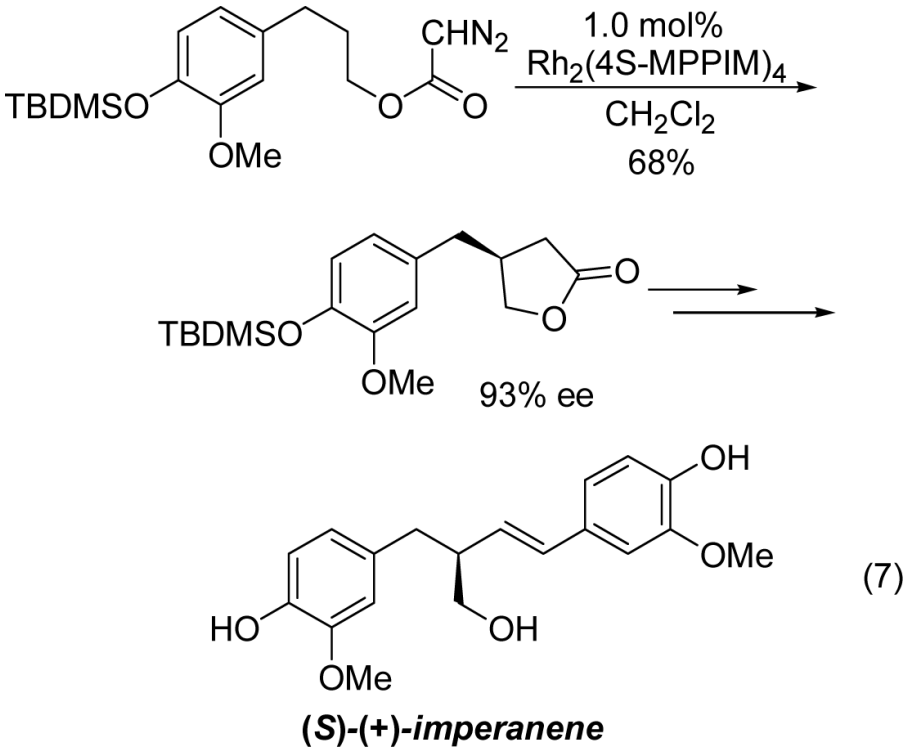
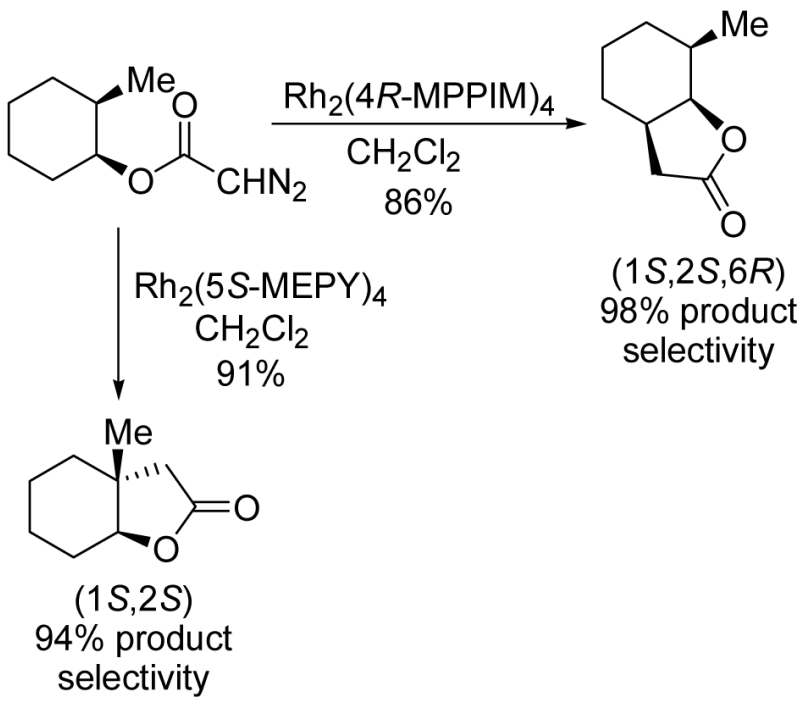


FIGURE 3.
Ring size versus %ee for reactions of with catalysts $CuPF_6$/bis-oxazoline (**1**) and Rh_2(4S-IBAZ)$_4$.



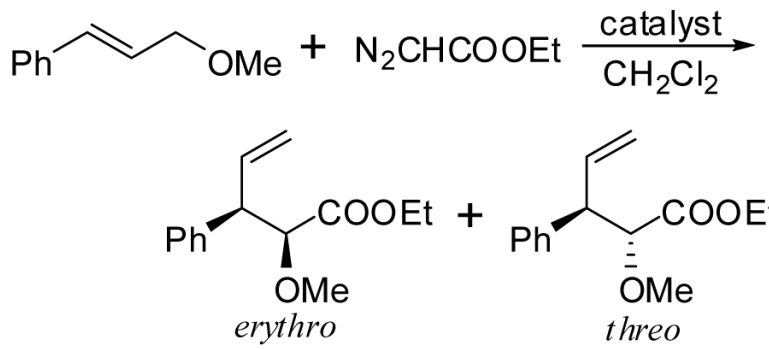
(7)

SCHEME 6.
Synthesis of *S*-(+)-imperanene via a carbon-hydrogen insertion reaction



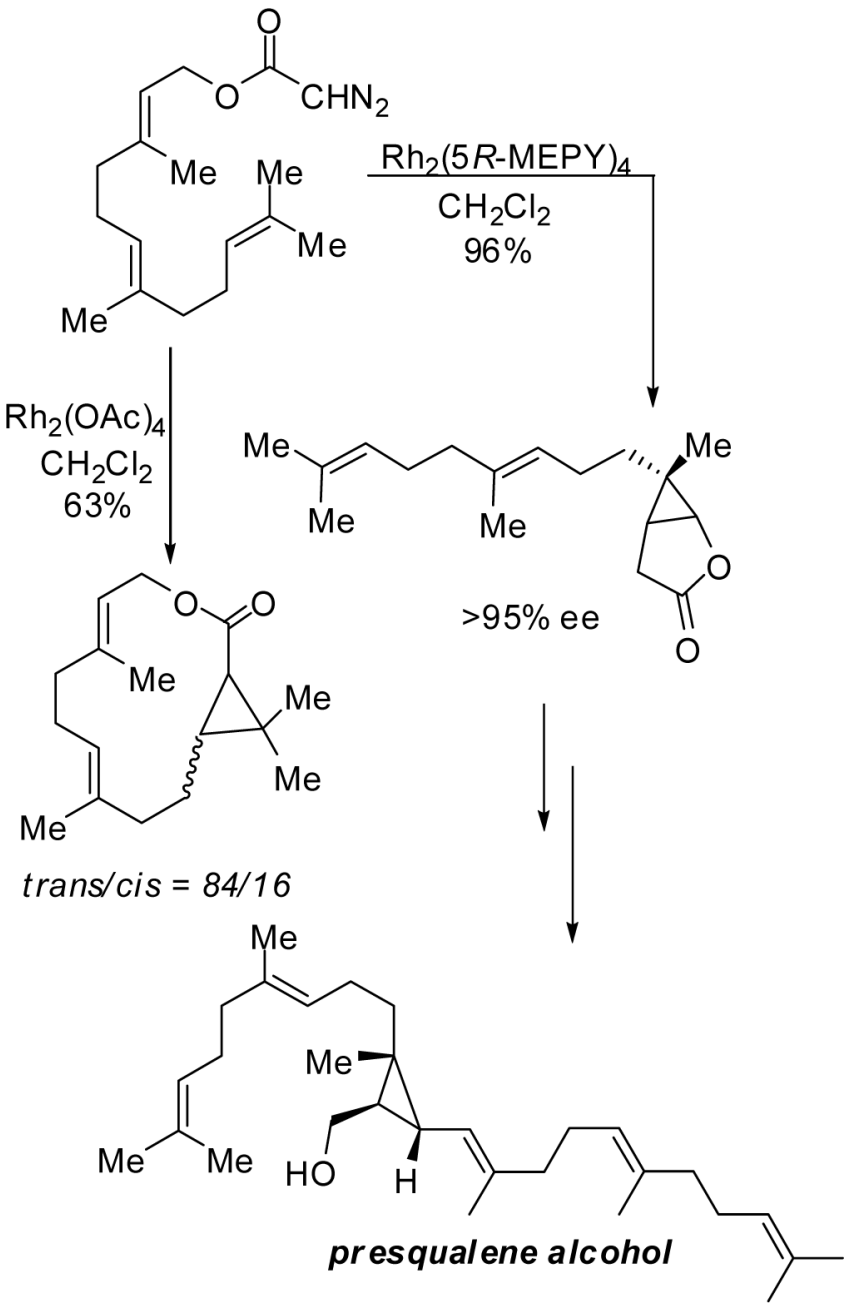
SCHEME 7.

Diastereoselectivity from match/mismatch of catalyst and substrate configurations in carbon-hydrogen insertion reactions



catalyst		
$Rh_2(OAc)_4$	83	17
$Rh_2(4S\text{-MEOX})_4$	15 (94% ee)	85 (98% ee)
$Rh_2(4R\text{-MEOX})_4$	15 (94% ee)	85 (98% ee)

SCHEME 8.
Dirhodium(II) catalysts for asymmetric oxonium ylide formation/[2,3]-sigmatropic rearrangement



SCHEME 9.
Contrast between catalysts in regioselective cyclopropanation of farnesyl diazoacetate