S-donor ligands such as SMe^-. Addition of MeI to **1**-Fe_2 produced extremely air sensitive, paramagnetic solutions, in contrast to the monomeric **1**-Ni complex, which yielded stable S-alkylated **2**-Ni.[1] The extent and sites of alkylation, iron, thiolate sulfur, or bridging sulfur, are under investigation.[4] In the presence of SPh^-, MeI cleaves the **1**-Ni_2Fe_2 dimer resulting in **2**-Ni and thiolato iron complexes, while MeI alone does not add to the complex. We are pursuing as well the intriguing possibility for heterobimetallic interactions, Fe···L···Ni, with small molecule donors and **1**-Ni_2Fe_2.

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Supplementary Material Available: Atom positional parameters for [(BME-DACO)Ni(μ-Cl)FeCl]$_2$ and [(BME-DACO)Fe]$_2$ (1 page). Ordering information is given on any current masthead page.

High Enantioselectivity in the Intramolecular Cyclopropanation of Allyl Diazoacetates Using a Novel Rhodium(II) Catalyst

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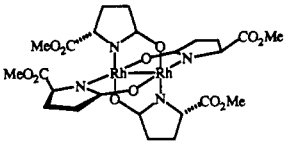
Interest in the synthesis and chemistry of the cyclopropane subunit may be attributed to a number of factors including its occurrence in natural products,[1] its biological significance,[2] its ability to function as a probe of reaction mechanisms,[3] and its utility as an intermediate in the preparation of complex molecules via vinylcyclopropane and homo-Cope rearrangements.[4] Given its important position, it is surprising that few general methods have been developed for preparing optically active cyclopropanes.[5] Although the metal-catalyzed decomposition of diazo carbonyl compounds in the presence of alkenes to give cyclopropanes is well-known in carbenoid chemistry,[6] few chiral catalysts have been designed that achieve high levels of enantioselectivity in these transformations.[7-15] Of those, only the chiral salicylaldimine copper(II) catalysts described by Aratani[7] and the chiral (semicorrinato)copper(II) catalysts designed by Pfaltz,[8] or their bisoxazoline analogues reported by Masamune,[9] appear to be capable of attaining high enantiomeric excesses in intermolecular cyclopropanations. In the course of several ongoing synthetic investigations, we required efficient access to optically pure, trisubstituted cyclopropanes. In order to address this need, we discovered a new class of catalysts for effecting enantioselective carbenoid transformations[16] whose suitability in intramolecular cyclopropanations of allylic diazoacetates is extraordinary.

The common strategic element found in approaches to designing catalysts for inducing enantioselective carbenoid transformations has consisted of attaching chiral ligands to a central metal atom.[7-15] To this end, we screened a series of dirhodium(II) amide complexes that were synthesized by ligand substitution.[17] Thus, dirhodium(II) tetrakis[methyl 2-pyrrolidone-5(*S*)-carboxylate] [Rh_2(5*S*-MEPY)$_4$ (**1**)] and dirhodium(II) tetrakis[methyl 2-pyrrolidone-5(*R*)-carboxylate] [Rh_2(5*R*-MEPY)$_4$ (**2**)] were conveniently prepared by ligand exchange with rhodium(II) acetate and the corresponding (5*S*)- or 5(*R*)-methyl pyroglutamate.[18] Like rhodium(II) acetamide[17] and rhodium(II) trifluoroacetamide,[19] these compounds possess four bridging amide ligands that are positioned so that each rhodium is sterically and electronically equivalent, and the two nitrogen donor atoms on each rhodium are in a cis arrangement.[20]



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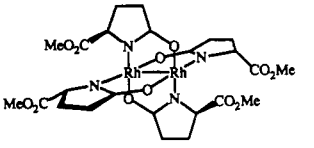

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(20) In support of this assignment, two NMR signals for the proton at the 5-position of Rh_2(MEPY)$_4$, either 5*S* or 5*R*, are observed (δ 4.35, dd, J = 8.7, 2.8 Hz and 4.05, d, J = 6.9 Hz). The methoxy resonance for Rh_2(MEPY)$_4$ consists of two singlets at δ 3.73 and 3.70. The trans isomer, which has C_2 symmetry, is expected to exhibit only one absorption for each of these protons. Further support of this assignment is provided by the ^{13}C NMR spectrum of **1**, which displays two signals for each carbon.

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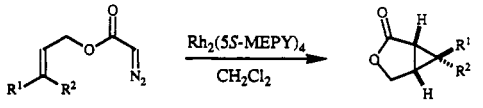
Table I. Enantioselectivity of $Rh_2(5S\text{-MEPY})_4$-Catalyzed Intramolecular Cyclopropanation Reactions

entry	3, synthetic method[a]	temp, °C	R^1	R^2	yield,[b] %	ee, %
a	A	25	H	H	74	88[c]
b	B	25	CH_3	CH_3	82	92[d]
c	A	40	H	C_6H_5	45	≥94[e,f]
d	B	25	C_6H_5	H	59	65[g]
e	A	40	H	CH_3CH_2	88	≥94[e,f]
f	B	25	$CH_3CH_2CH_2$	H	74	75[h]
g	A	40	H	$C_6H_5CH_2$	80	≥94[e,f]
h	A	40	H	c-$C_6H_{11}CH_2$	45	68[e]
i	A	40	H	$(CH_3)_2CHCH_2$	29	72[e]
j	A	40	H	$(n\text{-Bu})_3Sn$	78	≥94[e,f]

[a] Prepared from the corresponding allylic alcohols either by reaction with glyoxylic acid chloride (*p*-tolylsulfonyl)hydrazone (method A[21]) or by sequential diketene condensation, diazo transfer, and deacylation (method B[17]). [b] Isolated yield of purified (≥95% homogeneous) product. [c] $[\alpha]_D$ = +60.2° (*c* = 1.01, $CHCl_3$) relative to enantiomerically pure **4a**, $[\alpha]_D$ = +68.7° (*c* = 4.6, $CHCl_3$).[22] [d] $[\alpha]_D$ = +83.0° (*c* = 1.96 $CHCl_3$) relative to enantiomerically pure **4b**, $[\alpha]_D$ = +89.9° (*c* = 1.4, $CHCl_3$).[23] [e] Determined according to the method of Jones;[24] control experiments were executed with racemic mixtures of lactones. [f] The limit of accuracy of this NMR method based upon known mixtures of enantiomers was established to be ±1%. The limit of detection is generally accepted to be ±3%; therefore, % ee is denoted as ≥94% when only one enantiomer was detected.[24] [g] Determined by GLC separation of diastereomeric *l*-menthyl esters on a methylsilicone capillary column; a control experiment using racemic **4d** verified the absence of kinetic diastereoselection in ester formation. [h] Determined by GLC separation of diastereomeric (*S*)-(−)-1-phenylbut-1-yl esters on a Carbowax capillary column; a control experiment using racemic **4f** verified the absence of kinetic diastereoselection in ester formation.

The remarkable utility of these catalysts for effecting enantioselective intramolecular cyclopropanations was demonstrated in preliminary experiments with a series of allylic diazoacetates **3a–j** (Table I). Thus, slow addition (12–14 h) of **3a–j** to a solution of $Rh_2(5S\text{-MEPY})_4$ catalyst (1.0 mol %) in anhydrous CH_2Cl_2 delivered the corresponding 3-oxabicyclo[3.1.0]hexan-2-ones **4a–j** with very good to excellent enantioselectivities (65 to ≥94%). The absolute configuration of the lactones **4a–j** was assigned on the basis of comparison of the signs of rotation of the known cyclopropyl lactones **4a** and **4b**. Moreover, the structure of the (−)-menthyl ester of a derivative of lactone **4c** was established by single-crystal X-ray analysis.[25] The major competing reaction that accounted for the lower yields was the formation of carbene dimers. Examination of entries c–f reveals that intramolecular cyclopropanations of *Z* olefins proceeded with greater levels of enantioselectivity than the corresponding reactions of *E* isomers. The generality of this novel method for asymmetric synthesis of cyclopropanes was further enhanced by the fact that the readily available, enantiomeric $Rh_2(5R\text{-MEPY})_4$ catalyst **2** induced the intramolecular carbene additions of **3c,e,g–i** to give the enantiomers of **4c,e,g–i** with virtually identical efficiencies.



3a-j **4a-j**

In an attempt to increase the enantioselectivity of these processes, we replaced the methyl esters of **1** with isopropyl esters. However, no improvement for the cyclization of **3b** to give **4b** (89% ee, 83% yield) was observed when this catalyst was used. In preliminary experiments, we have also evaluated other chiral rhodium(II) catalysts having oxazolidinone ligands,[26] but these were found to be inferior to **1** and **2**.

Thus, rhodium(II) catalysts **1** and **2** offer unique advantages for enantioselective intramolecular cyclopropanations, since both enantiomers of a cyclopropyl lactone may be efficiently prepared with high enantioselectivity from a single allylic diazo ester. Studies are in progress to determine the scope and limitations of these catalysts to effect enantioselective cyclizations of other unsaturated systems as well as catalysis in other carbenoid transformations.

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Synthesis and Structural Characterization of Eight-Coordinate Geometrical Isomers of $[ReH_2(mhp)_2(PPh_3)_2]PF_6$ That Retain Their Structural Identity in Solution

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While the stabilization of geometric isomers of eight-coordinate complexes has been known to be possible in the solid state, the only examples of structurally characterized isomeric pairs are the lanthanide complexes *cis*- and *trans*-$SmI_2[O(CH_2CH_2OMe)_2]_2$,[1] and the two dodecahedral isomeric forms of $V(S_2CCH_3)_4$ that are present in single crystals of this complex.[2] In neither system is there evidence that the isomers retain a separate and distinct identity in solution.[3] Indeed, the preparation and characterization of such isomers *in solution* has generally been considered to be "difficult, if not impossible".[4] However, it has been recognized through the elegant studies of Archer and Donahue[5] on tungsten(IV) complexes with four bidentate or two tetradentate donors that, in some instances, eight-coordinate geometrical isomers can be separated and that such stereoisomers can be stereochemically rigid. Unfortunately, in none of these cases was it possible to assign a specific structure to any isomer although dodecahedral geom-

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