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Monomeric Rhodium(II) Catalysts for the Preparation of Aziridines and Enantioselective Formation of Cyclopropanes from Ethyl Diazoacetate at Room Temperature

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A family of bis(oxazoline) complexes of coordinatively unsaturated monomeric rhodium(II) (**2a**,**b**, **3a**,**b**) are described. These complexes serve as catalysts for cyclopropanation of olefins by ethyl diazoacetate, giving excellent yields (66−94%). Enantioselectivities for the cis product isomers are good (61−84%). The reaction shows an unusual preference for formation of the cis isomers. Catalytic aziridination of *N*-aryl imines with ethyl diazoacetate is also described.

Introduction

Three-membered ring compounds—particularly epoxides, cyclopropanes, and aziridines—are prevalent structures in biologically active molecules and valuable synthetic intermediates.[1,2] In the latter context, they are particularly attractive for generating useful optically active products from relatively simple starting materials. While the technologies for catalytic asymmetric synthesis of epoxides are highly advanced, the catalytic synthesis of cyclopropanes is a somewhat less developed field. The most common catalytic method of obtaining cyclopropanes involves transfer of a carbene moiety from a diazocarbonyl compound to an olefin. Although cyclopropanes can often be obtained in high yields and with excellent stereoselectivities with this technique, some challenges remain.[3−6] Essentially complete stereocontrol has been achieved in the intramolecular variants of this reaction, but intermolecular cyclopropanation reactions are more difficult to achieve with high levels of both diastereo- and enantioselection.[6,7] The most pronounced control problem in the intermolecular reaction is the tendency to form the thermodynamically favored trans isomers of the product cyclopropanes. This feature is particularly pronounced when the convenient, commercially available compound ethyl diazoacetate is used as the carbene source. Although it is relatively easy to find catalysts (particularly those based on Cu(I) or Ru(II)[8−12]) that form trans cyclopropanes in high yields and enantioselectivities with ethyl diazoacetate, catalysts that preferentially afford the cis isomers remain quite rare.[13−21]

Compared to epoxides and cyclopropanes, the synthesis of aziridines by catalytic asymmetric techniques is a very difficult challenge.[2,22,23] While several catalytic systems have been developed for the asymmetric transfer of nitrene fragments to olefins,[2] only scattered reports have demonstrated significant enantiocontrol in the complementary reaction, carbene transfer to imines.[24−29] This latter method represents an attractive complement to the nitrene transfer catalysis, as it involves readily accessible

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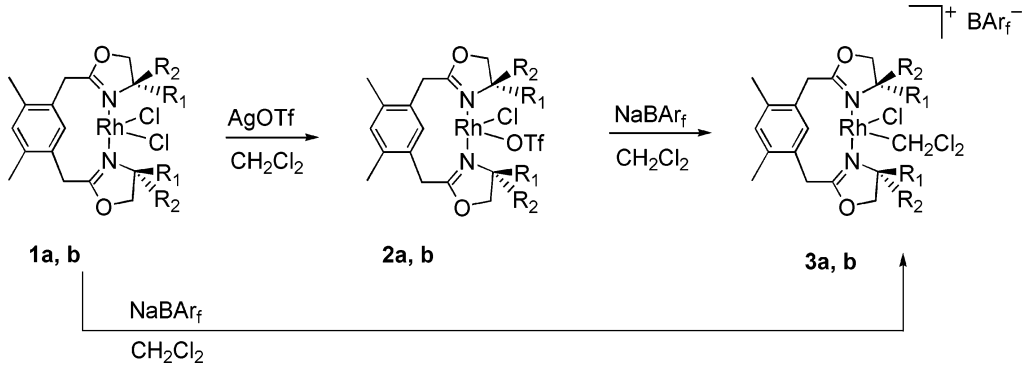
SCHEME 1. Synthesis of Unsaturated Rhodium(II) Complexes

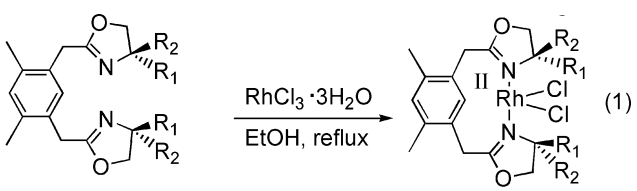


compounds (imines and diazocarbonyl compounds) and features dinitrogen as the sole reaction byproduct.

Carbene transfer reactions have been traditionally best catalyzed by one of two major catalyst types: dimeric complexes of Rh(II) or monomeric complexes of transition metals with C_2-symmetric ligands. Dimeric Rh(II) complexes have been shown to catalyze a variety of carbene transfer reactions, including cyclopropanation, aziridination, epoxidation, and C−H insertion. In many of these reactions, a chiral bridging ligand is used, giving modest to excellent enantioselectivities.[5,6] In contrast, the most successful monomeric transition metal catalysts for carbene transfer are Cu(I) and Ru(II) complexes of C_2-symmetric ligands, particularly bis(oxazolines).[5,6] The approach to carbene transfer catalysis described here involves a blend of the two chief catalyst structures: we have employed bis(oxazoline) ligands with monomeric Rh(II) metal centers, and applied these catalysts to the asymmetric synthesis of cyclopropanes by carbene transfer to alkenes. Additionally, catalytic synthesis of aziridines by carbene transfer to imines is described.

Results and Discussion

We recently reported the synthesis and characterization of rhodium(III) and rhodium(II) complexes based on a series of new benzyl bis(oxazoline) (benbox) ligands.[30,31] This class of ligands is related to the well-known phebox (phebox = bis(oxazolyl)phenyl) ligands by benzylic homologation. Preliminary molecular mechanics modeling suggested that homologation of phebox would widen the ligand's N−M−N bite-angle. We predicted this modification would draw the oxazolyl alkyl groups closer to the metal center, providing a sterically congested chiral environment. Surprisingly, when the most sterically congested benbox ligands were treated with $RhCl_3(H_2O)_3$, monomeric Rh(II) complexes (**1a**,**b**) were cleanly isolated in addition to the expected Rh(III) products (eq 1).



(1)

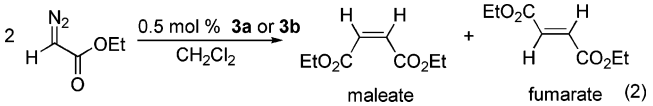
a-series: R_1 = ^{t}Bu, R_2 = H;
b-series: R_1, R_2 = Me

Compounds **1a**,**b** result from a failure of the ligand aryl ring to undergo cyclometalation, and hence they contain a bidentate ligand with an unusual nine-membered chelate ring.[32] Most known chemistry of rhodium is carried out on the Rh(I) and Rh(III) oxidation states. Although many Rh(II) dimers have been characterized, far fewer monomeric Rh(II) complexes have been isolated, and these complexes are generally quite air-sensitive.[33,34] Surprisingly, although they are formally 15-electron complexes, **1a**,**b** were isolated by column chromatography and found to be bench-stable for weeks. The remarkable air-stability of complexes **1a**,**b** is likely due to the steric shielding properties of the new benbox ligands.

Coordinatively Unsaturated Rh(II) Complexes. Catalytically active rhodium species were obtained by substituting a triflate or dichloromethane ligand for one of the apical chlorides of **1a**,**b**. The dichloride complexes **1a**,**b** were treated with AgOTf to give the chlorotriflato complexes **2a**,**b** (Scheme 1).

The dichloromethane adducts **3a**,**b** were obtained by treatment of either **1a**,**b** or **2a**,**b** with $NaBAr_f$ (BAr_f = tetrakis(3,5-(trifluoromethyl)phenyl)borate) in dichloromethane. An ORTEP diagram of **3a** is depicted in Figure 1. The apical dichloromethane ligand of **3a** was found to be highly disordered in the crystal structure. The structure of **3a** reveals the coordinative unsaturation of these monomeric rhodium(II) species—no unusually close intermolecular contacts were observed in the crystal structure, indicating that the compound is monomeric in the solid state. Furthermore, dissociation of the dichloromethane ligand of **3a** should be facile, suggesting that the BAr_f salts **3a**,**b** are good candidates for catalysis.

To test for possible activity in carbene transfer reactions, the catalysts were treated with ethyl diazoacetate. Addition of ethyl diazoacetate to a methylene chloride solution of **3a** or **3b** resulted in rapid formation ($t_{1/2}$ < 5 min) of the olefins diethyl maleate and diethyl fumarate (eq 2). The reactions proceeded stereoselectively, giving



(2)

an 84:26 ratio of maleate to fumarate with **3a** and a 75:

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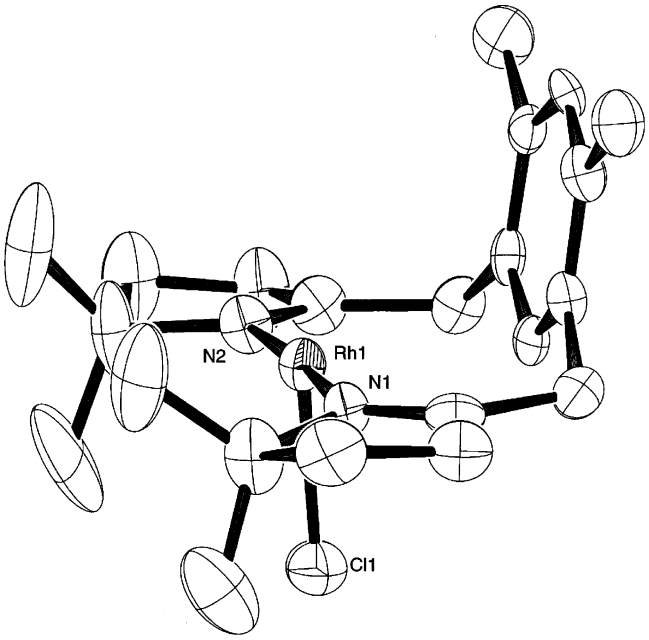
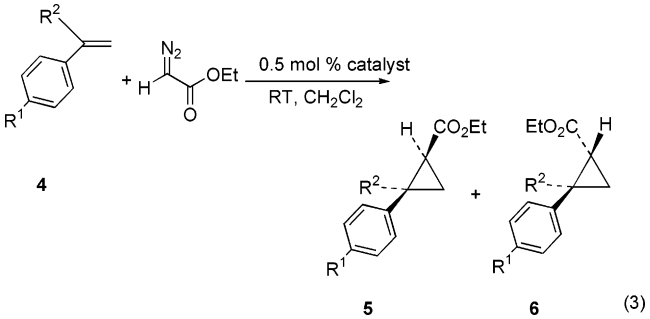


FIGURE 1. ORTEP drawing of **3b**. The BAr_f anion and methylene chloride ligand (disordered) are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Representative bond lengths (Å) and angles (deg): Rh(1)−Cl(1), 2.286(3); Rh(1)−N(1), 2.061(8); Rh(1)−N(2), 2.059(9); N(1)−Rh(1)−Cl(1), 90.9(2); N(2)−Rh(1)−Cl(1), 88.4(3); N(1)−Rh(1)−N(2), 176.1(4).

25 ratio of maleate to fumarate with **3b**. The observation of carbene dimerization suggested that metal−carbene moieties are formed in the presence of the monomeric Rh(II) catalysts. Furthermore, the selectivity observed in the formation of the olefin products indicated that stereoselectivity might be observed in carbene transfer reactions involving these catalysts.

Cyclopropanation of Olefins. The reaction of ethyl diazoacetate (EDA) with styrene is a classic transformation for which catalyst effectiveness in carbene transfer chemistry is often evaluated.[6,20] Addition of 1 mmol of EDA to room temperature solutions of **2a**,**b** or **3a**,**b** (0.005 mmol) and various substituted styrenes (**4a**−**e**, 5 mmol) resulted in the formation of the cis and trans cyclopropanes **5** and **6** (eq 3, Table 1).



(3)

Ethyl diazoacetate was delivered as a dilute solution by syringe pump to minimize the formation of maleate and fumarate relative to the desired cyclopropane products. Products were identified by GC and ^{1}H NMR, and yields were obtained by isolation of the products or by integration of peaks in the GC traces relative to that of an internal standard. For the products isolated by column chromatography, isolated yields were comparable to those obtained by GC.

TABLE 1. Cyclopropanation Reactions Catalyzed by 2a,b and 3a,b

entry	catalyst	olefin	R^1	R^2	yield, % (**5** + **6**)	cis:trans (**5**:**6**)	ee, % cis/trans[c]
1	**1a**	**4a**	H	H	<1[a]		
2	**1b**	**4a**	H	H	<1[a]		
3	**2a**	**4a**	H	H	5[a]		
4	**2b**	**4a**	H	H	19[a]	55:45	
5	**3a**	**4a**	H	H	87[b]	63:37	74/47
6	**3a**	**4b**	CH_3	H	94[b]	65:35	84
7	**3a**	**4c**	Cl	H	94[a]	64:38	73/46
8	**3a**	**4d**	CF_3	H	83[a]	66:34	80/35
9	**3a**	**4e**	H	CH_3	85[b]	60:40	61/74
10	**3b**	**4a**	H	H	66[b]	52:48	
11	**3b**	**4b**	CH_3	H	72[b]	57:43	
12	**3b**	**4c**	Cl	H	77[a]	46:54	
13	**3b**	**4d**	CF_3	H	67[a]	66:34	
14	**3b**	**4e**	H	CH_3	66[b]	59:41	

[a] Determined by integration (vs internal standard) of GC traces. [b] Combined isolated yields: products isolated by column chromatography. [c] Determined by GC on G-TA chiral column, compared to racemic product prepared with catalyst **3b**.

Although the triflato catalysts **2a**,**b** mediate the cyclopropanation reactions (Table 1, entries 3 and 4), the BAr_f catalysts **3a**,**b** provide higher yields (entries 5−14). It is clear that an accessible coordination site is required for catalysis, as **1a**,**b** were found to be ineffective catalysts for the cyclopropanation reaction (entries 1 and 2). The greater efficacy of **3a**,**b** relative to **2a**,**b** is likely due to the higher lability of the methylene chloride ligand relative to the triflate ligand. Other carbene sources were screened, including phenyl diazoacetate,[35,36] *tert*-butyl diazoacetate, and (trimethylsilyl)diazomethane. These reagents were found to be completely unreactive for carbene transfer with catalysts **2** and **3**. These alternative carbene sources did not appear to react with **2** or **3** at all in preliminary screening studies (no evidence of N_2 evolution or carbene consumption was observed). These results are presumably due to the steric shielding of catalysts **2** and **3**.

Product yields and enantioselectivities for the cyclopropanation reactions catalyzed by **3a**,**b** are uniformly high and comparable to results obtained for the cyclopropanation of styrene by EDA with dimeric Rh(II) catalysts.[20] In analogy to the findings of Doyle and coworkers, the enantioselectivities for the cis cyclopropanes generated by **3a** are higher than the enantioselectivities for the trans isomers.[4] Importantly, the use of either **3a** or **3b** for the cyclopropanation reaction results in preferential formation of the cis cyclopropane, **5**, over the thermodynamically preferred trans isomer, **6**. Furthermore, these results were obtained with catalyst loadings of **3a** or **3b** of only 0.5 mol %.

The vast majority of reported catalysts for cyclopropanation of olefins of the styrene type favor formation of the thermodynamically favored trans isomers, **6**. Rela-

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tively few systems have been reported that favor formation of the cis isomers, **5**, with good enantioselectivities.[19,21] Doyle has reported a family of chiral dimeric rhodium(II) catalysts that demonstrate modest cis selectivity in cyclopropanation of styrene (≤69:31 cis:trans).[5,6,18,20] The isolated yields of the styrene cyclopropanation product (**5a** + **6a**) in Doyle's system are good (62−74%), although not as high as the yield afforded by **3a** (87%).[18,20] The enantioselectivities of Doyle's cis-selective catalysts are comparable to those afforded by **3a**, although those catalysts were applied to a less broad range of substrates.[18,20] Importantly, while Doyle's dimeric systems involve syringe pump addition of the diazoacetate to refluxing dichloromethane solutions of olefin, catalysts **3a** and **3b** react readily at room temperature, offering a practical advantage.

In addition to the advantages described above, the catalysis of cyclopropanation by the monomeric Rh(II) complexes **2** and **3** represents a significant conceptual advance. Although dimeric Rh(II) complexes have been shown to be versatile catalysts for carbene transfer, relatively little is known about the metal-containing intermediates in these reactions.[37,38] It is generally assumed that the thermodynamically stable Rh(II) dimer stays intact, but no conclusive studies have demonstrated this point. Furthermore, no studies have conclusively ruled out the possibility of synergistic effects between the two rhodium(II) centers (e.g., the formation of bridging carbene moieties). This work represents the first demonstration that cyclopropanation can be accomplished by a monomeric Rh(II) complex.[39,40]

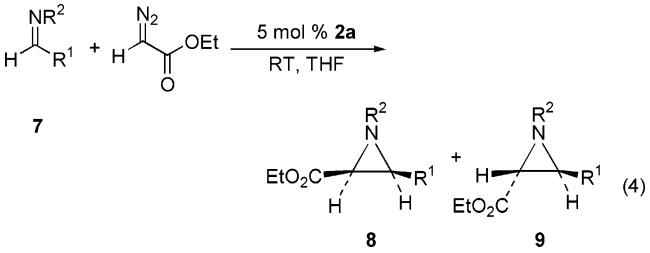
Aziridination of Imines. Reliable methods for the addition of carbenes to imines to form aziridines are much less common than reactions of carbene precursors with olefins to form cyclopropanes.[2] As aziridines are valuable synthetic intermediates, the general lack of reliable catalytic methodologies for their asymmetric synthesis represents an important area for development.[23] For asymmetric reactions, only two classes of imine substrates have been shown to be excellent substrates for carbene addition: activated imines with *N*-heteroatom bonds[25,29] (such as *N*-tosyl imines) and *N*-benzyl imines.[26,28] In contrast to *N*-activated and *N*-benzyl imines, the direct asymmetric synthesis of simple *N*-aryl and *N*-alkyl aziridines from the corresponding imines remains a difficult problem. In 1995 Jacobsen and co-workers used carbene transfer to synthesize *N*-aryl aziridines in 10−65% yield with modest enantioselectivities (22−67%) using a copper bis(oxazoline) catalyst.[24] Good yields and diastereoselectivties have been obtained in the Lewis acid-catalyzed racemic syntheses of *N*-aryl aziridines reported by Brookhart, Templeton, Jorgensen, and others.[41−48]

TABLE 2. Imine Aziridination Reactions Catalyzed by 2a

entry	imine	R^1	R^2	solvent	yield, %	cis:trans (**8**:**9**)
1	**7a**	C_6H_5	C_6H_5	THF	73,[a] 46[b]	75:25
2	**7b**	*p*-$H_3CC_6H_4$	C_6H_5	THF	60,[a] 43[b]	58:42
3	**7c**	C_6H_5	*p*-$H_3CC_6H_4$	THF	47[b]	73:27
4	**7d**	^{t}Bu	C_6H_5	THF	40[b]	70:30
5	**7e**	C_6H_5	$CH_2C_6H_5$	THF	12[b]	86:14
6	**7f**	*p*-ClC_6H_4	*p*-$H_3CC_6H_4$	THF	43[b]	71:29
7	**7g**	*p*-$NO_2C_6H_4$	C_6H_5	THF	29[b]	90:10
8	**7a**	C_6H_5	C_6H_5	CD_2Cl_2	36[b]	69:31
9	**7b**	*p*-$H_3CC_6H_4$	C_6H_5	CD_2Cl_2	18[b]	75:25
10	**7c**	C_6H_5	*p*-$H_3CC_6H_4$	CD_2Cl_2	10[b]	87:13

[a] Combined isolated yields: products purified by column chromatography. [b] Determined by integration (vs internal standard) of well-resolved peaks in the ^{1}H NMR.

Addition of EDA to a THF solution of **2a** and *N*-phenylbenzaldimine (**7a**) results in formation of the corresponding aziridines, **8a** and **9a** (eq 4) (Table 2, entry 1).



(4)

The reaction proceeds selectively, giving a 3:1 ratio of the cis-to-trans diastereomers. The diastereoselectivity and isolated yield of aziridine are comparable to those afforded by Jacobsen's system, although the enantioselectivities are poor (≤11%). As Jacobsen observed for this class of substrates, product yields erode upon substitution of the *N*-aryl group, although diastereoselectivities remain good (Table 2, entries 2−7). Catalyst **2b** is inactive for this reaction, and catalysts **3a** and **3b** gave only the olefin products of carbene dimerization. For all substrates, the reaction proceeds in higher yield in THF than in CH_2Cl_2. Interestingly, catalyst **2a** provides good yields without the use of syringe pump techniques. This is a difference in reactivity from the cyclopropanation reaction, and from several previously reported asymmetric imine aziridination protocols.

Conclusion

In conclusion, it was found that the monomeric Rh(II) catalysts **2a**,**b** and **3a**,**b** perform carbene transfer reactions. The catalysts are easy to prepare, store, and use. Complex **3a** is an excellent catalyst for asymmetric

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cyclopropanation of styrenes and α-methylstyrene, giving high yields and enantioselectivities, as well as an unusual selectivity for formation of the cis isomers of these compounds at very low catalyst loadings of 0.5 mol %. Furthermore, the catalysts offer a practical advantage in that they allow for operation at room temperature. Finally, it was found that complex **2a** catalyzes the aziridination of imines with good diastereoselectivity, albeit with poor enantioselectivity. Importantly, the cyclopropanation and aziridination reactions catalyzed by **2a**,**b** and **3a**,**b** show definitively that carbene transfer can be catalyzed by a paramagnetic monomeric rhodium(II) complex.

Experimental Section

Synthesis of [RhCl(OTf){benbox(Me$_2$)H}] (2a, 2b). To a yellow solution of [RhCl$_2${benbox(Me$_2$)H}] (**1**) (0.10 mmol) in methylene chloride (5 mL) at ambient temperature was added AgOTf (25.7 mg, 0.10 mmol) producing a yellow suspension. After being stirred overnight the suspension was filtered. The solvent was removed in vacuo, leaving an orange-yellow microcrystalline solid. Complexes **2a**,**b** can be recrystallized from benzene/pentane at room temperature.

[RhCl(OTf){(*S*,*S*)-tb-benbox(Me$_2$)H}] (2a). Yield: 65 mg, 97%. Mp: 152−154 °C dec. Anal. Calcd for $C_{25}H_{36}ClF_3N_2O_5RhS$: C, 44.68; H, 5.40; N, 4.17. Found: C, 44.92; H, 5.58; N, 3.90. IR (KBr, cm^{-1}): 1642, 1630 (ν(CN)). ^{1}H NMR (300 MHz, C_6D_6): δ 19.0, 18.6, 10.7, 9.6, −38.6. ^{19}F NMR (376.1 MHz, C_6D_6): δ −75.0. EI-MS (*m*/*z*): 670 [M − H]$^+$, 635 [M − HCl]$^+$, 521 [M − HOTf], 485 [M − HOTf − HCl]$^+$.

[RhCl(OTf){dm-benbox(Me$_2$)H}] (2b). Yield: 59 mg, 96%. Mp: 148−150 °C dec. Anal. Calcd for $C_{21}H_{28}ClF_3N_2O_5RhS$: C, 40.95; H, 4.58; N, 4.55. Found: C, 40.56; H, 4.68; N, 4.40. IR (KBr, cm^{-1}): 1643, 1632 (ν(CN)). ^{1}H NMR (300 MHz, C_6D_6): δ 19.8, 15.5, 9.8, −35.1. ^{19}F NMR (376.1 MHz, C_6D_6): δ −75.0. EI-MS (*m*/*z*): 479 [M − HCl]$^+$, 465 [M − HOTf], 430 [M − OTf − HCl]$^+$.

Isolation of Crystalline [RhCl(CH$_2$Cl$_2$){dm-benbox(Me$_2$)H}]BAr$_f$ (3b). To a yellow solution of [RhCl(OTf){dm-benbox(Me$_2$)H}] (**2b**) (12.8 mg, 25 mmol) in methylene chloride (2 mL) at ambient temperature was added a methylene chloride solution of NaBAr$_f$ (27 mg, 30 mmol) producing a dark orange suspension. After the solution was stirred for 1 h, precipitation of NaOTf was observed, and the suspension was filtered. Elemental analyses and NMR data indicate that in the absence of a good trapping ligand (e.g. styrene) **3a**,**b** are both thermally sensitive and unstable to vacuum. Hence, these compounds were used in situ without further characterization. However, **3b** was recrystallized from a concentrated dichloromethane/pentane solution at −30 °C to give a small quantity of X-ray quality crystals.

X-ray Structure Data for 3b. The X-ray crystal structure was determined by Drs. Fred Hollander and Allan Oliver at the UCB X-ray facility (CHEXRAY). The crystal was mounted on a glass fiber with Paratone N hydrocarbon oil. Measurements were made on a SMART CCD area detector with graphite monochromated Mo Kα radiation (λ = 0.71069 Å). The data were collected with a detector position of 60.00 mm. Data were integrated by the program SAINT, and were corrected for Lorentz and polarization effects. Data were analyzed for agreement and possible absorption with XPREP. The structures were solved by direct methods and expanded with Fourier techniques. The data were collected with use of 10-s frames with an ω scan of 0.3°. Empirical absorption corrections based on comparison of redundant and equivalent reflections were applied by using SADABS (T_{max} = 0.91, T_{min} = 0.80). The maximum peak in the final difference map was 1.99 e$^-$/Å^3, and the minimum peak was −0.96 e$^-$/Å^3.

Catalytic Cyclopropanation Reactions. A mixture of **2a** or **2b** (0.0050 mmol) and NaBAr$_f$ (4.5 mg, 0.0050 mmol) was stirred in dry CH_2Cl_2 (5 mL) in a glovebox for 2 h. The resulting solution of **3a** or **3b** was filtered, and the olefin (5.0 mmol) was added. The reaction flask was fitted with a septum and brought out to the benchtop. A CH_2Cl_2 solution (9 mL) of ethyl diazoacetate (105 μL, 1.0 mmol) was added to the reaction mixture via syringe pump over the course of 9 h. The reaction mixture was stirred for an additional 8 h, then the volatile materials were removed from the reaction mixture by rotary evaporation. The pure cyclopropanation products **5a**−**e** and **6a**−**e** were obtained by chormatographing the residual oil (silica gel, 5% ethyl acetate in hexane). ^{1}H NMR data for products **5a**−**e** and **6a**−**e** were compared to reported literature shifts for these compounds.[49] The enantiomeric excesses (ee) of **5a**−**e** and **6a**−**e** prepared with catalyst **3a** were determined by chiral capillary GC on a G-TA (Chiraldex) column. Enantioenriched samples were compared to racemic samples generated by catalyst **3b**.

Catalytic Aziridination of 7a and 7b. In the glovebox, catalyst **2a** (79 mg, 0.12 mmol), imine (430 mg, 2.3 mmol), and ethyl diazoacetate (300 μL, 2.8 mmol) were dissolved in THF (5 mL) in a glass vial equipped with a Teflon-coated stirbar. The vial was capped and the reaction mixture was stirred at room temperature for 8 h. The reaction vessel was uncapped occasionally (roughly once every 2 h) to prevent the buildup of a significant overpressure of nitrogen. After 8 h of stirring, the vial was brought out of the box and the reaction mixture was immediatedly chromatographed on silica gel (gradient elution: hexane → 2% ethyl acetate in hexane → 4% ethyl acetate in hexane). Product identities were confirmed by GC/MS, and by comparing ^{1}H NMR resonances to those reported in the literature.[24,41] For determination of the ee values of products prepared with **2a**, racemic aziridines **8a**,**b** and **9a**,**b** were prepared with TiCl$_4$(THF)$_2$ and purified by silica gel chromatography (conditions described above). For **8a**, the ee was determined by addition of Eu(hfc)$_3$ to an NMR sample (C_6D_6) of isolated product and compared to authentic racemic product. For **8b**, **9a**, and **9b**, ee values were determined by chiral HPLC (Chiraldex OD column: 0.7 mL/min, 10% isopropyl alcohol in hexane) of isolated product compared to isolated racemic samples. Representative data for the previously reported compounds **8a**, **9a**, **8b**, and **9b** are presented in the Supporting Information.

Catalytic Aziridination of 7c−7g. In the glovebox **2a** (4.0 mg, 0.0060 mmol), imine (0.12 mmol), and hexamethylbenzene (4.0 mg, 0.025 mmol) were dissolved in 300 μL of d_8-THF. An initial ^{1}H NMR spectrum was taken. To this mixture was added ethyl diazoacetate (15 μL, 0.14 mmol) by syringe. The NMR tube was flame sealed under vacuum and the reaction progress was monitored by ^{1}H NMR. The reaction was halted after 8 h, at which point product yields were determined by ^{1}H NMR integration of the aziridine ring protons versus internal standard. All products were identified in the crude reaction mixtures by GC/MS and ^{1}H NMR. The ^{1}H NMR data for products **8d**, **9d**, **8e**, **9e**, **8f**, **9f**, **8g**, and **9g** were compared to literature values for these compounds.[24,41,47] Authentic samples of products **8c** and **9c** were independently prepared and isolated by using the procedure described by Brookhart and co-workers for analogous compounds, and are described in the Supporting Information.[41]

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Supporting Information Available: General experimental notes, analytical data for **8a**−**c** and **9a**−**c**, and X-ray structure data for **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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