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# Highly *cis*-Selective Rh(I)-Catalyzed Cyclopropanation Reactions

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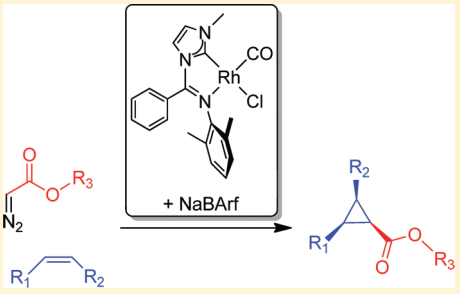
Supporting Information

**ABSTRACT:** The performance of recently reported highly *cis*-diastereoselective Rh(I) cyclopropanation catalysts has been significantly improved by a systematic study of different reaction parameters (catalyst activation, solvent, temperature, stoichiometry). The catalyst efficiency and diastereoselectivity were enhanced by changing the activating agent from AgOTf to NaBArf. With this new system, the Rh(I) catalyst was shown to be a highly efficient and *cis*-diastereoselective cyclopropanation catalyst in reactions between α-diazoacetates and a range of different alkenes and substituted derivatives. Particularly noteworthy is the remarkable reactivity and *cis*-diastereoselectivity displayed in the reactions between ethyl diazoacetate and cyclopentene, 2,5-dihydrofuran, and benzofuran, with yields up to 99% and *cis*-selectivities greater than 99%.




## INTRODUCTION

Cyclopropanes are highly interesting compounds, from both a biological and synthetic point of view. They are versatile molecules with numerous potential applications in organic synthesis.[1−3] Cyclopropanes are important substructures in many synthetic and naturally occurring biologically active compounds.[4−6] Reported biological activities include enzyme inhibition, antimicrobial, antibiotic, antitumor, and antiviral activities.[5] The most common catalytic method for generating cyclopropanes involves transfer of a carbene moiety from a diazocarbonyl compound to an olefin. In such a reaction, up to three new stereocenters can be formed. A challenge in intermolecular cyclopropanation reactions can be to achieve good diastereoselectivities, and preferably with simple, readily available diazo compounds such as ethyl diazoacetate (EDA). Consequently, great effort has been invested in developing methods and catalysts that are highly diastereoselective. There are quite a few reports on catalysts that are very efficient and highly selective for the formation of the thermodynamically favored *trans* isomer.[7−9] On the other hand, high diastereoselectivity and good yields in the formation of the unfavored *cis* isomer remain a greater challenge. There are few reports on highly *cis*-selective cyclopropanations.[9−14] Among the reported *cis*-selective catalysts is a Cu(I) homoscorpionate catalyst that gives very good yields and high *cis*-selectivities in the cyclopropanation reaction between EDA and styrene.[15] Mezzetti and co-workers have shown that some Ru-salen[16−20] complexes display very high *cis*-selectivities with EDA. Co-salen complexes have also been reported to give high *cis*-selectivitites using EDA[21] and *tert*-butyl diazoacetate,[10] and Ir-salen[22,23] complexes give high reactivity and *cis*-selectivities using *tert*-butyl diazoacetate.

Rh(II) carboxylates constitute one of the most extensively used classes of catalysts in cyclopropanation reactions.[8,9,24] While they are known to give excellent diastereoselectivities with bulkier or more substituted diazo compounds, there are not many examples of good diastereoselectivities using EDA as the diazo compound. There are only a few examples of highly *trans*-selective catalysts, and we have encountered only a couple of examples of Rh(II) carboxylate based catalysts that give good *cis*-selectivities in the cyclopropanation of styrene,[9,25−27] the best selectivity being 90:10. We recently reported the preparation of Rh(I) catalyst **1** with a chelating imine-functionalized N-heterocyclic carbene (NHC) ligand. Following activation with silver triflate (AgOTf), this catalyst was reported to display a remarkable high reactivity and *cis*-selectivity in the cyclopropanation reaction between EDA and styrene (Scheme 1).[28] These are among the highest *cis*-selectivities reported in this reaction and the highest *cis*-selectivity ever reported with a Rh catalyst. We here report a more detailed study of recent developments of this very promising catalytic system. The effects of changing different experimental parameters (catalyst activation,

**Scheme 1. Highly *cis*-Selective Cyclopropanation Reaction with Rh(I) Catalyst 1**[28]

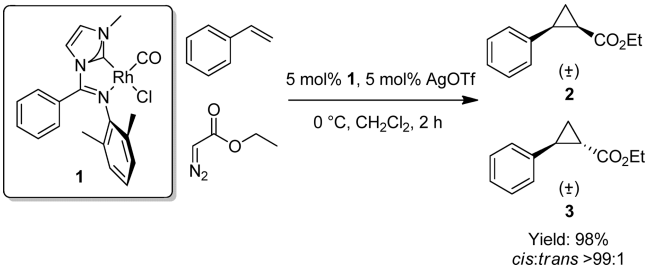



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**Table 1. Cyclopropanation Reaction between Styrene and EDA Catalyzed by 1 with AgOTf as the Activating Agent[a]**

| entry | catalyst loading (mol %) rel to EDA | equiv of styrene rel to EDA | AgOTf (mol %) | reaction time (h) | yield[b] (%) | *cis*:*trans*[c] |
|---|---|---|---|---|---|---|
| 1 | 5 | 5 | 5 | 2 | 98 | >99:1 |
| 2 | 2.5 | 5 | 2.5 | 3 | 89 | 94:6 |
| 3 | 1 | 5 | 1 | 48 | 50 | 92:8 |
| 4 | 5 | 2.5 | 5 | 24 | 47 | 95:5 |

[a] Reaction conditions: 1.00 mmol of EDA and given quantities of **1**, AgOTf, and styrene in 20 mL of $CH_2Cl_2$ at 0 °C. [b] Isolated yield based on EDA limiting reagent. [c] *cis*:*trans* ratio determined by $^1$H NMR and GC.

**Table 2. Cyclopropanation Reaction between Styrene and EDA Catalyzed by 1 Using NaBArf As the Activating Agent[a]**

| entry | catalyst loading (mol %) rel to EDA | equiv styrene rel to EDA | NaBArf (mol %) | reaction time (h) | yield[b] (%) | *cis*:*trans*[c] |
|---|---|---|---|---|---|---|
| 1 | 5 | 5 | 5 | 1 | 98 | >99:1 |
| 2 | 2.5 | 5 | 2.5 | 2 | 98 | >99:1 |
| 3 | 1 | 5 | 1 | 24 | 49 | 96:4 |
| 4 | 2.5 | 2.5 | 2.5 | 2 | 98 | 99:1 |
| 5 | 2.5 | 1 | 2.5 | 2 | 70 | 99:1 |

[a] Reaction conditions: 1.00 mmol of EDA and given quantities of **1**, NaBArf, and styrene in 20 mL of $CH_2Cl_2$ at 0 °C. [b] Isolated yield based on EDA limiting reagent. [c] *cis*:*trans* ratio determined by $^1$H NMR and GC.

catalyst loading, solvent, temperature, stoichiometry) in the catalytic system have been investigated in order to improve the catalytic performance. Several new alkenes and substituted derivatives as well as diazo compounds as carbenoid sources have also been tested in order to broaden and explore the scope of the catalytic process.

## RESULTS AND DISSCUSSION

**Catalyst Activation: Necessity To Form a Rh Cation.** In our recent communication on the performance of catalyst **1**,[28] it was demonstrated that in order to obtain catalytic activity, the catalyst had to be activated. The activating agent of choice in the first study was AgOTf, the role of which was presumed to be abstraction of the chloride ligand to create a vacant (or loosely solvated) coordination site. Activation of **1** with AgOTf for 20 min, followed by addition of styrene and EDA at 0 °C, furnished the *cis* and *trans* cyclopropanes **2** and **3**, respectively, in 98% isolated yield and with a better than 99:1 *cis*-diastereoselectivity (Scheme 1). The diazo compound could be added in one portion without any sign of formal carbene dimerization, a rather desirable and unusual feature of this catalyst. These results where obtained with a catalyst loading of 5 mol % of **1**, 5 mol % of AgOTf, and a 5-fold excess of styrene, all measured relative to EDA (Table 1, entry 1). When the catalyst loading (entries 2 and 3) or the amount of styrene (entry 4) were reduced, yields and diastereoselectivities both dropped. Under reaction conditions that led to reduced yields, formal carbene dimerization (as observed by formation of diethyl maleate and diethyl fumarate) was observed to be a major side reaction but the mechanistic implications are unclear. There were no signs of side products arising from the known[24] formal dipolar cycloadditions of EDA to maleate or fumarate.

It was obviously desirable to modify the reaction conditions in order to obtain a more efficient and versatile process. Triflate is a fairly small and slightly coordinating anion.[29,30] Previous reports have demonstrated that replacement of the triflate anion with the larger, more weakly coordinating[31] $BArf^-$ anion ($BArf^- = B[3,5\text{-}(CF_3)_2C_6H_3)]_4^-$) can significantly increase the reactivity in Rh(II)-catalyzed cyclopropanations.[32] Indeed, enhanced reactivity was seen also in our system. With the use of NaBArf as the activating agent, it was possible to reduce the catalyst loading from 5 to 2.5 mol % without detrimental effects on the reactivity or selectivity (Table 2, entries 1 and 2). However, with 1 mol % catalyst loading the yield and selectivity were significantly reduced (entry 3). It is not known whether these changes in yields and selectivities are due to catalyst destruction, deactivation, or modification facilitated by the prolonged reaction times that are needed for the reaction to proceed at lower catalyst loadings. Importantly, the new catalyst activation procedure made it possible to reduce the amounts of styrene to 2.5 and even 1 equiv relative to EDA while the high diastereoselectivities and good yields were still obtained (entries 4 and 5). This makes the catalyst more attractive for use in synthesis where it is not desirable to use an excess of the alkene. The fact that using the sodium salt NaBArf as the activating agent gave better results than salt AgOTf also rules out the involvement of Ag species in these cyclopropanation reactions, and supports the notion that the mode of activation is a straightforward chloride abstraction.

**Attempted Preparation of an Activation-Free Cationic Rh Catalyst.** A new cationic Rh(I) complex (**6**) was also synthesized, in which the CO and chloride ligands in **1** are replaced by the bidentate norbornadiene (nbd) ligand. It was envisioned that complex **6** might be a better catalyst for the cyclopropanation, without need for prior catalyst activation, provided that the nbd ligand would be sufficiently labile to provide a coordination site at Rh. The synthesis of complex **6** is depicted in Scheme 2.

The imidazolium salt **4** was reacted with in situ generated $[Rh(O\textit{t}\text{-}Bu)(nbd)]_2$ to furnish the 5-coordinated Rh complex **5**,[33] which was directly used in the next step. The stable cationic complex **6** was obtained by chloride removal from **5** with NaBArf, a well-established procedure for chloride abstraction in organometallic chemistry.[32] The driving force for chloride removal is the formation of NaCl, poorly soluble in $CH_2Cl_2$; this is quite analogous to the formation of AgCl when AgOTf is the activating agent. The $^{13}$C NMR spectrum of **6** exhibited a characteristic doublet for the carbene carbon at $\delta$ 177.8 with $J(^{103}Rh-^{13}C) = 61$ Hz. The IR $\nu_{C=N}$ absorption of the imine was lowered by 51 cm$^{-1}$ compared to that of the imidazolium salt **4**, strongly indicating that the iminocarbene ligand had formed the expected $\kappa^2$(C,N) chelate at Rh. An X-ray crystal structure of complex **6** is presented in Figure 1. The X-ray structure analysis confirmed that the iminocarbene ligand had formed a $\kappa^2$(C,N) chelate at Rh and the expected square planar geometry was assumed for the $d^8$ $ML_4$ complex. The Rh−C(nbd) bond distances are considerably longer for the part of the diene that


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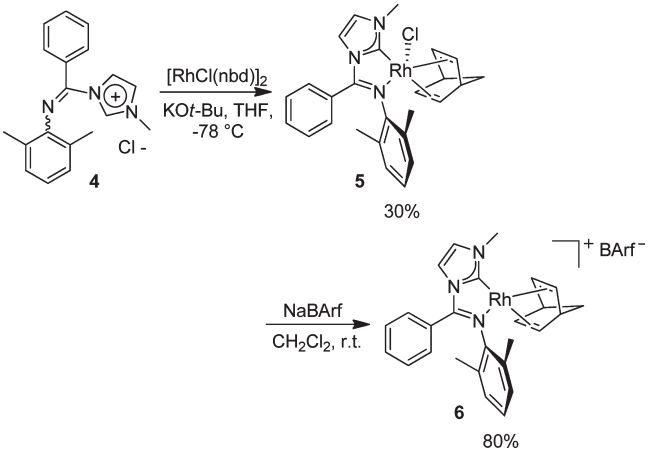
**Scheme 2. Synthesis of the Cationic Rh(I) Complex 6**



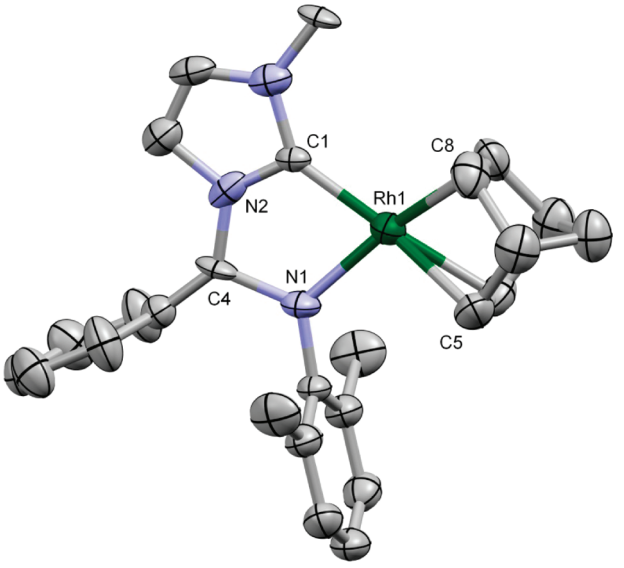




**Figure 1.** ORTEP drawing of **6** (hydrogen atoms and the $BArf^-$ counteranion have been removed for clarity, ellipsoids at 30% propability). Selected bond distances (Å) and angles (deg): Rh−N(1) 2.069(11), Rh−C(1) 1.991(12), Rh−C(8) 2.096(11), Rh−C(5) 2.184(11), Rh−C(1)−N(2), 118.7(8), Rh−C(1)−N(3) 140.3(10), N(1)−Rh−C(1) 76.1(5).

is *trans* to the NHC (2.19(1) Å) than for the part that is *cis* (2.10(1)) to the NHC ligand, as expected from the greater *trans* influence of the NHC ligand compared to the imine.[34,35]

Complex **6** was then tested in the cyclopropanation reaction between EDA and styrene by using 5 mol % of **6** and 5 equiv of styrene under the reaction conditions reported in Table 2. Unfortunately, the new catalyst gave rather low yields (39%) of the cyclopropanes **2** and **3** and only a slight excess of the *cis* isomer (*cis*:*trans* 66:44). Probably, the nbd ligand is not sufficiently labile to effectively create the necessary vacant coordination site. A more labile ligand than nbd is then obviously needed to furnish a more efficient and selective catalyst than the original catalyst **1**.

**Solvent Effects.** Dichloromethane, one of the most commonly used solvents in cyclopropanation reactions, was the solvent used in the initial study of **1**. A range of different solvents of highly variable polarities and donor strengths have now been tested in order to examine the solvent effects on the catalytic system (Table 3).

**Table 3. Testing of Solvent Effects[a]**

| entry | solvent | yield[b] (%) | *cis*:*trans*[c] |
|---|---|---|---|
| 1 | dichloromethane | 98 | >99:1 |
| 2 | trifluorotoluene | 65 | >99:1 |
| 3 | trifluoroethanol | 70 | 98:2 |
| 4 | toluene | 63 | 98:2 |
| 5 | fluorobenzene | 94 | 95:5 |
| 6 | nitromethane | 56 | 97:3 |
| 7 | ethanol | | |
| 8 | THF | | |
| 9 | acetonitrile | | |

[a] Reaction conditions: 1.00 mmol of EDA, 5 equiv of styrene, 2.5 mol % of **1**, 2.5 mol % of NaBArf in 20 mL of the given solvent at 0 °C. [b] Isolated yield based on EDA limiting reagent. [c] *cis*:*trans* ratio determined by $^1$H NMR and GC.

As can be seen in Table 3, the initially chosen solvent dichloromethane proved to be the best for yields and selectivities (entry 1). In trifluorotoluene (entry 2), which is similar in polarity and promoted as a "greener" alternative[36] to dichloromethane, the same excellent selectivity was observed but the yield was considerably lower. Good selectivities were also observed by using trifluoroethanol and toluene (entries 3 and 4), but the yields were moderate and products from formal carbene dimerization were observed in the $^1$H NMR spectra of the crude product mixture. No product from formal carbene insertion into the solvent O−H bond[24] was found with trifluoroethanol, but with ethanol (entry 7) the cyclopropanes (**2** and **3**) were not formed and instead the only products observed were those from O−H insertion and formal carbene dimerization. In fluorobenzene the yield was high, but the *cis*:*trans* selectivity dropped to 95:5 (entry 5). In nitromethane, the cyclopropanes were formed with good selectivity and moderate yields (entry 6). In the better donor solvents THF and acetonitrile the only products observed where those from formal carbene dimerization (entries 8 and 9). These solvents are presumably inefficient for cyclopropanation because of the donor properties, but it is not clear mechanistically how this leads to carbene dimerization.

**Scope of Reactants: Diazo Compounds.** As discussed above, Rh(I) catalyst **1** gives excellent results with commercially available EDA as the diazo compound. *tert*-Butyl diazoacetate was also tested under the conditions found to be best for EDA. As shown in Scheme 3 (top), similarly high yield and *cis*-selectivity were observed in the synthesis of cyclopropanes **7** and **8**.

Ethyl phenyl diazoacetate was also tested as a carbenoid precursor, Scheme 3 (bottom). The phenyl diazoacetates are known to have a high preference for formation of the *E* isomer.[37,38] Indeed, with Rh(I) catalyst **1**, the *E* isomer was the favored isomer with a selectivity of 26:74. With ethyl phenyl diazoacetate, the reaction temperature had to be raised from 0 °C to ambient and a catalyst loading of 10 mol % was necessary in order to furnish a reasonable 48% yield of the cyclopropanes **9** and **10**. A diastereomeric ratio of >99:1 in favor of the *E* isomer has been reported using a Cu catalyst in the same reaction.[39] Thus, catalyst **1** shows an enhanced *cis*-selectivity in its formal carbene additions when compared to other catalysts in the reactions between styrene and three different diazoacetate reagents.

**Scope of Reactants: Alkenes.** Cyclopropanations with catalyst **1** and EDA were previously tested on a range of different alkenes.[28] Some of these alkenes were now tested again with the new and more efficient system using NaBArf as the activating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**Scheme 3. Cyclopropanation of Styrene with *tert*-Butyl Diazoacetate and Ethyl Phenyldiazoacetate**

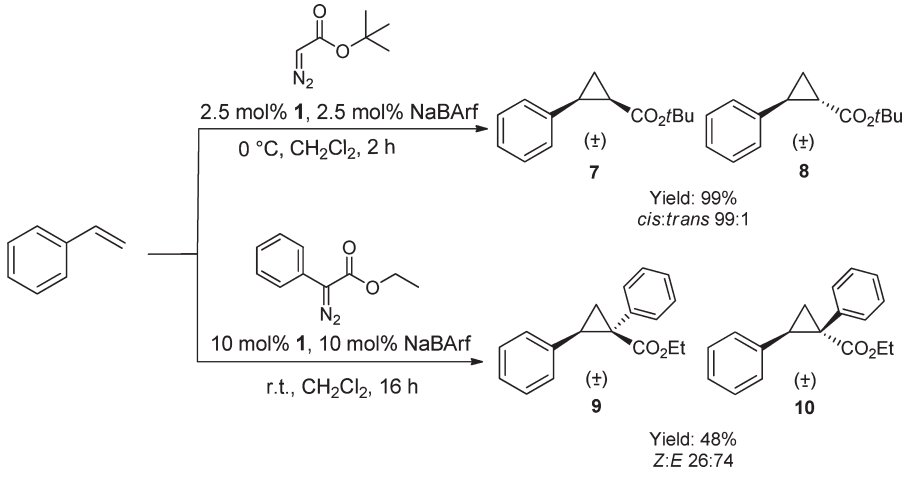



**Table 4. Cyclopropanation of Different Alkenes with EDA[a]**

| entry | alkene | yield[b,c] (%) | *cis*:*trans*[c,d] |
|---|---|---|---|
| 1 | styrene | 98 (98) | >99:1 (>99:1) |
| 2 | indene | 99 (98) | >99:1 (98:2) |
| 3 | cyclopentene | 99 (98) | 99:1 (99:1) |
| 4 | 1-octene | 95 (60) | 75:25 (78:22) |
| 5 | α-methylstyrene | 80 (38) | 75:25 (66:44) |

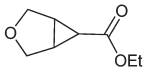
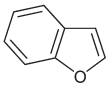
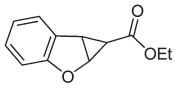
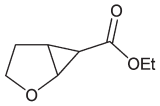
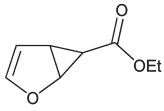
[a] Reaction conditions: 1.00 mmol of EDA, 5 equiv of alkene, 2.5 mol % of **1**, 2.5 mol % of NaBArf in 20 mL of $CH_2Cl_2$ at 0 °C. [b] Isolated yield based on EDA limiting reagent. [c] Numbers in parentheses refer to yields and selectivities reported with AgOTf activation.[11] [d] *cis*:*trans* ratio determined by $^1$H NMR and GC.

agent, and the results are presented in Table 4 (previously reported results shown in parentheses for comparison).

With NaBArf as the activating agent, the yields improved slightly for indene and cyclopentene (entries 2 and 3), and for indene the selectivity improved from 98:2 to >99:1. For both 1-octene and α-methylstyrene (entries 4 and 5) the yields improved significantly but the selectivities were still moderate. Thus, Rh(I) catalyst **1** displays very high reactivity and *cis*-selectivity in the reactions with indene and cyclopentene; for cyclopentene this is the highest yield and by far the highest *cis*-selectivity that has been reported in reactions with EDA. This unusual reactivity prompted us to investigate the reactivity toward a number of O-heterocyclic analogues, the furan derivatives in Table 5. The corresponding cyclopropanation products formed from these substrates can be important intermediates[40−42] or substructures in biologically active compounds, as for example in nucleoside derivatives which have been reported to have antiviral activity.[5] Cyclopropanated carbohydrates are also of particular interest.[3] The selected substrates and the results from their reactions with EDA using **1** as the catalyst with NaBArf activation are presented in Table 5.

An excellent yield and a selectivity of >99:1 in favor of the *cis* isomer was achieved with 2,5-dihydrofuran (entry 1). With benzofuran, the selectivity was also >99:1 in favor of the *cis* isomer, and a good yield was obtained (entry 2). No *trans* isomer was detected by $^1$H NMR or GC analysis in these experiments. For 2,3-dihydrofuran, yield and selectivity were moderate but still with a considerable *cis*-selectivity. In the reaction with furan, only traces of the cyclopropane products were

**Table 5. Cyclopropanation of 5-Ring Oxygen-Heterocyclic Alkenes with EDA[a]**

| entry | alkene | product | yield[b] (%) | *cis*:*trans*[c] |
|---|---|---|---|---|
| 1 |  |  | 98 | >99:1[d] |
| 2 |  |  | 70 | >99:1[d] |
| 3 |  |  | 33[e] | 88:12 |
| 4 |  |  | Trace amounts | not determined |

[a] Reaction conditions: 1.00 mmol of EDA, 5 equiv of alkene, 5 mol % of **1**, 5 mol % of NaBArf in 20 mL of $CH_2Cl_2$ at 0 °C. [b] Isolated yield based on EDA limiting reagent. [c] *cis*:*trans* ratio determined by $^1$H NMR and GC. [d] No *trans* product detected. [e] Yield determined by $^1$H NMR by use of benzaldehyde as internal standard.

observed. In these reactions a catalyst loading of 5 mol % of **1** had to be used in order to obtain good yields. No products arising from insertions into substrate C−H bonds[24] were observed in these reactions. This is in accord with our previously reported results[28] which also showed that catalyst **1** is a highly selective catalyst for cyclopropanation reactions vs C−H insertion. The selectivities observed in the reactions of 2,5-dihydrofuran and benzofuran open up the possibility of highly selective syntheses of interesting building blocks and potentially biologically active compounds.

## CONCLUSION

The efficiency and the scope of our recently developed highly *cis*-selective Rh(I) catalyst **1** has been improved through tuning of different experimental parameters in its cyclopropanation reactions. By changing the activating agent from AgOTf to NaBArf, the catalyst loading could be reduced and the yields and selectivities were

improved for several of the tested alkenes compared to the previously reported results. A screening of different solvents showed that the best results were obtained with $CH_2Cl_2$ as solvent. Bulkier substituents on the ester group in the diazo compound were found to have little effect on the high yields and selectivities, potentially broadening the synthetic utility of cyclopropanations catalyzed by catalyst **1**. Catalyst **1** is a very efficient and highly *cis*-selective catalyst in cyclopropanation reactions between EDA and sterically unhindered electron-rich alkenes. The high reactivity and selectivities observed in the reactions between EDA and the cyclic substrates cyclopentene, 2,5-dihydrofuran, and benzofuran are especially interesting, as these results suggest the possibility of highly selective syntheses of biologically interesting compounds. These are, to the best of our knowledge, the highest *cis*-selectivities and yields observed in cyclopropanation reactions with these substrates using EDA as the diazo compound.

Rh(I) catalyst **1** has been demonstrated to be an efficient, highly *cis*-selective cyclopropanation catalyst in reactions between simple commercially available diazo compounds and a range of different alkenes. The catalytic system is under continuing investigation in our laboratories.

## EXPERIMENTAL SECTION

**General Procedures.** All reactions involving organometallic compounds were carried out with use of drybox and inert atmosphere techniques unless otherwise noted. Solvents for reactions were dried according to standard procedures. THF, $CH_2Cl_2$, $Et_2O$, and $CH_3CN$ were dried using a MB SPS-800 solvent purifying system. NMR spectra were recorded at 25 °C. The assignments of $^1H$ and $^{13}C$ signals for complex **6** were aided by COSY 45, HMQC, and HMBC spectroscopy. For brevity, the following abbreviations are used for the assignment: Ph = phenyl, Dmp =2,6-dimethylphenyl; Ar = 3,5-bis(trifluoro)phenyl: $H_{o/m/p}$ and $C_{i/o/m/p}$ denote the *ipso*/*ortho*/*meta*/*para* atoms relative to the point of attachment to the imine nitrogen. Imidazolium salt **4** was synthesized according to previously reported procedures.[28,34] Where $CH_2Cl_2$ was found in the elemental analysis, this was also observed in the $^1H$ NMR spectra.

**General Procedure for Cyclopropanation.** The procedure is an adaption of the one used in our recent communication.[28] Rh complex **1** (0.0114 g, 0.025 mmol, 2.5 mol %) and NaBArf (0.0221 g, 0.025 mmol, 2.5 mol %) were stirred in dry $CH_2Cl_2$ (13.0 mL) at ambient temperature for 1 h under an argon atmosphere. The reaction mixture was cooled to 0 °C and the substrate was added. Ethyl diazoacetate (0.12 mL, 1.00 mmol, 1.0 equiv) in dry $CH_2Cl_2$ (7.0 mL) was then added in one portion. The reaction mixture was stirred at 0 °C. $CH_2Cl_2$ was removed in vacuo and the crude product was purified by flash chromatography (ethyl acetate:hexane) to afford the cyclopropanes. The *cis*:*trans* ratio and characterization of the cyclopropanes were determined by GC analysis and by comparison of $^1H$ NMR spectra with literature data.

Most of the cyclopropanation reactions described have exceptionally good isolated yields of pure products. We attribute this to the fact that when these reactions work well, only a simple and quick flash chromatography procedure is required to separate excess alkene from the cyclopropane products. We note that there are numerous reports in the literature of cyclopropanation reactions giving yields of 98% to "quantitative".[7,15,22,23,39,43]

**Ethyl *cis*-2-phenylcyclopropane-1-carboxylate (2):**[44]. $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 7.25 (m, 4H, Ph-**H**), 7.18 (m, 1H, Ph-**H**), 3.87 (q, 2H, $J$ = 7.1 Hz, OC**H**$_2$CH$_3$), 2.67−2.52 (m, 1H, cyclopropane-**H**), 2.06 (ddd, 1H, $J$ = 9.3, 7.9, 5.7 Hz, cyclopropane-**H**), 1.70 (ddd, 1H, $J$ = 9.3, 7.4, 5.3 Hz, cyclopropane-**H**), 1.40−1.23 (m, 1H, cyclopropane-**H**), 0.95 (t, 3H, $J$ = 7.1 Hz, OCH$_2$C**H**$_3$); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 170.8 (**C**=O), 136.5 (Ph-**C**), 129.2 (Ph-**C**H), 127.7 (Ph-**C**H), 126.5 (Ph-**C**H), 60.0 (O**C**H$_2$CH$_3$), 25.3 (cyclopropane-**C**H), 21.7 (cyclopropane-**C**H), 13.9 (OCH$_2$**C**H$_3$), 11.0 (cyclopropane-**C**H$_2$); EI-MS $m/z$ (%) 190 ($M^+$, 42), 162 (7), 145 (20), 117 (100), 91 (24).

**Rh(I) Iminocarbene Complex 6.** The method is an adaption of a published method for making related Rh(I) oxazolinylcarbene complexes.[33] KO*t*-Bu (0.0570 g, 0.508 mmol, 2.2 equiv) and $[RhCl(nbd)]_2$ (0.107 g, 0.231 mmol, 1.0 equiv) were mixed in the drybox. Dry degassed THF (7.5 mL) was added and the reaction mixture was stirred at ambient temperature for 30 min. The mixture was added dropwise to a solution of imidazolium salt **4** (0.150 g, 0.461 mmol, 2.0 equiv) in THF (15 mL) at −78 °C, and the reaction mixture was slowly heated to ambient temperature overnight. The reaction mixture was centrifuged, the resulting orange supernatant was separated, and the solvent was removed in vacuo. The crude product was recrystallized from $CH_2Cl_2/Et_2O$ and this gave **5** as an orange solid. The product was used directly in the following synthesis of **6**. $^1H$ NMR of **5** ($CD_2Cl_2$, 200 MHz) $\delta$ 7.48−7.32 (m, 5H, Ph-**H**), 7.14 (br s, 1H, NC**H**CHN), 6.97−6.90 (m, 3H, Dmp-**H**), 6.86 (d, 1H, $J$ = 2.2 Hz, NCHC**H**N), 3.72 (s, 3H, N-C**H**$_3$), 3.70−3.63 (m, 4H, nbd-**H**), 3.60−3.53 (m, 2H, nbd-**H**), 2.32 (s, 6H, Dmp-C**H**$_3$), 1.11−1.09 (m, 2H, nbd-**H**).[33]

A mixture of **5** (0.040 g, 0.080 mmol, 1.0 equiv) and NaBArf (0.042 g, 0.16 mmol, 2.0 equiv) was dissolved in $CH_2Cl_2$ (5.0 mL) and the reaction mixture was stirred at ambient temperature for 3 h under argon. The reaction mixture was centrifuged and the solvent was removed in vacuo. The product was recrystallized from $CH_2Cl_2/Et_2O$. This gave **6** as a purple solid (0.0862 g, 80%). $^1H$ NMR ($CD_2Cl_2$, 600 MHz) $\delta$ 7.74−7.71 (m, 8H, BArf-Ar-$H_o$), 7.57−7.55 (m, 4H, BArf-Ar-$H_p$), 7.54−7.52 (m, 1H, Ph-$H_p$), 7.43−7.38 (m, 2H, Ph-**H**), 7.23−7.19 (m, 2H, Ph-**H**), 7.01−7.0 (m, 3H, Dmp-**H**), 6.85 (d, 1H, $J$ = 2.3 Hz, NC**H**CHNCH$_3$), 6.80 (d, 1H, $J$ = 2.3 Hz, NCHC**H**NCH$_3$), 4.98 (dd, 2H, $J$ = 4.8, 2.6 Hz, nbd-**H**), 4.21 (dd, 2H, $J$ = 4.5, 1.8 Hz, nbd-**H**), 4.09−4.05 (m, 2H, nbd-**H**), 3.46 (s, 3H, NC**H**$_3$), 2.27 (s, 6H, Dmp-C**H**$_3$), 1.62 (dt, 1H, $J$ = 1.6, 8.8 Hz, nbd-**H**), 1.37 (dt, 1H, $J$ = 1.6, 8.8 Hz, nbd-**H**); $^{13}C$ NMR ($CD_2Cl_2$, 126 MHz) $\delta$ 177.8 (d, $^1J(^{103}Rh-^{13}C)$ = 60.8 Hz, NHC-**C**), 163.1 (**C**=N), 162.1 (q, $J$ = 49.9 Hz, BArf-Ar-**C**), 140.9 (Dmp-**C**), 135.2 (br s, BArf-Ar-$C_o$), 133.6 (Ph-**C**H), 129.6 (Ph-**C**H), 129.4 (Dmp-**C**H), 129.1 (br s, BArf-Ar-**C**), 128.4 (Ph-**C**H), 127.5 (Dmp-**C**), 126.0 (Ph-**C**), 123.9 (NC**H**CHNCH$_3$), 124.8 (q, $J$ = 304.5 Hz, BArf-C**F**$_3$), 119.0 (N**C**HCHNCH$_3$), 117.9 (m, BArf-Ar-$C_p$), 88.8, 88.7 (nbd-**C**H), 67.5, 67.4 (nbd-**C**H), 66.7, 66.6 (nbd-**C**H), 55.1, 55.0 (nbd-**C**H), 36.7 (N**C**H$_3$), 18.8 (Dmp-**C**H$_3$); ESI-MS ($CH_3CN$) $m/z$ 474 (Rh cation − nbd +2 × $CH_3CN$). Anal. Calcd for $C_{58}H_{39}F_{24}BRhN_3 \cdot 0.3CH_2Cl_2$: C, 50.9; H, 2.9; N, 3.1. Found: C, 51.0; H, 3.1; N, 3.1.

## ASSOCIATED CONTENT

**Supporting Information.** Characterization data and $^1H$ NMR of cyclopropanes, $^1H$ NMR and $^{13}C$ NMR spectra of Rh complex **6**, crystal data for **6**, and structural data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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