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Rhodium(II)-Catalyzed Enantioselective Intermolecular Aziridination of Alkenes

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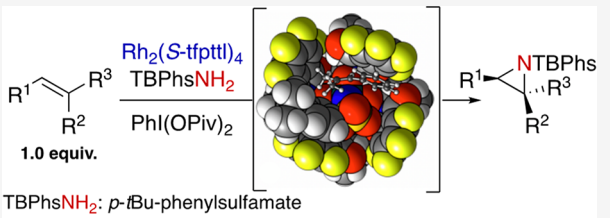
ABSTRACT: C_4-Symmetrical dirhodium(II) tetracarboxylates are highly efficient catalysts for the asymmetric intermolecular aziridination of substituted alkenes with sulfamates. The reaction proceeds with high levels of efficiency and chemoselectivity to afford aziridines with excellent yields of up to 95% and enantiomeric excesses of up to 99%. The scope of the alkene aziridination includes mono-, di-, and trisubstituted olefins as well as the late-stage functionalization of complex substrates. The reaction can be performed on a gram-scale with a catalyst loading of 0.1 mol %. Our DFT study led us to propose a two-spin-state mechanism, involving a triplet Rh−nitrene species as key intermediate to drive the stereocontrolled approach and activation of the substrate.



TBPhsNH$_2$: *p*-*t*Bu-phenylsulfamate

- *Low catalyst loading: 0.1 to 1 mol%*
- *Large scope (>35 examples): mono-, di-, or tri-substituted aziridines*
- *Excellent yields up to 95% and e.r. up to 99.5:0.5*
- *Two-spin state mechanism*
- *Stereochemical model rationalizing the enantiocontrol*

INTRODUCTION

Aziridines are the smallest but not the least of saturated nitrogen heterocycles.[1,2] Long considered as epoxides' ugly cousins,[1] they gained a broad acceptance as useful scaffolds in organic chemistry. They are important motifs in bioactive products as well as versatile intermediates for the synthesis of functionalized amines.[3−7] Particularly, trisubstituted aziridines hold a paramount importance because they can give access to products incorporating a tetrasubstituted carbon center.[8,9] Thus, the design of catalytic methods for the asymmetric synthesis of aziridines is of utmost interest for the preparation of enantiopure nitrogen-containing molecules.

Catalytic asymmetric reactions from alkenes or imines are reported for the stereoselective synthesis of aziridines.[10] However, few of them are described for the formation of optically pure trisubstituted derivatives. Catalytic additions to imines[11−14] or to α,β-unsaturated carbonyl derivatives[15−18] only give access to aziridine-2-carbonyl derivatives (Scheme 1a). By comparison, the application of catalytic nitrene transfer to alkenes leads to a greater variety of substituted aziridines.[19−21] Seminal reports from the groups of Evans and Jacobsen demonstrated the efficiency of chiral C_2-symmetrical bis(oxazoline) or salen ligands in the metal-catalyzed asymmetric alkene aziridination with iminoiodinanes (Scheme 1b).[22−26] On the other hand, the design of D_2-symmetrical Co(II)-porphyrin complexes has led to enantioselective processes with azides.[27−29] However, these intermolecular aziridination reactions apply mostly to monosubstituted alkenes and α,β-unsaturated carbonyl compounds. The rare examples of asymmetric reactions with poly-substituted alkenes were reported only for intramolecular processes.[29−31]

Chiral rhodium(II) complexes are another class of catalysts that were first reported by Müller in the enantioselective alkene aziridination.[32] However, studies in rhodium(II)-catalyzed asymmetric aziridination have not led to efficient processes so far. Moderate enantiomeric excesses were reported for intramolecular reactions,[33−35] while the best results for intermolecular reactions were described for diastereoselective aziridinations using a chiral nitrene source.[36,37] Issues raised by rhodium(II) complexes include their propensity to catalyze the competitive allylic C(sp^3)−H amination, thereby leading to mixtures of products from alkenes.[38] Moreover, these Lewis acidic complexes are able to mediate the in situ ring opening of aziridines.[39,40] Yet, the unique symmetry of rhodium(II) complexes with ligands derived from α-*N*-(imidoyl)amino acids offers opportunities in alkene aziridination. These compounds adopt an "all-up" conformation that leads the imido groups to delineate a tunable C_4-symmetrical pocket into which the rhodium-bound reacting species can form.[41−44] In this article, we report that they are perfectly suited to catalyze the asymmetric aziridination of alkenes with sulfamates in the presence of a mild iodine(III) oxidant.

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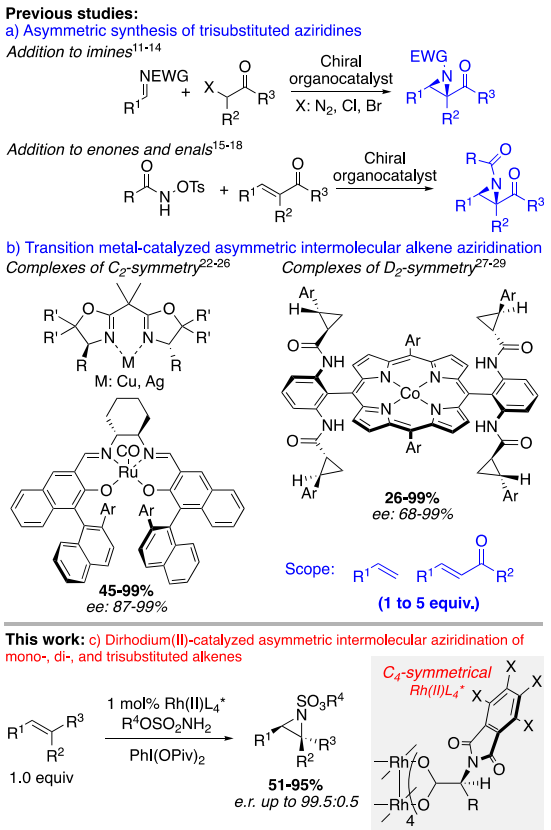
Scheme 1. State-of-the-Art Asymmetric Intermolecular Alkene Aziridination



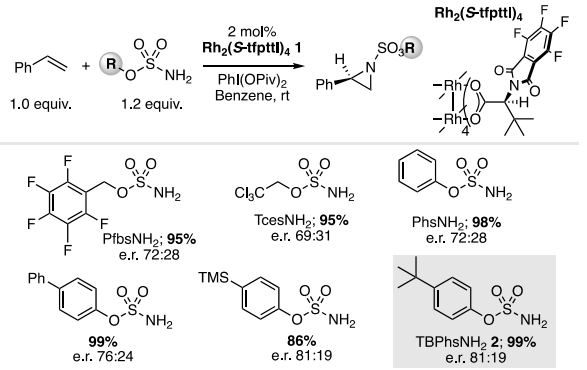
Particularly, high levels of enantiocontrol and chemoselectivity can be reached for the formation of enantiopure trisubstituted aziridines (Scheme 1c).

RESULTS AND DISCUSSION

Optimization of the Rhodium(II)-Catalyzed Asymmetric Aziridination with Sulfamates. The use of chiral C_4-symmetrical dirhodium(II) tetracarboxylates was reported for catalytic asymmetric benzylic C(sp^3)−H amination.[45−48] Very good conversions and enantiomeric excesses were obtained particularly for the reactions involving a benzylic sulfamate as the nitrene source.[47] Thus, inspired by these results, we decided to screen various combinations of rhodium(II) complexes and sulfamates for enantioselective alkene aziridination.

We initially focused on sulfamates in the intermolecular enantioselective aziridination of styrene used as the limiting component, with the commercially available chiral complex dirhodium(II) tetrakis[*N*-tetrafluorophthaloyl-(*S*)-*tert*-leucinate] (Rh_2(*S*-tfpttl)$_4$) **1** (Scheme 2). The first experiments with benzylic sulfamates confirmed the high reactivity of the pentafluorobenzyl derivative $PfbsNH_2$.[47] The corresponding aziridine was isolated in 95% yield and with an enantiomeric ratio (er) of 72:28. However, the latter could not be improved by changing the aromatic substitution (SI Scheme S1). Testing aliphatic sulfamates such as $TcesNH_2$ reported for the intermolecular C(sp^3)−H amination[49−51] led to comparable results both in terms of yield and enantioselectivity. Then we turned our attention to aromatic sulfamates and found that the simple phenol-derived reagent $PhsNH_2$[51] was as efficient and selective as $PfbsNH_2$. Pleasingly, a significant increase in the er

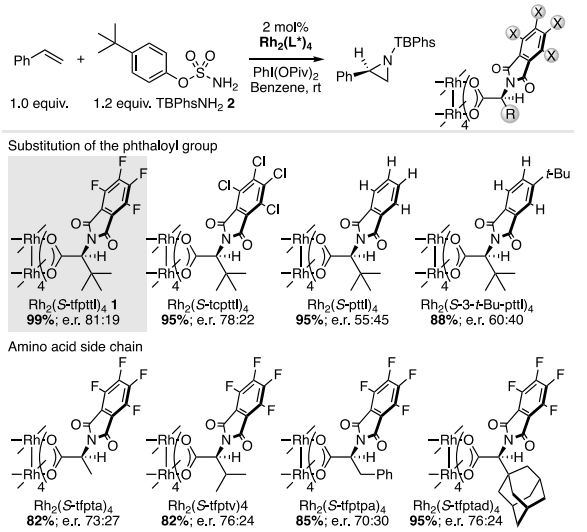
Scheme 2. Screening of Sulfamates with the Rh_2(*S*-tfpttl)$_4$ Complex 1



was obtained following the introduction of a substituent at the *para* position of the aromatic ring, while substitution of the *meta* and *ortho* positions proved to be deleterious (SI Scheme S1). In this context, a *t*-butyl group proved to be optimal in terms of yield and selectivity. The *p*-*t*Bu-phenylsulfamate ($TBPhsNH_2$) **2** affords the aziridine from styrene in quantitative yield and with an er of 81:19. This readily available sulfamate was chosen to further optimize the conditions.

Next, the screening of catalysts revealed the superiority of complexes having ligands derived from *α*-*N*-(phthaloyl)amino acids (Scheme 3 and SI Scheme S2). The influence of the

Scheme 3. Screening of Chiral Rhodium(II) Complexes with $TBPhsNH_2$ 2



nitrogen protecting group and the side chain of the amino acid ligand installed on the dirhodium core was evaluated and the *t*-butyl derivative (Rh_2(*S*-tfpttl)$_4$) **1** proved to give the highest yield and level of enantioselectivity. Worth of mention are the variable influence of the side chain, as the presence of the more sterically demanding adamantyl group in the Rh_2(*S*-tfptad)$_4$ complex led to a lower er of 76:24, and the critical role of the perhalogenated phthaloyl group on the enantiocontrol that might be attributed to the stabilization of the chiral crown conformation through noncovalent interactions.[42,44]

Optimization of the iodine(III) oxidant, the solvent and the temperature was next performed with the combination of

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sulfamate **2** and the rhodium(II) complex **1** (SI Tables S1, S2, and S3). The best compromise in terms of reactivity and enantioselectivity was achieved by running the reaction with commercially available $PhI(OPiv)_2$ as the oxidant, at −15 °C in toluene. Under these conditions, the aziridine derived from styrene was isolated in 85% yield and with an er of 87.5:12.5. Finally, we studied the influence of additives on the level of enantiocontrol as previously investigated for several selective rhodium(II)-catalyzed diazo transfers.[52] Whereas the use of a Lewis base did not prove conclusive, the addition of 1 equiv of a Brønsted acid had a beneficial effect on the selectivity (SI Table S4).[53,54] Thus, the expected *N*-(TBPhs)-2-phenylaziridine was isolated in 87% yield with an er of 90:10 in the presence of pentafluorobenzoic acid. How this acidic additive interacts with the catalyst and/or reactants is at this stage difficult to rationalize, however, we were pleased to note that its presence led to obtain the same improved yield and selectivity with a catalyst loading reduced to 1 mol %.

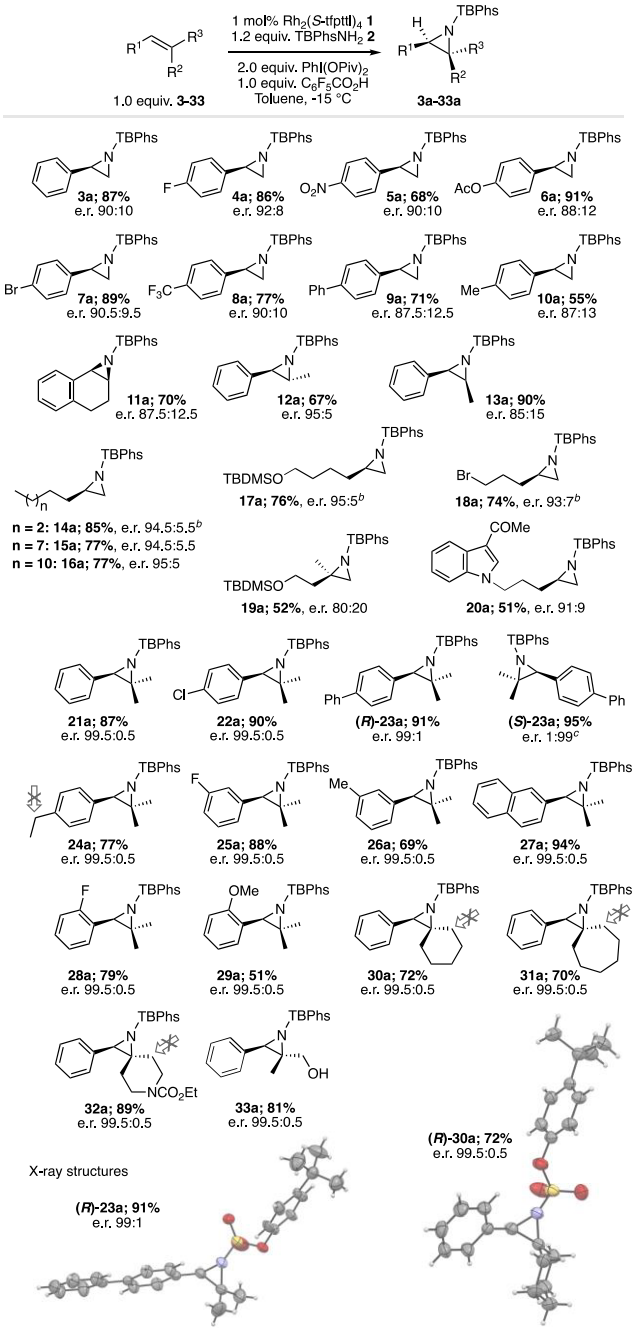
Scope of the Rhodium(II)-Catalyzed Asymmetric Aziridination with Sulfamates. The scope of the aziridination reaction was first investigated in the presence of aromatic alkenes (Scheme 4). The optimal conditions efficiently apply to several monosubstituted styrene derivatives bearing either an electron-withdrawing (**4a**−**8a**) or an electron-donating (**9a** and **10a**) group at the *para* position. It should be mentioned that in the case of electron-rich substrates **9a** and **10a**, the yields were improved by performing the reaction in the absence of pentafluorobenzoic acid to avoid the in situ nucleophilic ring opening of the aziridine.[40,55] Disubstituted aromatic alkenes were also relevant substrates for the asymmetric aziridination reaction. Particularly, *trans*- and *cis*-methylstyrene exclusively afforded the corresponding *trans*- and *cis*-aziridines **12a** and **13a**, a result indicating that this catalytic process is stereospecific.

The reaction was also applied to aliphatic alkenes having various functional groups but also secondary allylic positions likely to undergo C(sp^3)−H amination.[20] Pleasingly, the corresponding aziridines **14a**−**20a** were isolated with complete chemoselectivity, in very good yields up to 85% and high er up to 95:5. In some specific cases where amination of toluene is observed because of the low reactivity of the alkenes, toluene-d_8 can alternatively be used as the solvent to avoid this side product and improve the yields as demonstrated with simple examples (**14a**, **17a**, and **18a**).

Even higher levels of enantiocontrol were observed from trisubstituted alkenes.[56,57] Various *β*,*β*-dimethylstyrene derivatives were converted to the aziridines **21a**−**29a** with yields in the 51−95% range and er of 99:1 or 99.5:0.5. Importantly, the reaction tolerates both electron-withdrawing (**22a**, **25a**, and **28a**) and electron-donating (**23a**, **24a**, **26a**, and **29a**) substituents located either at the *para*, *meta*, or *ortho* position. As shown for the aziridine **23a**, each enantiomer is accessible by reaction with the (*S*)- or (*R*)-enantiomer of complex **1**. In addition, the X-ray structure of the aziridine **23a** resulting from the reaction with the (*S*)-catalyst **1** demonstrated that it has a (*R*)-configuration.

It is worth highlighting the complete chemoselectivity observed with substrates displaying benzylic and allylic C(sp^3)−H bonds that can react with nitrenes under metal catalysis. Previous studies have indeed demonstrated the key influence of the metal and the nitrene source on the competitive formation of the aziridine or the aliphatic amine.[58,59] Here, in the case of the *p*-ethylstyrene derivative

Scheme 4. Catalytic Asymmetric Aziridination of Diversely Substituted Alkenes[a]



[a]Reaction conditions: substrate (0.5 mmol), sulfamate (0.6 mmol), $PhI(OPiv)_2$ (1.0 mmol), $C_6F_5CO_2H$ (0.5 mmol), and rhodium catalyst (1 mol %) in toluene (1.0 mL) at −15 °C. [b]Reaction performed in toluene-d_8. [c]Reaction performed with the (*R*)-enantiomer of complex **1**.

24, we observed the exclusive formation of the corresponding aziridine although the ethyl group includes benzylic C(sp^3)−H bonds that are highly prone to react with a rhodium-bound nitrene (vide infra).[47] Moreover, highly chemoselective alkene aziridination proceeds from trisubstituted alkenes **30**−**32** that display potentially reacting allylic C(sp^3)−H bonds. The resulting aziridines **30a**−**32a** show that catalytic allylic amination does not occur under these conditions. Enantiopure spiro nitrogen heterocycles were isolated in high yields and

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complete enantiocontrol. Again, the X-ray structure of **30a** confirmed the (*R*)-configuration induced by the (*S*)-catalyst. Finally, starting from an alkene bearing three different substituents, the aziridination reaction again proceeds in a stereospecific manner to afford the corresponding aziridine **33a** with the same excellent level of enantiocontrol. Taken together, these results in terms of chemoselectivity are in line with previous studies that demonstrated the strong bias of electrophilic rhodium−sulfamoylnitrenes for intermolecular functionalization of weaker more electron-rich π-bonds over amination of σ-bonds.[60]

Synthetic Applications of the Rhodium(II)-Catalyzed Asymmetric Aziridination with Sulfamates. The functional group tolerance of the reaction was further investigated by applying the conditions to the late-stage derivatization of complex substrates (Figure 1). The catalytic alkene aziridination efficiently proceeds in the presence of ester, ketone, imide, lactam, or sulfonyl groups. More importantly, the reaction proved to be chemoselective in the case of polyenes such as the cinnamyl derivative **34a**, the fislatifolic ester **35a**, or geranyl acetate **36a**. The addition of the electrophilic rhodium−nitrene proceeds at the more electron-rich *gem*-dimethyl π-bond because the presence of the electron-withdrawing ester group (**34a**) or acetyl group (**36a**) deactivates the other alkene. Regarding compound **35a**, we postulate that an optimal interaction between the substrate and the catalytic Rh_2-nitrene cavity as depicted by the computational studies for β,β-dimethylstyrene (vide infra) would favor the functionalization of the β,β-dimethylstyryl moiety. Aziridination also proceeds with high chemoselectivity for compounds **37a**−**39a** that possess benzylic or tertiary C(sp^3)−H bonds likely to undergo C−H amination,[50,51,61] a result that confirms the preferential reactivity of rhodium−sulfamoylnitrenes toward alkenes.

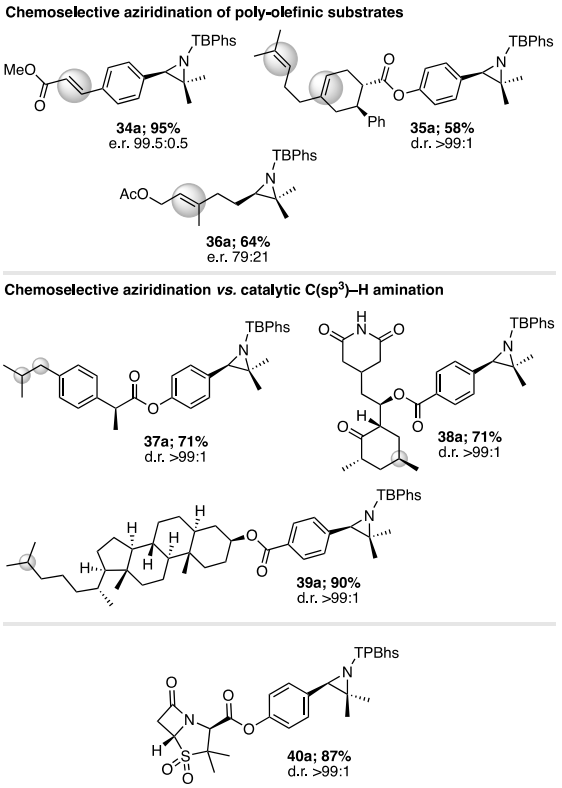
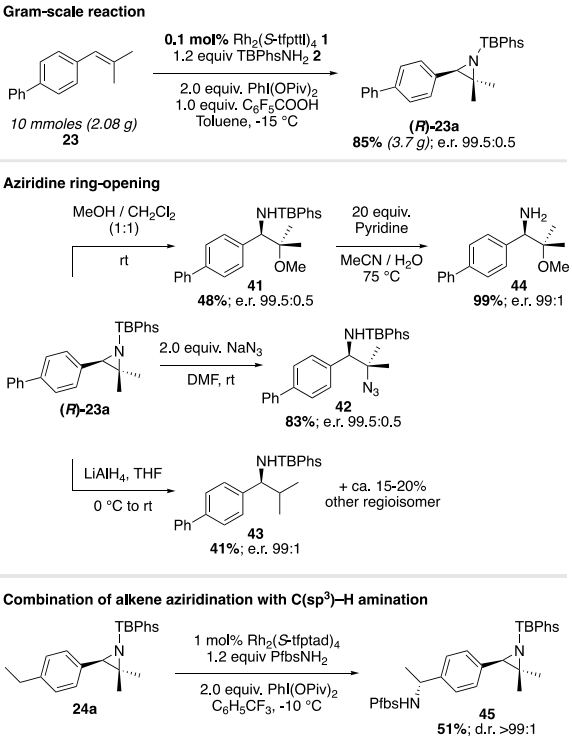


Figure 1. Catalytic diastereo- and chemoselective aziridination for the late-stage functionalization of complex molecules.

To highlight the practicality of our method, a catalytic alkene aziridination reaction was performed on a gram-scale with equal efficiency using only 0.1 mol % of the rhodium catalyst **1**. Starting from 10 mmol of olefin **23**, the corresponding aziridine (*R*)-**23a** was isolated in 85% yield and with an er of 99.5:0.5 (Scheme 5). Then compound (*R*)-**23a** was reacted with various nucleophiles to provide the corresponding enantiopure benzylic amines **41**−**43** with non-optimized yields of 41−83%. These compounds result from a selective ring opening at the more substituted carbon center. Joullié's group previously described the same regioselectivity for the ring opening from 2,2,3-trisubstituted aziridines. This would be the result of unfavorable electronics in the transition state regarding the attack at the less substituted benzylic center.[62]

Scheme 5. Synthetic Opportunities Provided by the Catalytic Asymmetric Alkene Aziridination



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The sulfamoyl group can be cleaved by simple treatment with pyridine in a 2:1 mixture of acetonitrile and water at 75 °C, as shown from compound **41** that was converted to the free amine **44** in quantitative yield without loss of enantiopurity. Product **44** can be considered as an analogue of α-*t*-butyl- and α-*i*-propyl-benzylamines that are important motifs for the design of bulky chiral carbene ligands.[63] Thus, the catalytic aziridination of trisubstituted alkenes stands as a streamlined strategy for the preparation of new optically pure sterically demanding benzylic amines. Finally, starting from aziridine **24a**, we were able to obtain the optically pure diaminated product **45** that results from the combination of two catalytic nitrene transfers, i.e. an enantioselective alkene aziridination followed by a diastereoselective benzylic (sp^3)−H amination.[47]

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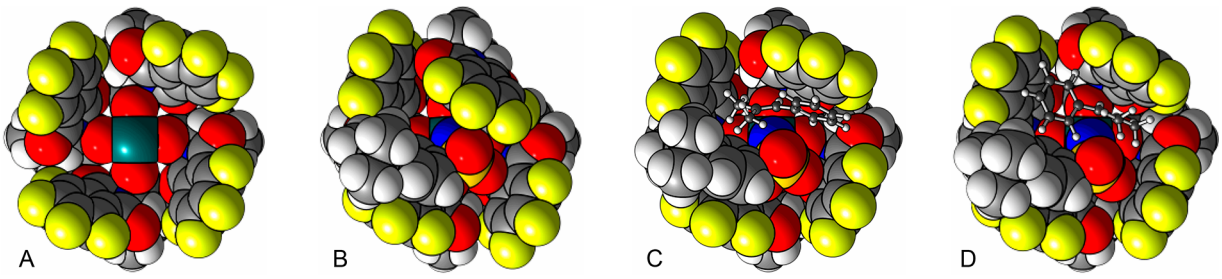

Figure 2. Views showing $^{3}Rh_2$ (A), $^{3}Rh_2N$ (B), $^{3}RhN{:}Styr_{Si}$ (C), and $^{3}RhN{:}Styr_{Re}$ (D). Different representations are used to provide evidence that the substrate (ball and sticks) fits in the catalytic pocket (van der Waals spheres). H, white; C, gray; N, blue; O, red; F, neon green; S, yellow.

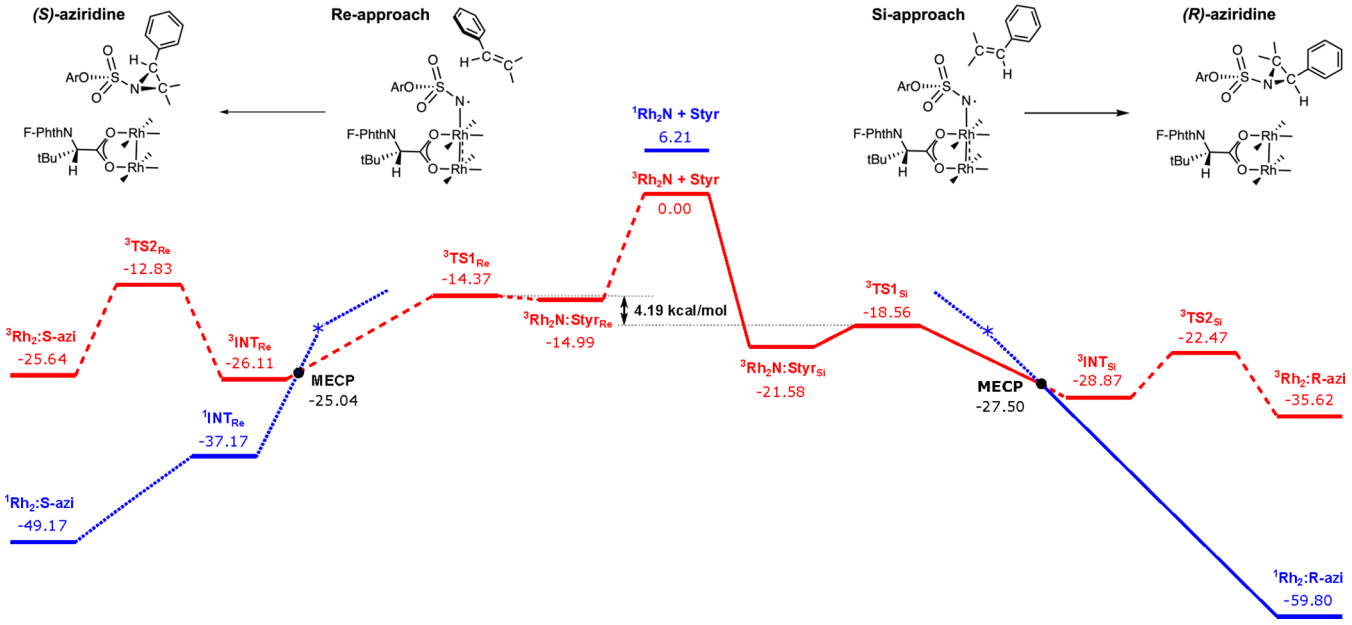

Figure 3. Extract of the computed two spin state mechanism (triplet in red, singlet in blue) showing the favored energy profile in plain line ($\Delta G_{258\ K}$ in kcal/mol); * indicates the position of pseudo-TS.

Computational Investigations to Rationalize the High Level of Stereocontrol in the Catalytic Aziridination of Trisubstituted Alkenes. In order to propose a mechanistic rationalization of the excellent enantioselectivity of the rhodium-catalyzed alkene aziridination, a DFT study was conducted. Geometry optimization were performed using the D3BJ[64] dispersion corrected OPBE[65,66] functional in combination with the mixed basis set 6-31G(d) for C,H,O,N,S/StuRSC(+f) for Rh.[67−70] This method was benchmarked against the X-ray structure of the Rh_2(*S*-tfpttl)$_4$(OH_2)$_2$ complex (SI Table S5 and Figure S1). The full energetic profile and the structures of the different intermediates discussed below are given in the SI Figures S8−S11.

As a model reaction, the aziridination of *β*,*β*-dimethylstyrene **21** with the TBPhsNH_2 sulfamate was examined. First, the geometry and spin state of the relative Rh_2(*S*-tfpttl)$_4$-nitrene intermediate was investigated. The naked Rh_2(*S*-tfpttl)$_4$ precursor is stabilized in a singlet state ($^{1}Rh_2$) and offers two binding sites, one with a hindered *t*Bu environment (Rh_A) and the other (Rh_C) buried in the chiral pocket shaped by the four interacting phthaloyl rings (Figure 2A and SI Figure S2). In agreement with the observed enantioselectivity, binding of the nitrene to Rh_A was found neatly disfavored in both singlet and triplet spin states, compared to Rh_C (>13 kcal/mol, SI Table S6 and Figure S3). Regarding Rh_C binding, three different conformers were assessed depending on the rotation of the nitrene chain along the N−S bond (SI Figure S4). As in $^{1}Rh_2$, intramolecular interactions hold the phthaloyl rings in these Rh−nitrene species, but the encapsulation of the nitrene moiety results in a desymmetrisation of the pocket. Notably, for the most stable conformer (noted $^{3}Rh_2N$, Figure 2B), the aryl of the nitrene stacks with one phthaloyl moiety of the catalyst while the nitrene seems to anchor the opposite phthaloyl ring (Figure 2B and SI Figures S5 and S6). A tight dissymmetric catalytic pocket is thus obtained that prefigures a constrained substrate approach. Intermediate $^{3}Rh_2N$ is best described as a mixed valence $Rh_2^{II,III}$−nitrene radical species and is 6.21 kcal/mol more stable than the corresponding closed shell state, and 5.70 to 7.95 kcal/mol more stable than the other triplet conformers (SI Table S6). We thus considered the activation of the dimethylstyrene from this triplet rhodium−nitrene species.

Two different approaches of the substrate into the catalytic Rh_2−nitrene cavity were envisioned, with the dimethylstyrene presenting either its *Si* or *Re* face to the N-atom of the nitrene, while pointing away the bulkier phenyl substituent (SI Figure S1). Taking the dirhodium−nitrene substrate pair ($^{3}Rh_2N$ + Styr) as a reference, both $Styr_{Re}$ and $Styr_{Si}$ insertions of the substrate in the catalyst pocket were found exergonic, with a gain of 21.58 kcal/mol for the *Si* approach leading to

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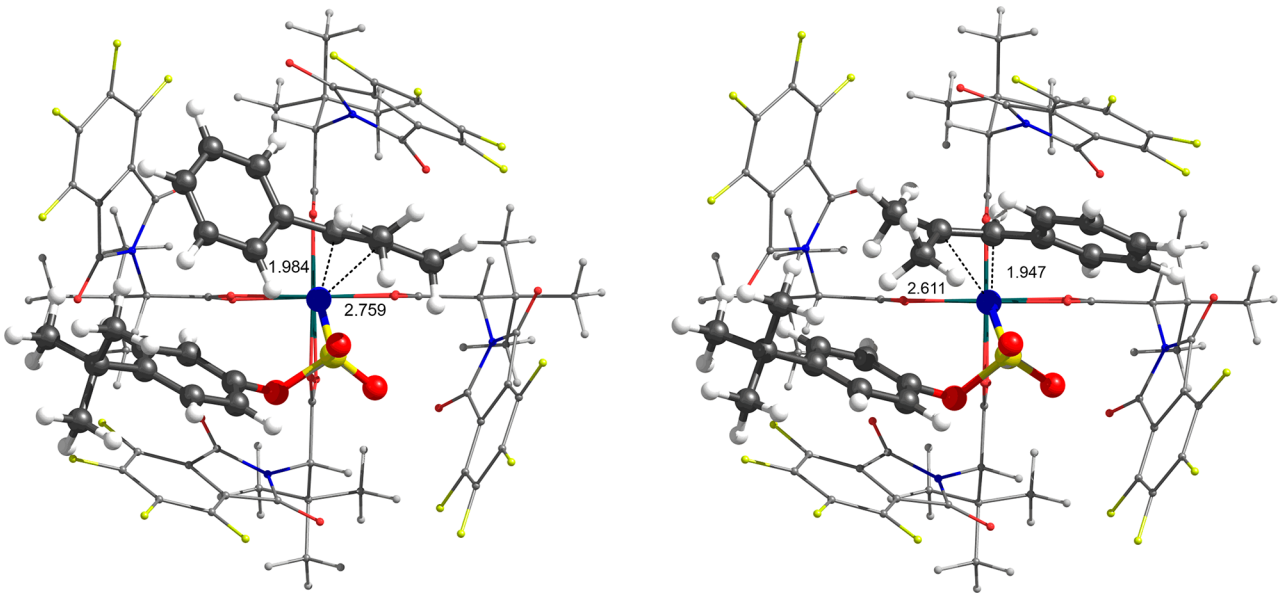

Figure 4. 3D views along the N−Rh−Rh axis of the two TS involved in the enantioselective step with C−N distances in Å (*Re* approach on the left, *Si* approach on the right).

intermediate $^{3}Rh_2N$:$Styr_{Si}$ and only 14.99 kcal/mol for $^{3}Rh_2N$:$Styr_{Re}$ (Figure 2C,D). This energy difference can be explained by comparing the geometry of the two intermediates with those of the catalyst and substrate taken separately. Interestingly, minimal deformation of the catalytic site was observed for $^{3}Rh_2N$:$Styr_{Si}$ except for the opening of the phthalimide arm opposite to the nitrene. In contrast, the *Re* approach requires a bigger reorganization, that involves a 10° rotation of the nitrene along the Rh−N axis. Meanwhile, $Styr_{Re}$ must adapt its geometry to fit in the catalytic pocket, while $Styr_{Si}$ remains in its most favored conformation (SI Figure S7). The room designed by the ligand pocket and the nitrene chain is indeed perfectly suited for the $Styr_{Si}$ to accommodate both the aryl ring and the *gem*-dimethyl substituent.

From these two intermediates, aziridination proceeds by a radical pathway, starting with formation of a first C−N bond at the less hindered and most accessible benzylic position.[71,72] As shown in Figures 3 and 4, the corresponding transition state (TS) is favored when the N−CH bond forms at the *Si* face of the substrate ($^{3}TS1_{Si}$, −18.56 kcal/mol) compared to the *Re* ($^{3}TS1_{Re}$, −14.37 kcal/mol), where the substrate is held farther from the nitrene (SI Figure S8). Along the triplet surface, $^{3}TS1_{Si}$ then connects to the radical intermediate $^{3}INT_{Si}$ lying at −28.87 kcal/mol (Figure 3, right, red). Ring closure along the triplet path would then involve transition state $^{3}TS2_{Si}$ (−22.47 kcal/mol). However, any attempts to optimize the related ^{3}Rh-(*R*)-aziridine product only yielded a partially converged geometry at −35.62 kcal/mol (Figure 3, right, dashed red). In contrast, the singlet analog was found at −59.80 kcal/mol. We therefore looked for a possible two-spin-state mechanism, as it has already been reported in related studies.[73−75] Scanning the singlet potential energy surface from the $^{1}Rh_2N$ + Styr pair did not permit to locate any first order saddle point. However, a pseudo-transition state associated with a single imaginary frequency was identified. Starting from this geometry and that of $^{3}TS1_{Si}$ enabled us to find a minimum energy crossing point (MECP) at −27.50 kcal/mol, preceding $^{3}INT_{Si}$ along the reaction coordinate path (SI Figure S9). This MECP directly connects to the singlet aziridine product $^{1}Rh_2$:*R*-azi at −59.80 kcal/mol (Figure 3, right, plain blue). No genuine TS was located along the singlet recombination surface between the MECP and the product. Following the *Re* approach, the $^{1}Rh_2$:*S*-azi isomer product is located at −23.53 kcal/mol from its triplet analog and +10.63 kcal/mol from its *R* isomer. This alternative product can be obtained from $^{3}TS1_{Re}$ by spin crossing to the singlet potential energy surfaces at −25.04 kcal/mol (Figure 3, left). In that case, the costless formation of a singlet $^{1}INT_{Re}$ intermediate (−37.17 kcal/mol) was evidenced between the MECP and the product.

Accordingly, this computational study points to the formation of the first C−N bond as the enantioselective step, as both the starting rhodium−nitrene:styrene adduct and the resulting triplet transition state are favored with the *Si* approach. Thus, a calculated activation energy difference of 4.19 kcal/mol predicts an enantiomeric ratio of 99.97:0.03 in agreement with the experimental observation (99.5:0.5).[76] This TS then converges to the corresponding singlet product via spin cross over, bypassing the formation of ^{3}INT, from which olefin isomerization could have occurred. This result is in line with the stereospecificity observed for *trans*- and *cis*-aziridines **12a** and **13a**.

CONCLUSION

In conclusion, this study demonstrated that highly efficient catalytic asymmetric alkene aziridination reactions can be performed with chiral C_4-symmetrical dirhodium(II) tetracarboxylates in the presence of aromatic sulfamates and an iodine(III) oxidant. From a synthetic aspect, the key features of the process are (1) its excellent level of chemo- and enantioselectivity with enantiomeric excesses of up to 99%, (2) the low catalyst loading and its scalability to the multigram level, (3) its wide scope including mono-, di-, and trisubstituted alkenes, (4) its application to the late-stage functionalization of complex products, and (5) its ability to afford a streamlined access to sterically hindered enantiopure benzylic amines. In addition, our computational study allowed to draw a two-spin-state mechanism for the alkene aziridination that involves the formation of a discriminating

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triplet transition state to explain the origin of the enantioselectivity. Particularly, the DFT analysis was helpful to identify the key interactions in the hydrophobic pocket of the (*S*)-rhodium complex between the phthaloyl rings, the sulfamoyl nitrene and the alkene that are responsible for the preferential aziridination of the *Si* face of the alkene. These results will provide valuable insights for the future design of selective rhodium(II)-catalyzed nitrene additions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c07337.

Experimental procedures, reaction optimization, characterization data, spectra for all new compounds, HPLC, crystallographic data, and details of the computational studies (PDF)

Accession Codes

CCDC 2152250−2152251 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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(55) For example, aziridine **10a** was isolated with a higher yield of 89% but a lower er of 83:17 when the reaction was performed in the absence of pentafluorobenzoic acid.
(56) Worth mentioning is the test experiment performed in the absence of the acidic additive in the case of alkene **22**. The corresponding aziridine **22a** was isolated with the same yield of 90% and ee of 99%. This revealed that the addition of $C_6F_5CO_2H$ is not necessary to obtain excellent enantiomeric excesses in the case of trisubstituted alkenes.
(57) As a limitation of the method, a test experiment involving a tetrasubstituted alkene, α,β,β-trimethyl styrene did not afford the expected aziridine. See the Supporting Information for other unsuccessful alkenes.
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