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Mechanism of the Rhodium-Catalyzed Asymmetric Isomerization of Allylamines to Enamines

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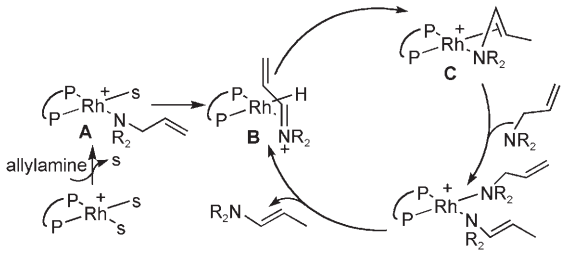
Abstract: A theoretical study of the mechanism of the rhodium-catalyzed asymmetric isomerization of allylamines to enamines by using density functional theory with the B3LYP functional leads us to discard the so far accepted nitrogen-triggered mechanism, in which the isomerization occurs on N-bonded intermediates and transition states, in favor of a variation of the classical allylic mechanism for olefin isomerization. The modified allylic mechanism consists of four main steps: 1) N-coordination of the allylamine to Rh^{I}; 2) intramolecular isomerization from κ^1-(N)-coordination to η^2-(C,C)-coordination of the allylamine; 3) oxidative addition of C^1–H to form a distorted octahedral η^3-allyl complex of Rh^{III}; and 4) hydrogen transfer to C^3 (reductive C^3–H elimination). The two hydrogen transfer steps (oxidative addition and reductive elimination) have the highest barriers of the overall process. The oxidative addition barrier, which includes solvent effects, is 28.4 kcal mol^{-1}. For the reductive elimination, the value in solvent is 28.6 kcal mol^{-1}, very similar to the oxidative addition barrier.

Keywords: alkenes · amines · enantioselectivity · isomerization · rhodium

Introduction

The highly enantioselective asymmetric isomerization of allylamines to enamines catalyzed by cationic BINAP–rhodium complexes (BINAP: 2,2′-bis(diphenylphosphino-1,1′-binaphthyl) is a most paradigmatic example of the successful application of an academic study to satisfy industrial demand. It was developed by Noyori to produce the asymmetric isomerization of diethylgeranylamine or diethylnerylamine to citronellal (*E*)-diethylenamine, a precursor in the industrial production of (−)-menthol.[1,2] The asymmetric isomerization requires, in addition to a face-selective interaction of the double bond of the prochiral enamine with the chiral catalyst, a stereoselective hydrogen transfer leading to double-bond migration. The catalytic cycle shown in Scheme 1 was initially proposed[3] and involves a C^1–H elimination in **A** to give **B**, followed by H re-addition to the terminal carbon atom of the coordinated iminium moiety (C^3) to afford a coordinated enamine in intermediate **C**.



Scheme 1. Catalytic cycle in the literature for the asymmetric isomerization of allylamine to enamine.

The double-bond isomerization in this mechanism is achieved in a sequence that differs from the two classical olefin isomerization mechanisms: hydride addition–elimination mechanism [Eq. (1)]; and the π-allyl mechanism, which results in an intramolecular 1,3-hydrogen shift [Eq. (2)]. A new name, the nitrogen-triggered mechanism, was coined

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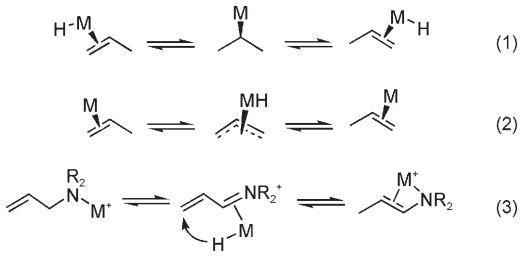
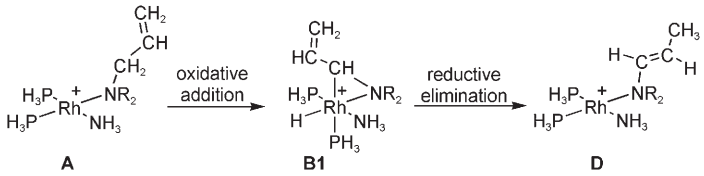
Supporting Information for this article is available on the WWW under http://www.chemeurj.org/ or from the authors and contains: Other mechanistic aspects; cartesian coordinates; absolute energies and free energies in the gas phase and in acetone for all optimized structures; and figures that include the geometries of selected intermediates and transition states.

for it, as it is initiated by a β-H elimination from the N-coordinated allylamine and the N atom plays a pivotal role throughout the process [Eq. (3)].



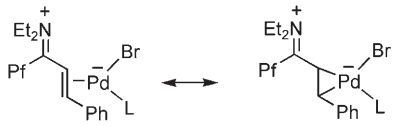
A slight modification of the mechanism was later proposed on the basis of an ab initio molecular orbital study which suggested that iminium coordination in intermediate **B** was closer to a metallacyclopropane-like structure (**B1**, Scheme 2). Moreover, **D** was calculated to be more stable



Scheme 2. Literature modification of the hydrogen-transfer step.

than **C**. It was then proposed that **D** should form from **A** by means of intramolecular oxidative addition of the C^1–H bond of the allylamine to the Rh^I center, to give a distorted-octahedral Rh^{III}–hydride intermediate (**B1**), followed by allylic transposition accompanied by reductive elimination (Scheme 2).[5,6] This ab initio study supported that the proposed intermediates were thermodynamically plausible, but transition states and activation energies, which decide whether the transformations are kinetically feasible, were not calculated.

Note that **B** and **B1** formally contain a vinyliminium moiety coordinated to Rh through the C=N bond, with little (Rh^I, **B**) or a lot of (Rh^{III}, **B1**) back donation from rhodium. Very recently, in the course of our studies on carbene transmetalation to palladium and subsequent carbene migratory insertion into a Pd–C_6F_5 bond,[5,7] we happened to isolate a palladium complex that contained a coordinated vinyliminium moiety.[8] Our complex has the same ambiguity of the formal Pd oxidation state (Pd^0 in **E**, or Pd^{II} in **E1**, Scheme 3) as Noyori's system has on the Rh oxidation state (Rh^I in **B**, or Rh^{III} in **B1**). At variance with the vinyliminium moiety in Noyori's cycle, ours lacks H on its C^1 atom, possessing instead a C_6F_5 group. This prevents the double-bond isomerization, which hypothetically needs to mobilize that hydrogen to occur. What matters in the context of this paper is that, interestingly, in contrast with the proposed structures in Rh, the iminium moiety is bonded to Pd



Scheme 3. Resonance structures for an olefin coordinated to Pd^0.

through the C=C bond rather than through the C=N bond. DFT calculations showed that the observed C=C-bonded structure in the Pd complex is 7.3 kcal mol^{-1} more stable than the nonobserved C=N bonded isomer.[8]

These results, prompted us to revisit the proposed N-triggered mechanism and examine the energies involved in the plausible reaction pathways, including those of transition states, as a complete theoretical study has never been carried out. We suspected that looking for the possible participation of C=C bonded to metal intermediates might lead the cycle back to one with the classically admitted mechanism for olefin isomerization [Eqs. (1) and (2)], as turns out to be the case.

Computational details: The calculations were performed by using the Gaussian 03 package.[9] The geometries of the minima and transition states were fully optimized by using density functional theory with the B3LYP functional.[10] For the Rh atom, the lanl2dz effective core potential has been used to describe the innermost electrons,[9,11] whereas their associated double-ζ basis set has been employed for the remaining electrons; an extra series of *f*-polarization functions has also been added (exp. 1.350).[12] The rest of the atoms have been described by the 6-31G(d,p) basis set.[13] The structures of the reactants, intermediates, transition states, and products were fully optimized without any symmetry restriction. Frequency calculations were performed on all optimized structures, by using the B3LYP functional, to characterize the stationary points as minima or transition states. Single-point solvent calculations were performed at the optimized gas-phase geometries, by using the CPCM approach,[14] which is an implementation of the conductor-like screening solvation model (COSMO) in Gaussian 03.[15] Acetone was the solvent of choice for some of the experiments to match the experimental conditions (dielectric constant $\varepsilon = 2.247$).

Results and Discussion

As in the literature studies,[3,4] our theoretical calculations were carried out for the isomerization of allylamine NH_2–CH_2–CH=CH_2 to the enamine NH_2–CH=CH–CH_3. This isomerization is calculated to be thermodynamically favorable by 8.3 kcal mol^{-1}. *cis*-$[Rh(PH_3)_2]^+$ was taken as a model of the fragment $[Rh(binap)]^+$ of the real catalyst. At least a third coordination site on Rh must be taken by the reactant allylamine. As for the fourth coordination site, we assumed

that it is initially occupied by another N-coordinated amine (whether allylamine or enamine), modeled by a NH_3 molecule.[16]

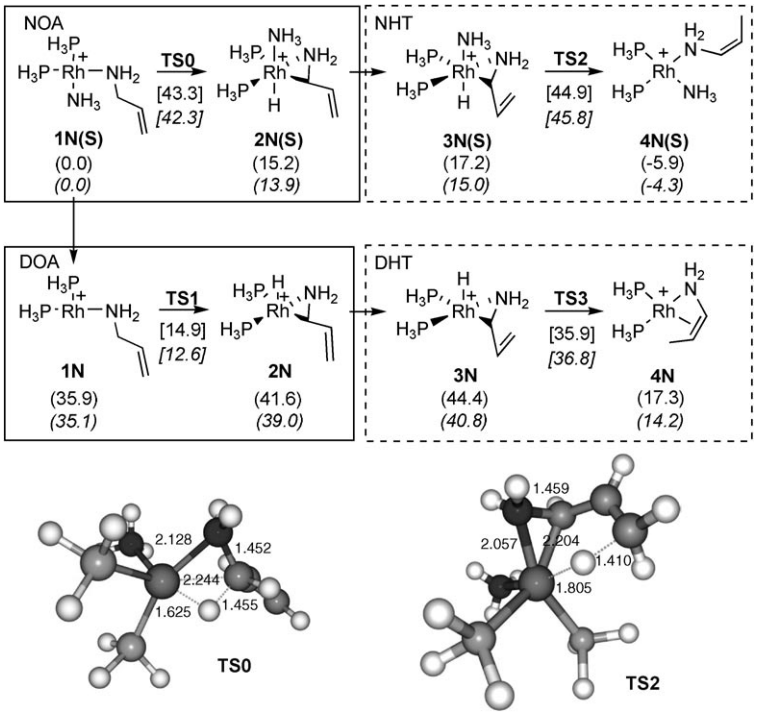
In the absence of external sources of hydride to trigger the classical isomerization shown in Equation (1), only the allylic [Eq. (2)] and the N-triggered [Eq. (3)] mechanisms need to be evaluated. Both involve two general steps: oxidative addition of C^1–H to Rh and hydrogen transfer from Rh to C^3. In the text and schemes to follow, the minima have been labeled with letters representing the mechanism (**N** for nitrogen triggered and **A** for the allylic mechanism) and numbers (**1**, **2**, **3**, etc.) in order of appearance. Finally, (**S**) indicates a geometry that contains an ancillary NH_3 ligand modeling the amine. The transition states are labeled in order of appearance. The energy values of the transition states and the intermediates are given in the schemes, for calculations in vacuum (normal style) and in continuum solvent (acetone; numbers in italic). The energies commented in the text are in continuum solvent, unless otherwise specified. Details for calculations and geometries of the TS's are given in the Supporting Information.

N-triggered mechanism: In the N-triggered mechanism (Scheme 4), the oxidative addition (NOA) starts at the square-planar N-coordinated Rh complex **1N(S)**, which undergoes β-H elimination (C^1–H oxidative addition) to give **2N(S)**, with the Rh center adopting a distorted octahedral geometry with the two phosphines and the "iminium" ligand in an equatorial plane, and the NH_3 and hydride ligands in axial positions. This step has a fairly high **TS0** energy of 42.3 kcal mol^{-1}, and the product lies 13.9 kcal mol^{-1} above the reactants.

Decoordination of NH_3 from **1N(S)** to give **1N**, preceding the oxidative addition, was also considered to check whether this would reduce the oxidative addition barrier (DOA, Scheme 4). Indeed the energy barrier for the oxidative addition step drops to 12.6 kcal mol^{-1} (**TS1**) but, as the energy cost to dissociate NH_3 from **1N(S)** is 35.1 kcal mol^{-1}, this pathway is in fact more energy demanding (47.7 kcal mol^{-1}) than NOA. Moreover, the product of this reaction (**2N**), a square pyramidal complex with the hydride in an apical position, is a less-stable intermediate, with a relative energy, 39.0 kcal mol^{-1}, above **1N(S)**. Considering Gibbs energies, the DOA would be slightly favored in front of the NOA mechanism, mainly due to the entropy variation in a dissociative process in the gas phase.[17] In the DOA mechanism, the formation of **1N** requires 22.1 kcal mol^{-1} and the subsequent oxidative addition has a relative free-energy barrier of 13.3 kcal mol^{-1}. Thus, the Gibbs energy barriers for the DOA and NOA mechanisms are 35.4 and 39.7 kcal mol^{-1}, respectively. These energy barriers are still fairly high.

The hydrogen transfer to the terminal carbon atom C^3 in the N-triggered mechanism (NHT) consists of the insertion of the C=C bond into the Rh–H bond from **2N(S)** (Scheme 4). All attempts to find a TS that keeps the nitrogen of the enamine bonded to Rh while the hydride is transferred to C^3, as proposed in Equation (3),[3,4] were unsuccessful, unless the conformation of the vinyliminium moiety was changed to give intermediate **3N(S)**, from which the H transfer becomes feasible. This conformational change is easily achieved by an essentially barrierless σ-bond rotation. The TS energy for hydrogen transfer from **3N(S)** is 45.8 kcal mol^{-1}, and affords the wrong (*Z*)-enamine isomer. The DHT mechanism is not any more advantageous, as it also produces the wrong isomer with even higher overall energy barriers: $\Delta E =$ 77.6 kcal mol^{-1}, $\Delta G = 64.7$ kcal mol^{-1}.

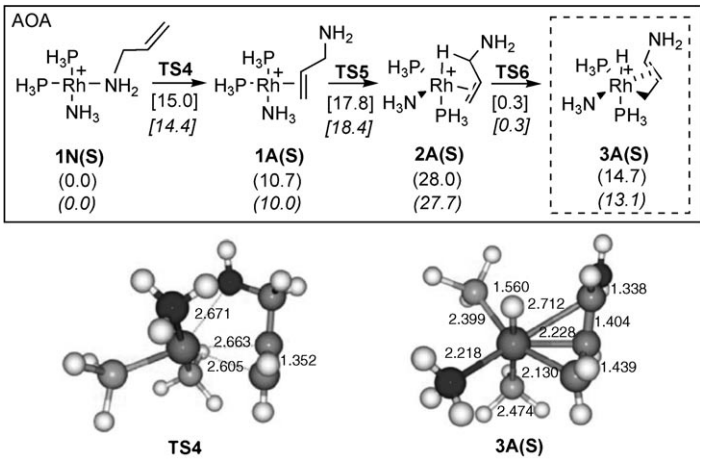
Thus, the reported N-triggered mechanism consists of two steps: 1) oxidative addition of C^1–H from the N-allylamine complex to form the distorted octahedral "iminium" complex **2N(S)**, with a **TS0** energy of 42.3 kcal mol^{-1} and 2) insertion of the C=C bond into the Rh–H bond, with an overall energy barrier of 60.8 kcal mol^{-1} above **1N(S)**. Both steps



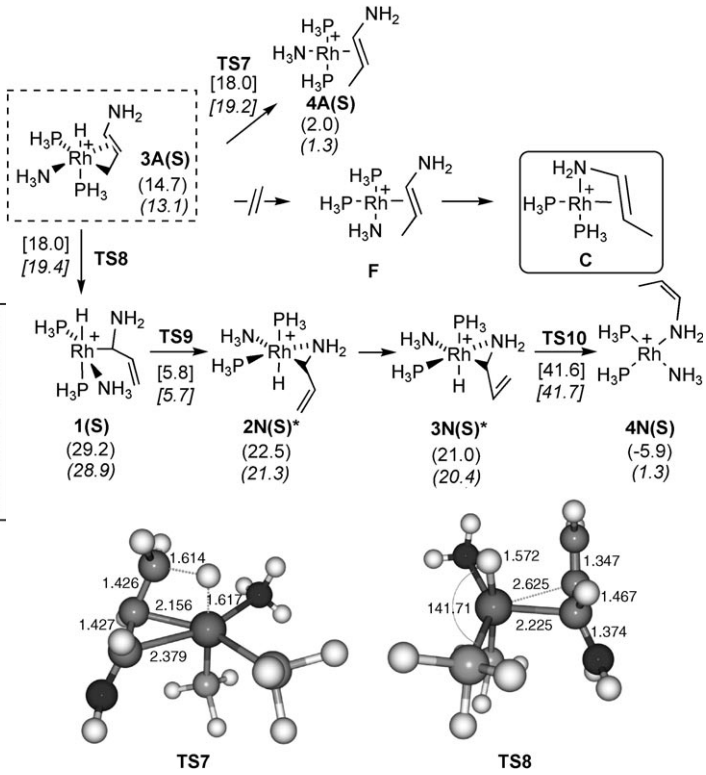
Scheme 4. Calculation results for the N-triggered mechanism proposed in the literature.

have a very high energy barrier. Moreover, this mechanism affords the wrong *Z* isomer of the enamine. Consequently it can be discarded.

Allylic mechanism for the hydrogen transfer and double-bond isomerization: In the allylic mechanism (AOA) the C^1-H oxidative addition requires a previous isomerization to coordinate the amine through the C=C bond (Scheme 5).



Scheme 5. Calculation results for the oxidative addition step in the allylic mechanism.



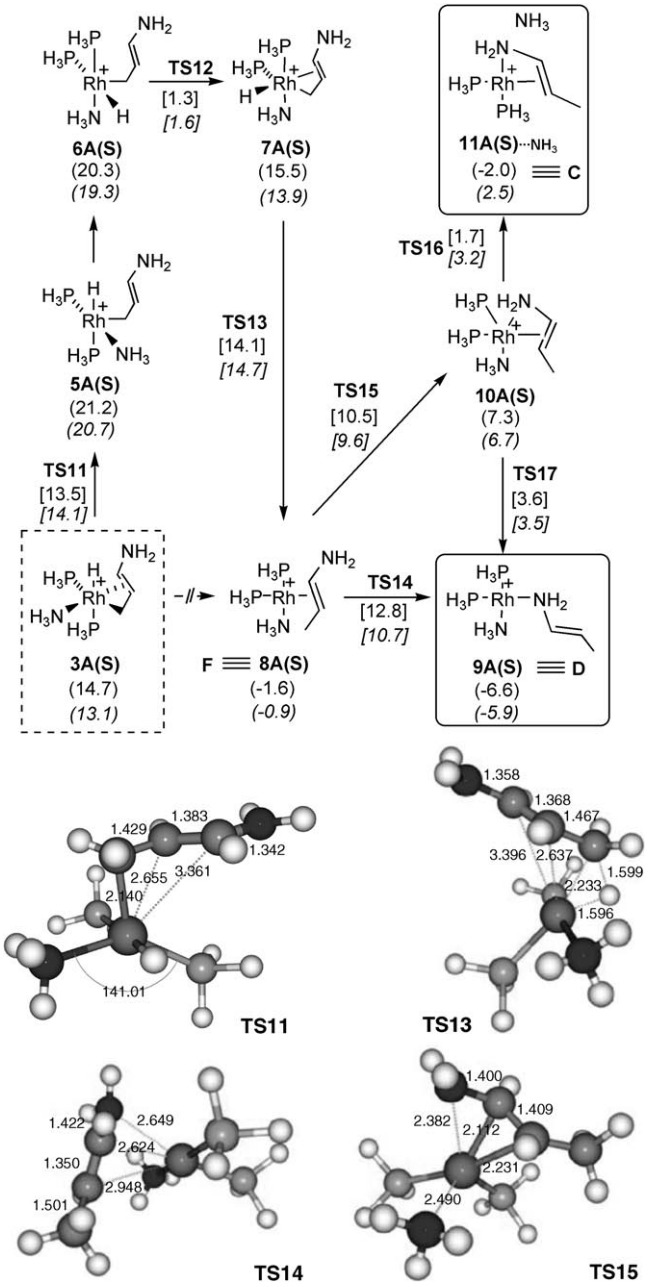
Scheme 6. Calculation results that turn out not to be productive for the hydrogen-transfer step in the allylic mechanism.

Although coordination through the amine nitrogen is more stable by 10.0 kcal mol^{-1}, the intramolecular substitution switching from κ^1-(N) to η^2-(C,C) through **TS4** (shown in Scheme 5) has an accessible energy barrier of 14.4 kcal mol^{-1}. From **1A(S)**, the oxidative addition of C^1–H goes through **TS5** (18.4 kcal mol^{-1}) to form an agostic intermediate **2A(S)** with an energy of 27.7 kcal mol^{-1} with respect to **1N(S)**. From there, an essentially barrierless oxidative addition (**TS6**, 0.3 kcal mol^{-1}) gives the η^3-allyl intermediate **3A(S)**, with an energy of 13.1 kcal mol^{-1}. This intermediate has a distorted octahedral geometry (shown in Scheme 5) in which one PH_3, the NH_3 ligand, and the η^3-allyl group of the allylamine are occupying four equatorial positions while the other phosphine and the hydride ligand take the axial positions.

Thus, taking as reference the starting complex **1N(S)**, the oxidative addition is much more favorable for the allylic mechanism (AOA) (28.4 kcal mol^{-1} including the cost of the initial intramolecular isomerization to **1A(S))** than for the N-triggered mechanism (NOA, 42.3 kcal mol^{-1}), which is a further reason to discard the latter.[18]

Let us examine now the possible pathways for hydrogen transfer in the allylic mechanism (AHT). From the different alternatives tried, those that proved nonproductive can be seen in Scheme 6. A direct hydride transfer to C^3 from complex **3A(S)** to give **F** (and then **C**) was not found. In contrast, a direct transfer was found that led to **4A(S)** (the *trans* isomer of **F**) with an accessible barrier (19.2 kcal mol^{-1}) but, as the real ligand, BINAP, cannot give a *trans* isomer, it had to be discarded. On the other hand, two pathways led to hydrogen transfer, all starting with the transformation of the η^3-allyl into a σ-allyl. The σ-allyl can be formed through C^1 or C^3. From these, the former is nonproductive: the formation of σ-allyl through C^1 has an energy barrier of 19.4 kcal mol^{-1} (**TS8**). Then, from the intermediate **1(S)**, easy coordination of the NH_2 group provides **2N(S)***, an isomer of **2N(S)** (Scheme 3), in which the spectator ligands NH_3 and PPh_3 have exchanged their positions. The evolution then continued as described for the NHT mechanism. The formation of the coordinated iminium intermediate **2N(S)*** from complex **1N(S)** has an overall energy barrier of 34.6 kcal mol^{-1} (**TS9**). The highest energy step is the hydrogen transfer (**TS10**), imposing an energy cost of 62.2 kcal mol^{-1} and affording the wrong isomer, (*Z*)-enamine. Consequently this pathway was also discarded.

The productive AHT process starts with a conversion of the η^3-allyl to a σ-allyl bonded to Rh through C^3 (formally equivalent to "ligand dissociation" of a C=C bond) and ligand topomerization to eventually allow for the orbital interaction that leads to H–C^3 coupling. This takes place through transition-state **TS11** (14.1 kcal mol^{-1}, Scheme 7), and affords a distorted square-pyramidal intermediate **5A(S)**. An essentially barrierless rotation around the Rh–C^3 bond in **5A(S)** followed by recoordination of the double bond produces the η^3-allyl Rh^{III} intermediate **7A(S)**, which undergoes direct H transfer to C^3 of the η^3-allyl through **TS13** (14.7 kcal mol^{-1}, Scheme 7) to give **8A(S)**. In contrast

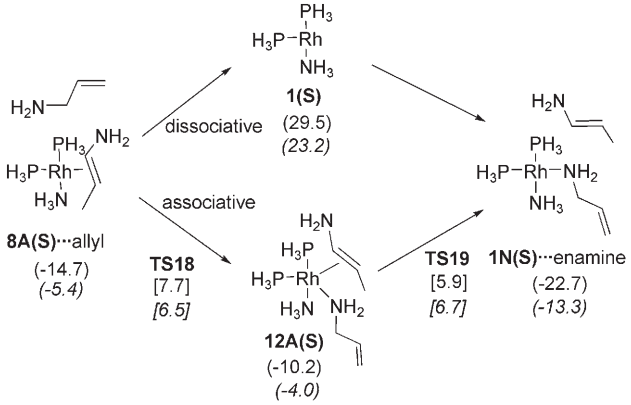


Scheme 7. Calculation results of the productive pathway for the hydrogen-transfer step in the allylic mechanism.

to **4N(S)** in Scheme 4, the coordinated enamine has the correct *E* conformation. Note that in contrast to **4A(S)** in Scheme 6, the two PH_3 ligands remain *cis* throughout the pathway, compatible with the modeled BINAP chelate.

From **8A(S)**, a number of intermolecular alternatives connected by low-energy paths are available: 1) Direct *intramolecular* switching from η^2-(C,C) to κ^1-(N) leads to **9A(S)** labeled **D** in Scheme 2, with an energy barrier of 10.7 kcal mol^{-1} (**TS14**, Scheme 7). 2) This transformation is also possible through a two-step intramolecular substitution of NH_3 for the pendant NH_2, with an energy barrier of 9.6 kcal mol^{-1} (**TS15**, Scheme 7); this leads to the pentacoordinated intermediate **10A(S)**, which evolves to **9A(S)** by decoordination of the double bond. 3) Alternatively, decoordination of NH_3 from **10A(S)** leads to **11A(S)**, which corresponds to intermediate **C** in the introduction (Scheme 1).

Which complex is exactly the complex preferred at the end of the reaction is unimportant, as **8A(S)**, **9A(S)**, and **11A(S)** are connected through very low energy barriers. For the sake of simplicity, we will choose to represent the closing of the catalytic cycle from **8A(S)**, regardless of the possible participation of **9A(S)**, **10A(S)**, and **11A(S)** as intermediates or resting states. To get to **1N(S)**, there are basically two alternatives (Scheme 8): 1) associative substitution of



Scheme 8. Easy pathways to transform the possible end products.

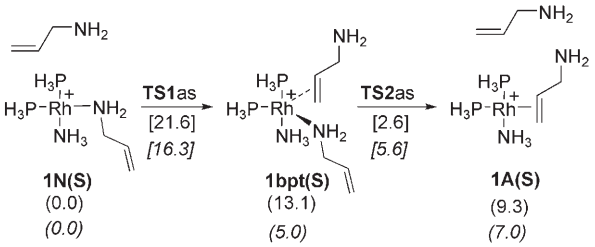
η^2-enamine for κ^1-(N) allylamine or 2) the dissociative substitution of both ligands. The energy barrier obtained was 8.1 kcal mol^{-1} for the former process, and 24.1 kcal mol^{-1} for the second. Thus, the associative process is favored. This still holds for ΔG values that include the entropic effects, in which the energy barrier is 13.3 kcal mol^{-1} for the associative mechanism and 23.9 kcal mol^{-1} for the dissociative.

In conclusion, the highest barrier after the oxidative addition corresponds to the hydrogen transfer (reductive elimination of the enamine, **TS13**) and amounts to 28.6 kcal mol^{-1}.[19]

Overall, the catalytic cycle for the allylic mechanism that leads to the correct *E* enamine isomer consists of three main steps, once the allylamine is N-coordinated to Rh^I: 1) isomerization from κ^1-(N) coordination to η^2-(C,C) coordination of the allylamine; 2) oxidative addition of C^1–H to form a distorted octahedral allylic complex of Rh^{III}; and 3) hydrogen transfer to C^3 (reductive C^3–H elimination). This last step takes place on a η^3-allyl intermediate, but a previous η^3- to σ-allyl ligand isomerization with ligand topomerization is required to reach the orbital interaction that leads to C–H coupling. The two hydrogen-transfer steps (oxidative addition and reductive elimination) have the highest barriers of the overall process. For the oxidative addition, the values obtained for the barriers (**TS5** and **TS6**) are 28.4 and 28.0 kcal mol^{-1}. For the reductive elimination

(**TS13**), the value is 28.6 kcal mol^{-1}, very similar to the oxidative addition barriers.

What about a fully classic allylic mechanism? From what we have discussed so far, the isomerization of allylamine to enamine starts (Scheme 5) with a N-coordinated complex **1N(S)** that isomerizes intramolecularly to a η^2-C=C coordinated one, **1A(S)**, through **TS4** (activation energy equals 14.6 kcal mol^{-1} in acetone). The question arises as to whether **1A(S)** should not be more easily reached by intermolecular associative substitution of a leaving N-coordinated allylamine for an entering η^2-C=C-coordinated allylamine (Scheme 9), in which case, the initial allylamine complex should be considered just a resting state of the catalyst, out of the catalytic cycle, and the isomerization would fully correspond to a classic allylic mechanism.



Scheme 9. Calculation results for the associative substitution of N-coordinated for η^2-C=C coordinated allylamine.

Looking at the calculated energy values in vacuum, it seems that the intermolecular associative substitution in Scheme 9 (**TS1as** = 21.6 kcal mol^{-1}) could be safely discarded in favor of the intramolecular N-triggered process in Scheme 5 (**TS4** = 15.20 kcal mol^{-1}; a dissociative ligand substitution has an even higher value (**TS1dis** = 31.6 kcal mol^{-1}). However, if the values in solvent (acetone) are considered, the decision is much less clear-cut because **TS1as** is greatly stabilized in solvent and falls to a value of 16.3 kcal mol^{-1}, fairly close to the value 14.64 kcal mol^{-1} found in Scheme 5. Yet, two factors are in favor of the N-triggered intramolecular isomerization as represented in Scheme 5: 1) The experimental results found by Noyori show that the reaction is markedly retarded by addition of NEt_3 and is unaffected by the addition of 2-methyl-2-butene;[3] this supports Scheme 5 for the isomerization of **1N(S)** into **1A(S)**, in preference to Scheme 9. 2) The entropic effects are more unfavorable for intermolecular **TS1dis** than for intramolecular **TS4**, again in favor of the mechanism in Scheme 5. Considering Gibbs energies, the values for **TS4** and **TS1as** are 16.4 and 24.0 kcal mol^{-1}, respectively.

Conclusion

Figure 1 shows the energy profiles in solvent (acetone) for the N-triggered mechanism, initially proposed when the process was developed,[3,4] as compared to the allylic mechanism proposed here. The transition states found for the N-triggered mechanism are noticeably higher. Moreover, the product formed is the wrong conformation of the enamine. Consequently, this mechanism [Eq. (3)] should be discarded in favor of the more favorable allylic mechanism [Eq. (2)] in which the intermediate hydride is formed from a C=C-coordinated allylamine. These conclusions are the same whatever the thermodynamic magnitude considered.

It is worth noting, however, that the lowest kinetic barrier to the C=C-coordinated allylamine complex **1A(S)** is not found for a direct C=C coordination of the allylamine through intermolecular ligand substitution, but for an initial N-coordination of the allylamine that then intramolecularly isomerizes to the C=C-coordinated product. Thus, in a way, the mechanism is still N-triggered, although in a very different way than was previously thought. In effect, in the new cycle (Scheme 10), the nitrogen atom of the amine undergoing isomerization remains uncoordinated during the hydrogen transfer from C^1 to C^3. This is in sharp contrast with the old mechanism, in which the nitrogen was the pivotal piece for the whole transformation. The change in coordination mode of the allylamine (N to C=C coordination), and the two high energy processes (the oxidative addition to form the allyl and the reductive elimination to release the enam-

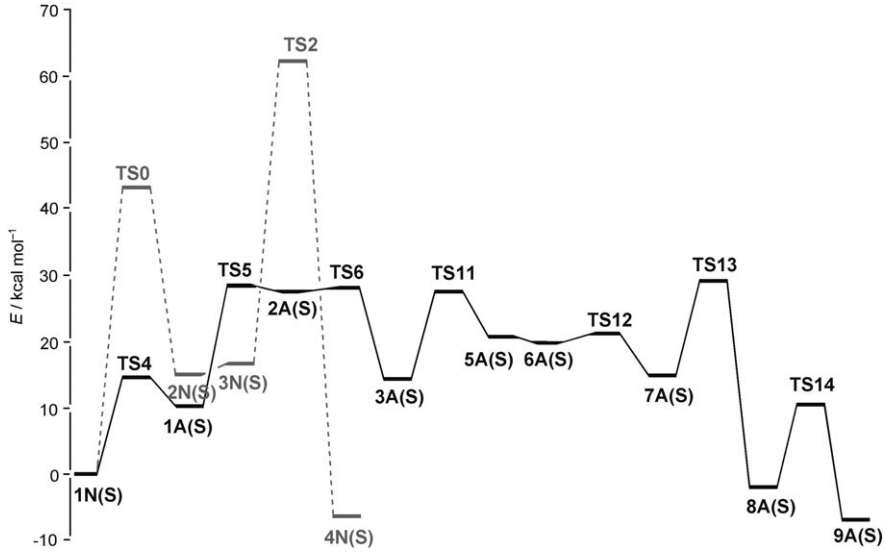
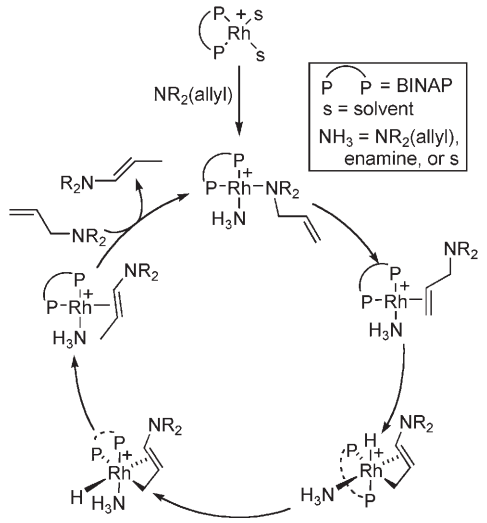


Figure 1. Compared plot of the literature N-triggered (-----) and the N-initiated (——) allyl mechanism proposed here.



Scheme 10. The catalytic cycle for asymmetric isomerization of allylamines to enamines.

ine) are the steps highlighted in the abbreviated catalytic cycle (Scheme 10) as they define the main features of the new mechanism for the Rh-catalyzed isomerization of allylamines.

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[16] Amine complexes are much more stable than acetone complexes. Moreover, if the 4-position was occupied by a molecule of solvent the essence of the discussion would not be altered. This is shown in the Supporting Information.
[17] Note, however, that calculation of bond dissociation energies in solution, albeit possible, is quite sensitive to the computational method. Reactions in which one molecule breaks into two have large entropic effects in the gas phase, and it is not clear to what extent these entropic effects are conserved in solution, taking into account the entropy values arising from solvent effects. See, for instance: A. C. C. Braga, G. Ujaque, F. Maseras, *Organometallics* **2006**, *25*, 3647.
[18] Considering Gibbs energies, the same conclusion is obtained, thus energy barriers of 27.4 and 39.7 kcal mol^{-1} are obtained for the allylic and the N-triggered mechanism, respectively.
[19] The Gibbs energy barrier for this process is 26.5 kcal mol^{-1}, which along with the reductive elimination are the highest energy barriers of the process.

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