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Aromatic-Amide-Derived Olefins as a Springboard: Isomerization-Initiated Palladium-Catalyzed Hydrogenation of Olefins and Reductive Decarbonylation of Acyl Chlorides with Hydrosilane

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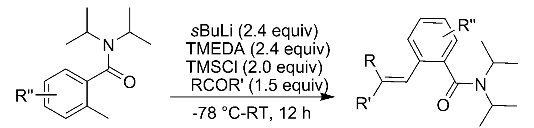
Abstract: A highly efficient catalytic protocol for the isomerization of substituted amide-derived olefins is presented that successfully uses a hydride palladium catalyst system generated from [$PdCl_2(PPh_3)_2$] and $HSi(OEt)_3$. The Z to E isomerization was carried out smoothly and resulted in geometrically pure substituted olefins. Apart from the *cis–trans* isomerization of double bonds, the selective reduction of terminal olefins and activated alkenes was performed with excellent functional group tolerance in the presence of an amide-derived olefin ligand, and the products were obtained in high isolated yields (up to >99 %). Furthermore, the palladium/hydrosilane system was able to promote the reductive decarbonylation of benzoyl chloride when a (Z)-olefin with an aromatic amide moiety was used as a ligand.

Keywords: alkenes · decarbonylation · isomerization · palladium · reduction

Introduction

Highly efficient regio- and chemoselective synthesis of substituted olefins containing different carbon-linked functional groups is still a challenge of particular importance in organic synthesis.[1] Functional alkenes represent key and basic structural features in organic compounds and are arguably the most important and basic building blocks in organic transformations. Preparative methods for the construction of carbon–carbon double bonds have provided useful platforms from which challenging complex targets and synthetic goals can be reached.[2] Especially in recent years, significant achievements have been made in the synthesis of substituted olefins through various protocols, such as the Wittig reaction,[3] the Bamford–Stevens–Shapiro olefination,[4] the Corey–Winter olefination,[5] the Julia–Lythgoe olefination,[6] the Peterson olefination,[7] the Takai reaction,[8] or by alkene metathesis.[9] Unavoidably, in these studies, the olefinations still resulted in mixtures of *cis-* and *trans*-alkenes. It would therefore be very useful to develop a reliable, mild, and facile method for the conversion of alkene mixtures to geometrically pure substituted olefins through isomerization. Although much attention has been focused on the versatile and selective construction of carbon–carbon double bonds, there is a continuous demand to develop synthetic methods for the synthesis of task-specific functional olefins. In addition, the functionalization and transformation of olefins is an everlasting, synthetically important problem in organic synthesis. Specifically, in the field of the application of functional olefins in homogeneous catalysis, the significance of substituted olefins in transition-metal-based catalysis is reflected in the potential application of such olefin-containing compounds as ligands.[10,11]

Very recently, we have reported the preparation of amide-derived substituted olefins by an unprecedented lateral sequential lithiation/silylation/Peterson condensation of tertiary aromatic amides (**1**), which provides an efficient method to build-up functional olefins that could be used as a ligand in palladium catalysis in good yields (Scheme 1).[12] However, similar to previous reports on olefination, mixtures of *cis-* and *trans*-alkenes were formed unavoidably in most cases. Although recent advances have been made using the transition-metal-catalyzed isomerization of olefins or based on photochemistry,[13] it was found that amide-derived olefins containing bulky groups were very stable under many



1

2
55-90% yield
mixtures of (Z/E)-isomers

Scheme 1. The synthesis of amide-derived olefins; TMEDA = tetramethylethylenediamine.

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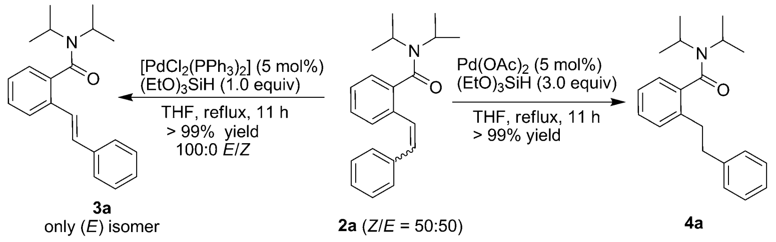
previously reported E/Z interconversion conditions.[12,13] Therefore, the development of a novel protocol of isomerization for the preparation of substituted olefins as a single isomer is highly desired. Herein, we report on the development of a new method of isomerization that is promoted by palladium in the presence of hydrosilanes. Furthermore, inspired by the palladium-catalyzed isomerization of olefins with hydrosilanes, the influence of the amide-derived olefin on the palladium-catalyzed hydrogenation of olefins and reductive decarbonylation of acyl chlorides was studied in this manuscript. Instead of dihydrogen gas, we found that functional olefins with tertiary aromatic amides could act as a highly efficient initiator or promoter in the palladium-catalyzed reduction of activated olefins and terminal non-substituted olefins with hydrosilanes. In addition, in a further study, we found the aromatic amide-derived olefin also exhibited dramatic ligand effects on the reductive decarbonylation of aromatic acyl chlorides to the corresponding aromatics.

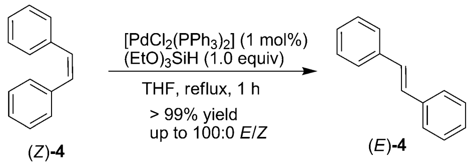


Scheme 2.

Results and Discussion

Isomerization of aromatic-amide-derived olefins: Previous studies have demonstrated that palladium can promote the isomerization of *cis*-alkenes to give *trans*-alkenes.[14] In particular, it was found that palladium hydrides were efficient catalysts in the isomerization of double bonds conjugated to aromatic systems in the presence of hydrogen (H_2) or tributyltin hydride (Bu_3SnH). Very recently, Lindhardt and Skrydstrup[14j] reported the application of an in situ generated bulky palladium(II) hydride catalyst derived from a mixture of $Pd(dba)_2$, $P(tBu)_3$, and isobutyryl chloride in the *cis–trans* isomerization of double bonds. However, the drawbacks of previous protocols are unavoidable, such as highly toxic reagents, high pressure conditions, and expensive palladium complexes, or use of an air-sensitive phosphane ligand; therefore, it is highly desirable to develop a novel and efficient approach to provide an effective palladium catalyst for isomerization that is also beneficial for the chemistry of palladium.

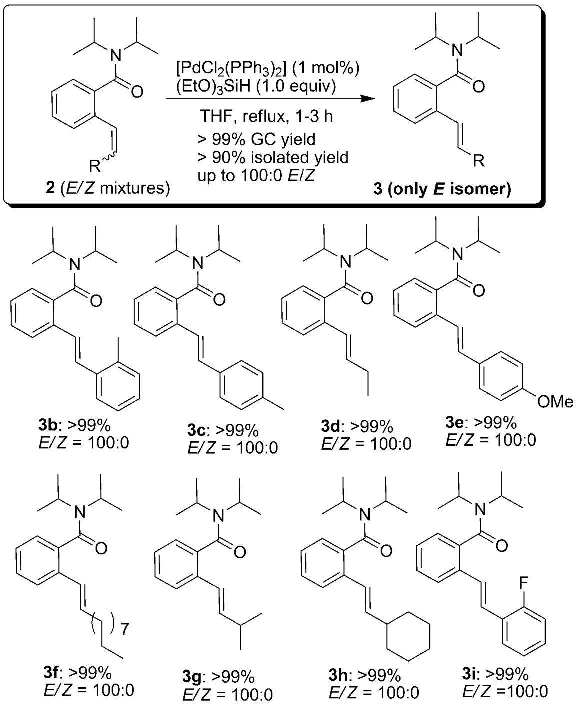
Initially, to obtain the geometrically pure isomer of the functional olefins with tertiary aromatic amides (**2**), we found it was difficult to provide the geometrically pure (*Z*)- or (*E*)-isomer completely under the palladium-catalyzed isomerization conditions reported previously. Inspired by previous findings, we hypothesized that hydrosilane could be used as a hydride source for the in situ formation of a highly efficient palladium hydride catalyst for the isomerization of double bonds. The screening of transition-metal catalysts revealed that [$PdCl_2(PPh_3)_2$] could afford full isomerization of (*Z/E*)-isomer mixtures of **2a** to the corresponding (*E*)-isomer **3a** in the presence of triethoxysilane ($HSi(OEt)_3$; Scheme 2). Control experiments proved that the palladium source, the phosphine, or the $HSi(OEt)_3$ individually or in a combination of two could not catalyze the isomerization. Interestingly, the type of palladium source is also crucial to the *cis–trans* double-bond isomerization because $Pd(OAc)_2$ resulted in complete hydrogenation of **2a** in the presence of excess $HSi(OEt)_3$ (Scheme 2, >99% yield). It was also shown that other transition metal catalysts, such as [$RhCl(PPh_3)$] and $RuCl_3$, were not able to catalyze the isomerization fully to give the geometrically pure (*E*)-isomer (see the Supporting Information). On the basis of these promising findings, we considered that the reaction conditions, [$PdCl_2(PPh_3)_2$], and $HSi(OEt)_3$, could be exploited for the isomerization of (*Z*)-1,2-diphenylethene. The result confirmed that the in situ generated palladium hydride complex was an efficient catalyst for the isomerization of the carbon–carbon double bond of (*Z*)-1,2-diphenylethene, and only (*E*)-1,2-diphenylethene was detected (Scheme 3).



Scheme 3.

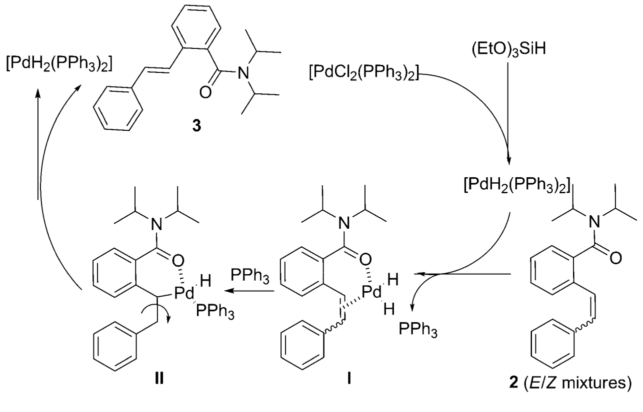
With the optimized conditions in hand, we decide to investigate the reactivity of the palladium catalyst system on different (*Z/E*)-isomer mixtures of olefins with tertiary aromatic amides. In all cases in Scheme 4, applying a 1 mol% palladium catalyst loading promoted the quantitative isomerization of (*Z/E*)-isomer mixtures of **2** in the presence of 1.0 equivalent of $HSi(OEt)_3$. Only the (*E*)-isomer was obtained under the reaction conditions (Scheme 4). Thus, the isomerization makes the amide-derived olefins (**3**) useful in organic synthesis due to the geometrically pure conformation.

An isomerization mechanism of the palladium-catalyzed *cis–trans* conversion of double bonds under a H_2 atmosphere has been reported previously.[14] This mechanism involves the formation of palladium hydride complexes by a repeated olefin addition and β-hydride elimination. In our proposed mechanism of palladium-catalyzed isomerization of amide-



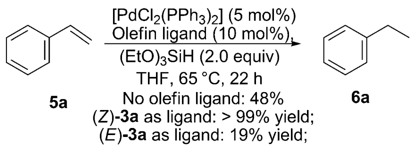
Scheme 4. Palladium-catalyzed isomerization of amide-derived olefins.

derived olefins **2**, an equilibrium between a palladium(dihydrido)–substrate complex and palladium hydride complexes was possible, followed by hydride addition to the olefin and β-hydride elimination to complete the *cis–trans* isomerization (Scheme 5).



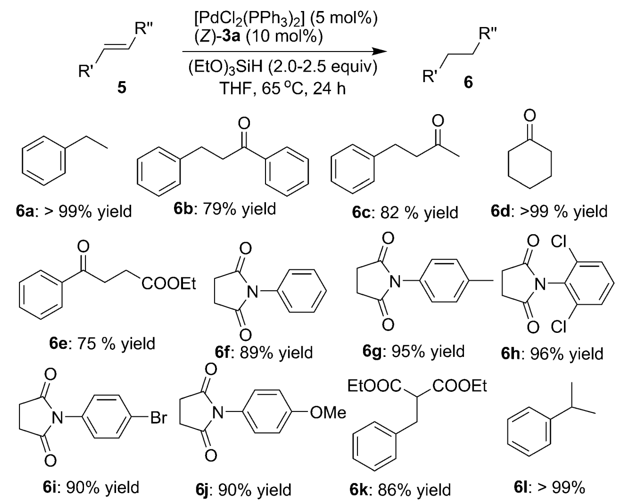
Scheme 5. The mechanistic process of palladium/HSi(OEt)$_3$-promoted *cis–trans* isomerization of double bonds.

Aromatic-amide-derived olefin-assisted palladium-catalyzed reduction of olefins: To elucidate the role of amide-derived olefins (**2**) in organic synthesis based on the mechanistic process of the palladium-catalyzed isomerization, we hypothesized that the palladium(dihydrido)olefin (**2**) complex (**I** or **II**) could be a highly efficient in situ generated palladium intermediate for hydrogenation of terminal olefins or activated olefins, which would be beneficial to the understanding of ligand effects of amide-derived olefins in the isomerization. A previous report indicated that the amide-derived olefin proved to be an effective ligand in the palladium-catalyzed Suzuki cross-coupling reaction.[12] All of this information and our hypothesis prompted us to extend the study of isomerization to selective hydrogenation. With HSi(OEt)$_3$ as the reductant, palladium-catalyzed hydrogenation of styrene was not an easy transformation due to side hydrosilylation. We found that the ratio of selective hydrogenation to hydrosilylation was low (48:15 of yield) in the presence of Pd(OAc)$_2$ as the catalyst. Interestingly, further result showed that only hydrogenated product was detected in the presence of [PdCl$_2$(PPh$_3$)$_2$] under the same reaction conditions, although the yield was moderate (48%). Although palladium-based catalysts are known to catalyze hydrosilylation reactions and coupling reactions, to our surprise, these side reactions were not observed in the presence of amide-derived olefin (*Z*)-**3a**. To obtain an improved conversion, we expected that the amide-derived olefin (*Z*)-**3a** could be used as a ligand on the basis of the illustration of palladium-catalyzed isomerization. As expected, under the same reaction conditions, 1-ethylbenzene was obtained quantitatively and no hydrosilylated product, triethoxyphenylethylsilane, was detected (Scheme 6). Note, that free triphenylphosphine was confirmed in solution, which supported the existence of an equilibrium between the palladium(dihydrido)olefin complex and the palladium(dihydrido) triphenylphosphine complex. Similar to a previous report,[12] the (*Z/E*) isomer mixture of **2a** and (*E*)-**3a** exhibited poorer activity than that of the corresponding (*Z*)-isomer. From these findings, it was concluded that the palladium(dihydrido)olefin complex in situ generated from (*Z*)-**3a** exhibited excellent activity in hydride transfer, thus resulted in the complete hydrogenation of styrene. Notably, when the amide-derived olefin ligand (*Z*)-**3a** was analyzed after the reaction, only (*E*)-**3a** was observed, with no trace of hydrogenated product.



Scheme 6. The effect of the amide-derived olefin in the palladium-catalyzed hydrogenation of styrene.

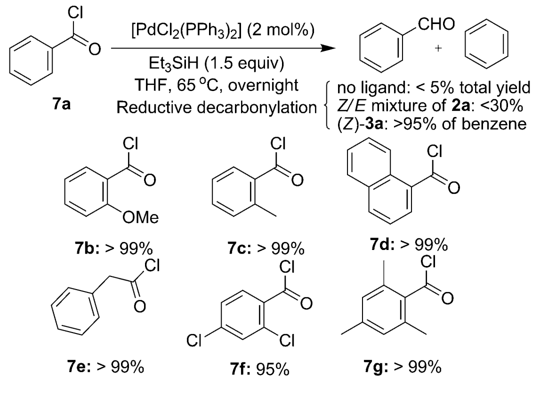
With the optimized conditions established in the palladium-catalyzed reduction of styrene in the presence of hydrosilane and to further investigate the utility of amide-derived olefin (*Z*)-**3a** in the palladium catalyzed hydrogenation of olefins, reduction reactions of activated alkenes and terminal olefins were examined. As shown in Scheme 7, the reduction of these substrates was performed in THF with [PdCl$_2$(PPh$_3$)$_2$], HSi(OEt)$_3$, and aromatic-amide-derived olefin (**2a** or **3a**). In most cases, complete conversion to the



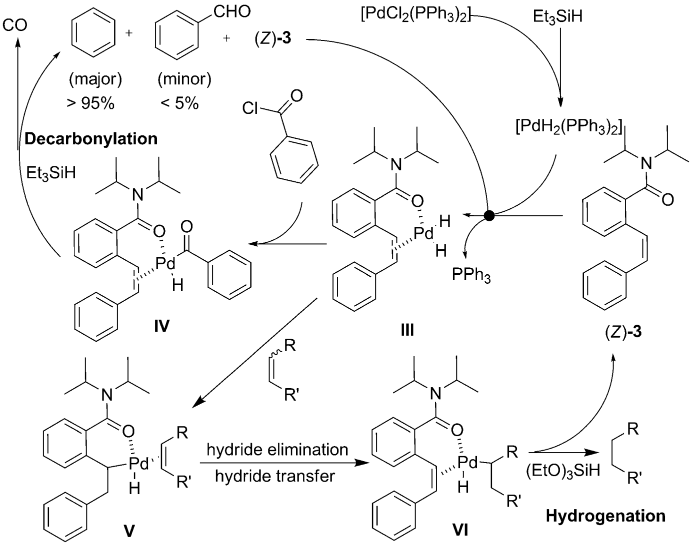
Scheme 7. Palladium-catalyzed hydrogenation of olefins promoted by amide-derived olefin ((Z)-**3a**.

corresponding reduction product was achieved under mild conditions. For example, the reaction of terminal olefins, cyclohexenone, and maleimide-derived alkenes, led to excellent isolated yields. No further purification was necessary to afford pure material. Although aromatic enones underwent complete conversion, trace hydrosilylated product was detected so that the isolated yields of corresponding products were only in the range of 75 to 82 %.

Aromatic-amide-derived olefin-assisted palladium-catalyzed reductive decarbonylation of acyl chlorides: To gain more insight into the palladium(II) hydride catalysis, the effect of the amide-derived olefin ligand was examined in the selective reduction of benzoyl chloride under identical reaction conditions. As shown in Scheme 8, reductive decarbonylation occurred in the presence of olefin ligand (*Z*)-**3a**, whereas the reaction was sluggish with trace conversion and the starting material remained in the absence of olefin ligand or in the presence of (*E*)-**3a**. This may prove to be a useful process for, for example, removal of traceless linkers and unwanted functional groups. Similar to the above findings, in the reductive decarbonylation reaction, the olefin ligand (*Z*)-**3a** was transformed to (*E*)-**3a** in the last step. It appears that because the palladium(dihydrido)olefin complex derived from (*Z*)-**3a** easily adds to benzoyl chloride, then the predominant reaction is palladium-catalyzed decarbonylation. Although the mechanism of the (*Z*)-**3a**-promoted palladium-catalyzed hydrogenation of olefins and reductive decarbonylation of acyl chloride has not yet been confirmed accurately, we assumed that the reaction proceeded through the process illustrated in Scheme 9 on the basis of experimental results. In the catalytic cycle, the amide-derive olefin (*Z*)-**3a** acted as a highly efficient ligand and substrate successively, which means that the amide-derived olefin used in these palladium-catalyzed reduction reactions is not only a simple olefin ligand but also a springboard to activated palladium catalysts.



Scheme 8. Palladium-catalyzed reductive decarbonylation promoted by the amide-derived olefin (*Z*)-**3a**.



Scheme 9. The mechanistic process of the amide-derived olefin (*Z*)-**3a**-promoted palladium-catalyzed hydrogenation of olefins and reductive decarbonylation of acyl chlorides.

Conclusion

A highly efficient catalytic protocol for the isomerization of substituted amide-derived olefins was presented using a hydride palladium catalyst system generated from [$PdCl_2(PPh_3)_2$] and $HSi(OEt)_3$. The *Z* to *E* isomerization was carried out smoothly and resulted in geometrically pure substituted olefins. The hydrosilane-promoted palladium-catalyzed isomerization could also be applied to the isomerization of diphenylethene. Apart from the *cis–trans* isomerization of double bonds, with the aid of the amide-derived olefin ligand, the selective reduction was performed with excellent functional group tolerance and the products were produced in high isolated yields. Furthermore, the palladium/hydrosilane system was able to promote the reductive decarbonylation of benzoyl chloride in the presence of the amide-derived olefin. Although the mechanism via a palladium(dihydrido)olefin complex needs to be supported by direct evidence, reaction results revealed that the in situ generated hydride palladium complex was a key catalyst in the presence of the amide-derived olefin. In other words, the amide-derived olefin used as a special olefin ligand directed palladium-catalyzed selective hydrogenation of activated olefins or terminal olefins and the reductive decarbonylation of acyl chlorides in the presence of hydrosilanes successfully. Finally, based on the above findings and the possible mechanistic process, we have established a novel concept of relay palladium catalysis, that is, the palladium-catalyzed isomerization of an olefin ligand to initiate/activate a palladium-catalyzed organic transformation. Additional investigations are ongoing to obtain more reaction performances and more transformations with regard to the amide-derived olefin with a chiral auxiliary used as a chiral ligand in transition-metal catalysis.

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