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Reduction

A General and Selective Rhodium-Catalyzed Reduction of Amides, *N*-Acyl Amino Esters, and Dipeptides Using Phenylsilane

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Abstract: This article describes a selective reduction of functionalized amides, including *N*-acyl amino esters and dipeptides, to the corresponding amines using simple [Rh(acac)(cod)]. The catalyst shows excellent chemoselectivity in the presence of different sensitive functional moieties.

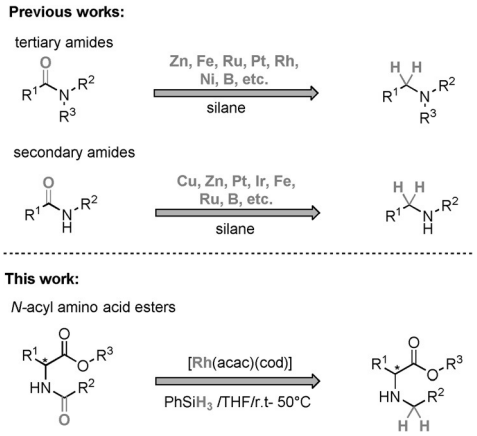
The synthesis of amines and their derivatives is of key importance for the development of novel bioactive compounds, especially in today's pharmaceutical and agrochemical industries.[1] Although numerous methodologies for their synthesis have been reported, novel strategies are still the focus of intense investigations in the scientific community.[2] Amides, through reduction, represent a desirable feedstock for the synthesis of amines due to their wide availability and facile synthesis.[3] In recent years, the hydrosilylation of secondary and tertiary amides has been intensively investigated; however selective reduction of more challenging amides, such as α-amino acid ester derivatives, is still underrepresented today.[4] Notably, these latter substrates represent the key structural unit for peptides and proteins, and they constitute valuable chiral pool intermediates, which are of actual interest as building blocks for drug discovery.[5] Apparently, chemoselective reductions of amino acid derivatives offer straightforward access to a variety of biologically interesting compounds for chemical biology studies and potential pharmaceutical applications.

Regarding the synthesis of *N*-alkylated amino acid derivatives, the classical Strecker reaction is well documented for the racemic products.[6] Nowadays, a plethora of asymmetric versions of this landmark reaction has been developed utilizing both stoichiometric and catalytic amounts of chiral sources. Additionally, the Petasis three-component reactions applying boronic acids, amines, and glyoxylic acid are employed for the diastereoselective synthesis of α-amino acid ester derivatives.[7] Other versatile approaches consist of the addition of electrophiles to glycine enolate derivatives, and conversely, of the addition of nucleophiles to electrophilic glycine templates, both of which have been used successfully as methodologies to access unnatural amino acid derivatives.[8] Moreover, catalytic Mannich reactions offer elegant access for the synthesis of β-amino esters.[9]

Interestingly, the straightforward direct reduction of amido esters has been completely overlooked for the synthesis of chiral amino esters. Obviously, for the reduction of amido ester derivatives to the corresponding amino esters, the tolerance of the ester moiety and racemization are of major concern. For that purpose, the application of stoichiometric amounts of metal hydrides failed due to their poor selectivity.[10] In addition, tedious purifications, removal of concomitant byproducts formed during the reduction might be troublesome. In contrast, catalytic procedures offer alternative strategies for selective reductions under milder conditions and might allow for improved chemo- and regioselectivities.[11] Obviously, catalytic hydrogenation would be an ideal option for this type of reduction but unfortunately lack of a general catalytic hydrogenation of amides requires other methodologies.[12]

Complementary to hydrogenations, catalytic hydrosilylations are operationally simple to perform and often allow for improved chemoselectivity and regioselectivity.[13] Hence, metal-catalyzed hydrosilylations of amides and related carboxylic acid derivatives have received considerable interest during the last decades.[14] More specifically, catalyst systems based on Rh,[15] Ru,[16] Mo,[17] In,[18] Pt,[19] Zn,[20] Cu,[21] Co,[22] and Fe[23] have proven to be effective for the reduction of amides (Scheme 1). It should be noted that the vast majority of these metal catalysts were used only for the reduction of nonchiral tertiary amides.

Recently, we established the first selective hydrosilylation of amino acid esters and peptides using specific rhodium cata-



Scheme 1. Catalytic reduction of amides using silanes.

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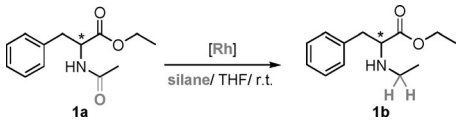
lysts. Although the optimized $[Rh(cod)_2]BF_4$/dppp system tolerated a wide variety of functional groups, only amino acid derivatives with tertiary amides could be reduced.[15d] In continuation of this work and based on our previous experience,[24] we present herein a more general reduction of secondary and tertiary amides, including amino acid esters, dipeptides, and functionalized derivatives.

Initially, we investigated the reduction of *N*-acetyl L-phenyl alanine ethyl ester (**1 a**) towards ethyl 2-(ethylamino)-3-phenylpropanoate (**1 b**) with phenyl silane using various catalysts as a model reaction. Unfortunately, Zn-[20b] and Cu-based[21] catalysts, which have been described for the reduction of secondary amides, proved not to be successful. In order to improve the reactivity, we focused on the use of Rh catalysts (Table 1).[25]

Table 1. Rhodium-catalyzed reduction of *N*-acetyl L-phenylalanine ethyl ester.[a]



1a **1b**

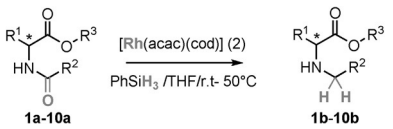
Entry	[Rh] (mol%)	silane (equiv)	Yield [%][b]
1	–	$PhSiH_3$ (2)	–
2	$RhCl_3 \cdot xH_2O$ (2)	$PhSiH_3$ (2)	5
3	$Rh(NO_3)_3 \cdot xH_2O$ (2)	$PhSiH_3$ (2)	20
4	$[Rh(Cl)(PPh_3)_3]$ (2)	$PhSiH_3$ (2)	28
5	[Rh(cod)(*S,S*-deguphos)]BF_4 (2)	$PhSiH_3$ (2)	–
6	[Rh(acac)(cod)] (2)	$PhSiH_3$ (2)	80
7	[Rh(acac)(cod)] (2)	$PhSiH_3$ (1)	55
8	$[Rh(cod)_2]BF_4$ (1.5)	$PhSiH_3$ (2)	–
9	$[RhH(CO)(PPh_3)_3]$ (1.5)	$PhSiH_3$ (2)	–
10	[Rh(acac)(cod)] (2)	Ph_2SiH_2 (2)	60
11	[Rh(acac)(cod)] (2)	TMDS (3)	3
12	[Rh(acac)(cod)] (2)	$(EtO)_2MeSiH$ (3)	–
13	[Rh(acac)(cod)] (2)	$(EtO)_3SiH$ (3)	–
14	[Rh(acac)(cod)] (2)	Et_3SiH (3)	–

[a] Reaction conditions: **1 a** (0.5 mmol), THF (2 mL), r.t., 24 h. [b] Detemined by GC using *n*-hexadecane as an internal standard. acac = acetylacetonate; *S,S*-deguphos = *S,S*-3,4-bis(diphenylphosphino)-1-(phenylmethyl)-pyrrolidine.

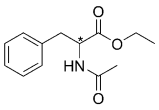
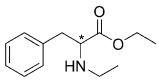
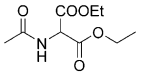
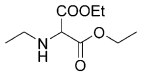
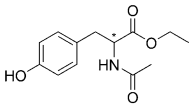
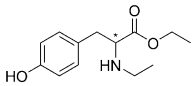
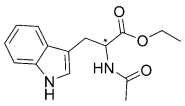
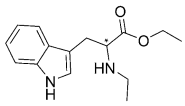
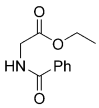
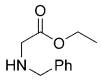
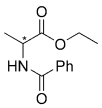
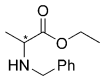
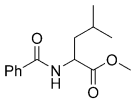
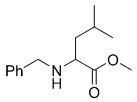
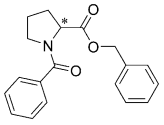
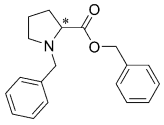
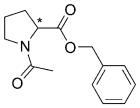
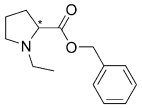
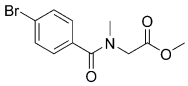
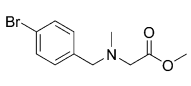
As expected, no activity was found in the absence of any rhodium catalyst (Table 1, entry 1). Applying a catalytic amount of $RhCl_3\ xH_2O$, 5% yield of the corresponding product was achieved (entry 2). The product yield slightly increased on switching to $Rh(NO_3)_3\ xH_2O$ and $[Rh(Cl)(PPh_3)_3]$ (entries 3–4). To our delight, formation of 2-(ethylamino)-3-phenylpropanoate reached 80% in the presence of [Rh(acac)(cod)] (entry 6). Notably, other rhodium complexes, such as [Rh(cod)*S,S*-deguphos]BF_4, $[Rh(cod)_2]BF_4$, and $[RhH(CO)(PPh_3)_3]$ did not lead to any conversion (entries 5, 8–9). Next, applying the commercially available [Rh(acac)(cod)] catalyst, we examined the effect of various silanes for the reduction of *N*-acetyl L-phenyl alanine ethyl ester. In addition to phenyl silane, diphenylsilane showed moderate reactivity. In the presence of other silanes, such as tetramethyldisiloxane (TMDS), $(EtO)_2MeSiH$, $(EtO)_3SiH$, and Et_3SiH, only poor or no reactivity at all was observed (entries 10–14).

Notably, our optimized reaction protocol proceeded smoothly on a 10 mmol scale without special precautions and loss of reactivity (Table 2, entry 1). Removal of the resulting siloxane was easily achieved by treatment of the reaction mixture with saturated ammonium fluoride solution followed by aqueous work up and purification by column chromatography. With optimized conditions in hand, the scope and limitations of this novel Rh-catalyzed reductive hydrosilylation of *N*-acetyl amino

Table 2. Reduction of *N*-acyl amino acid esters.[a]



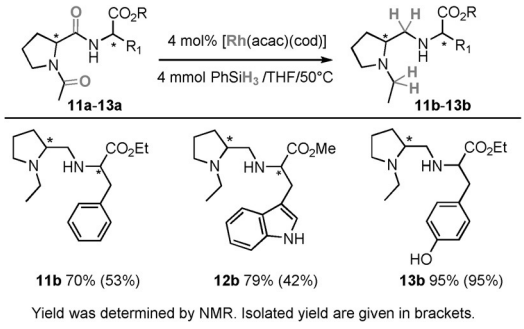
1a-10a **1b-10b**

Entry	Substrates		Products		Yield [%][b]
1		**1 a**		**1 b**	75, 75[c]
2		**2 a**		**2 b**	70
3		**3 a**		**3 b**	74
4		**4 a**		**4 b**	82
5		**5 a**		**5 b**	75
6		**6 a**		**6 b**	73
7		**7 a**		**7 b**	71
8[d]		**8 a**		**8 b**	75
9[d]		**9 a**		**9 b**	73
10[d]		**10 a**		**10 b**	70

[a] Reaction conditions: substrate (0.5 mmol), catalyst (2 mol%), silane (2 mmol), THF (2 mL), 24–72 h, r.t. [b] Isolated yield. [c] 10 mmol scale experiment. [d] 50 °C.

acid esters were explored. Indeed, 10 different amino acid derivatives, including aromatic, heteroaromatic, and aliphatic ones, were smoothly reduced in good yields (up to 82%). In most cases reduction took place at room temperature. Amino acid esters, including phenyl alanine, alanine, tyrosine, tryptophan, leucine, and glycine, led to high yields of the corresponding products. Interestingly, the reduction of three proline and sarcosine derivatives gave best product yields at higher temperature (50 °C; entries 8–10).

Having demonstrated the selective reduction of *N*-acyl amino acid esters, we applied this methodology for the chemoselective reduction of dipeptides. For this purpose, three different dipeptides (Scheme 2, **11a**–**13a**) were synthesized combining *N*-acetyl L-proline and corresponding amino acid esters (Scheme 2). Notably, here the hydrosilylation using



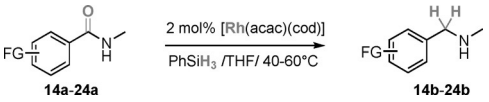
Scheme 2. Reduction of dipeptides.

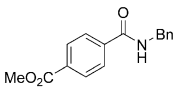
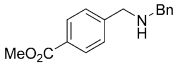
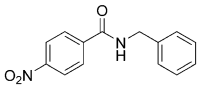
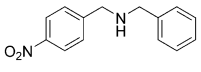
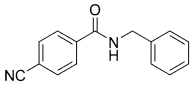
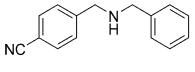
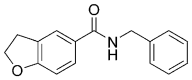
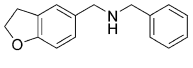
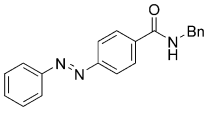
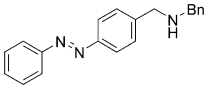
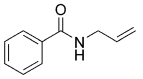
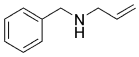
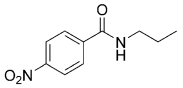
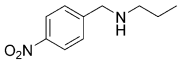
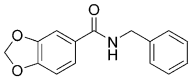
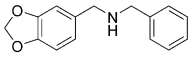
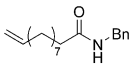
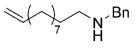
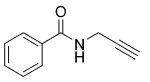
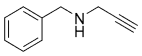
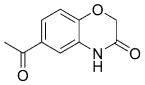
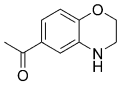
[Rh(acac)(cod)] catalyst proceeded smoothly and the corresponding amino esters were isolated in 42–95% yields. Remarkably, the reduction took place on both amide moieties and in none of the cases we observed any reaction of the ester group. However, in the case of **11b** and **12b**, the difficult purification led to lower isolated yields. Performing the catalytic experiments under mild conditions, sensitive functional groups, such as unprotected indole, and free hydroxyl group in tyrosine are well tolerated too.

Encouraged by all these results, finally we were interested to show the usefulness of our catalytic protocol for the chemoselective reduction of functionalized and structurally diverse secondary amides (Table 3). Steric as well as electronic influences of selected functional groups on the reaction have been studied by positioning these functionalities either at the aryl or at the amine part of the amide moiety. To our delight, nitrile, azo, nitro, ether, and ester substituents were well tolerated without further optimization, providing the corresponding amines in good to excellent yields. In addition, double and triple bonds are not affected under these conditions (entries 6, 9, and 10). Interestingly, even the selective reduction of a secondary amide bond in the presence of a ketone is possible (entry 11).

In summary, we have developed a highly selective rhodium-catalyzed hydrosilylation of secondary amides in the presence of other sensitive functional groups. For the first time, the reduction of secondary α-amido esters to the corresponding α-amino esters is possible under mild reaction conditions in an operational simple way.

Table 3. Chemoselective catalytic reduction of secondary amides.[a]



Entry	Substrates	Products	Yield [%][b]
1		**14a** 	**14b** 75
2		**15a** 	**15b** 72
3		**16a** 	**16b** 73
4		**17a** 	**17b** 72
5		**18a** 	**18b** 70
6		**19a** 	**19b** 70
7		**20a** 	**20b** 73
8		**21a** 	**21b** 74
9		**22a** 	**22b** 75
10		**23a** 	**23b** 68
11		**24a** 	**24b** 47[c]

[a] Reaction conditions: substrate (0.5 mmol), catalyst (2 mol%), silane (2 mmol), THF (2 mL), 24 h, 50 °C. [b] Isolated yield. [c] 48 h, 60 °C.

Experimental Section

A 10 mL dried Schlenk tube containing a stirring bar was charged with the rhodium catalyst (2 mol%) and *N*-acetyl amino acid ester (0.5 mmol). After, the Schlenk tube was vacuumed and purged with argon three times. Under Ar flow, dry THF (2 mL) and $PhSiH_3$ (2 mmol) were added, and the mixture was stirred at r.t.–50 °C for 24 h. Then, the reaction mixture was cooled to room temperature. Next, saturated solution of ammonium fluoride (3 mL) was added very slowly to the reaction mixture (caution! reaction is vigorous and exothermic), and it was kept for overnight stirring. After then

an aqueous work up was done using excess ethyl acetate, and the organic phase was dried by Na_2SO_4 and concentrated under vacuum. The residue was purified by silica gel column chromatography.

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Keywords: amides · esters · hydrosilylation · peptides · rhodium

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