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Efficient and Highly Chemoselective Direct Reductive Amination of Aldehydes using the System Silane/Oxorhenium Complexes

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Abstract: This work reports a novel method for direct reductive amination of aldehydes with silanes catalyzed by several high-valent oxorhenium(V) and oxorhenium(VII) complexes. The catalytic system $\text{PhSiH}_3/\text{ReIO}_2(\text{PPh}_3)_2$ (2.5 mol%) was very efficient for the synthesis of secondary amines and highly chemoselective, tolerating a wide range of functional groups such as $-\text{NO}_2$, $-\text{CF}_3$, $-\text{SO}_2\text{R}$, $-\text{CO}_2\text{R}$,

$-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{CN}$, $-\text{OH}$, $-\text{OCH}_3$, $-\text{SCH}_3$, $-\text{NCOR}$, and double bonds. This novel method was also employed in the synthesis of tertiary amines with moderate yields.

Keywords: amines; C–N bond formation; homogeneous catalysis; oxorhenium complexes; reductive amination; silanes

Introduction

Amines and their derivatives exist in many biologically important molecules, and are relevant intermediates in the synthesis of pharmaceutically active substances, dyes, and fine chemicals. Consequently, the synthesis of amines is an active field in medicinal chemistry and modern organic synthesis.

Direct reductive amination is a powerful tool to synthesize a higher order amine from a carbonyl compound and an amine, which proceeds through the formation of an imine intermediate, followed by an *in situ* reduction. The importance of reductive amination procedures is exemplified by the enormous number of its synthetic uses.

A variety of methods have been developed to accomplish direct reductive amination including catalytic hydrogenation,^[1] or using a reducing agent such as NaBH_4 ,^[2] NaBH_3CN ,^[3] $\text{NaBH}(\text{OAc})_3$,^[4] pyridine- BH_3 .^[5] However, in terms of functional group tolerance, and side reactions, most of these reagents may have one or more drawbacks. For example, catalytic hydrogenation is incompatible with compounds containing other reducible functional groups such as double and triple bonds, nitro, and cyano groups. NaBH_4 sometimes requires harsh reaction conditions, cyanoborohydride is highly toxic and generates toxic by-products such as HCN or NaCN, and pyridine- BH_3

is unstable to heat and must be handled with extreme care.

In contrast, organosilanes are mild and environmentally benign reducing agents, and in recent years, several reagent systems containing silanes such as $\text{Et}_3\text{SiH}/\text{InCl}_3$,^[6] $\text{Et}_3\text{SiH}/[\text{IrCl}(\text{COD})]_2$,^[7] $\text{PhSiH}_3/\text{Bu}_2\text{SnCl}_2$,^[8] $\text{PhSiH}_3/\text{MoO}_2\text{Cl}_2$,^[9] polymethylhydrosiloxane (PMHS)/ $\text{Ti}(\text{O}-i\text{-Pr})_4$,^[10] and polymethylhydrosiloxane (PMHS)/trifluoroacetic acid (TFA)^[11] have also been employed in reductive amination.

Due to the biological and chemical importance of amines, the search for novel catalyst systems, leading to efficient and highly chemoselective methods for their synthesis, remains an important target in organic synthesis.

In recent years, Toste's group^[12] and our group^[13] have demonstrated that oxomolybdenum and -rhenium complexes activate the Si–H and B–H bonds. Toste^[13] has also reported that the catalytic system $\text{PhMe}_2\text{SiH}/\text{ReIO}_2(\text{PPh}_3)_2$ is very efficient for the hydrosilylation of aldehydes and ketones, tolerating several functional groups such as $-\text{NO}_2$, $-\text{Br}$, ester and double bonds. We have also described the efficient hydrosilylation of aldehydes and ketones,^[13] and the reduction of several functional groups such as aromatic nitro compounds,^[14] imines,^[15] amides,^[16] esters,^[17] sulfoxides,^[18,13c] pyridine *N*-oxides,^[18a] and alkenes^[19] to the corresponding amines, alcohols, sul-

fides, pyridines, and alkanes using the catalytic systems silane/oxo-complexes or borane/oxo-complexes.

Very recently, we investigated the catalytic activity of oxo-complexes in C–C, C–S and C–P bond formation. We demonstrated that MoO_2Cl_2 catalyzes Friedel–Crafts acylation and sulfonylation, affording aromatic ketones and sulfones in moderate to good yields.^[20] We also reported the use of MoO_2Cl_2 as an excellent catalyst for the addition of HP(O)(OEt)_2 to aldehydes or imines, producing α -hydroxyphosphonates or α -aminophosphonates in excellent yields.^[21,22] These results show that MoO_2Cl_2 is an excellent catalyst for C–C, C–S and C–P bond formation.

In continuation of our interest in developing organic reductions and C–X bond forming reactions catalyzed by high-valent oxo-complexes, herein, we report a novel method for C–N bond formation through direct reductive amination of aldehydes.

Results and Discussion

The condensation of 4-nitrobenzaldehyde with aniline was chosen as the model reaction for studying the influence of catalysts, silanes and critical reaction parameters such as solvent and temperature (Table 1, Table 2 and Table 3). The progress of the reactions was monitored by thin layer chromatography and by ^1H NMR.

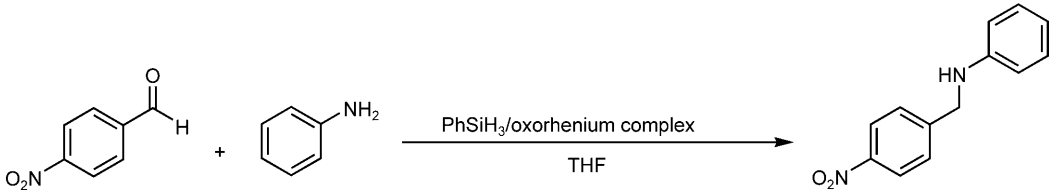
In order to compare the catalytic activity of oxorhenium complexes, the reaction of 4-nitrobenzaldehyde with aniline was carried out with PhSiH_3 (120 mol%) in the presence of the catalysts $\text{ReIO}_2(\text{PPh}_3)_2$, $\text{ReOCl}_3(\text{PPh}_3)_2$, Re_2O_7 , MTO (CH_3ReO_3), and $\text{ReOCl}_3(\text{dppm})$ in refluxing THF under air atmosphere, as summarized in Table 1. In general, all the

oxorhenium complexes were very efficient, affording high conversions of the amine. However, the reaction catalyzed by 2.5 mol% of $\text{ReIO}_2(\text{PPh}_3)_2$ was very fast (10 min), producing the amine with 96% conversion (Table 1, entry 1). A similar reaction using only 1 mol% of $\text{ReIO}_2(\text{PPh}_3)_2$ required 5 h 10 min (Table 1, entry 2). At room temperature, the reductive amination was much slower, taking 15 h (Table 1, entry 3). No reductive amination was observed with phenylsilane in the absence of $\text{ReIO}_2(\text{PPh}_3)_2$ (Table 1, entry 8), demonstrating the catalytic role of the oxorhenium complex.

Direct reductive amination of aldehydes was also studied with several silanes, namely, phenylsilane, dimethylphenylsilane, triethylsilane, triphenylsilane and polymethylhydrosiloxane (PMHS). Of these silanes, phenylsilane and dimethylphenylsilane were the most efficient reagents, affording the desired amine in excellent conversions (Table 2, entries 1 and 2). However, the reaction with PhSiH_3 was much faster, required only 10 min (Table 2, entry 1). Moderate conversions were obtained with Et_3SiH and PMHS (Table 2, entries 3 and 4). No reaction was observed using triphenylsilane (Table 2, entry 5) or in absence of silane (Table 2, entry 6).

The influence of the solvent on the direct reductive amination of aldehydes was also explored (Table 3). THF was the best solvent at reflux temperature, affording the amine in 96% conversion after only 10 min (Table 3, entry 1). At room temperature, this reaction required 15 h (Table 3, entry 2). Chloroform, toluene, and benzene also gave excellent conversions of the amine (Table 3, entries 3–5), however, the reaction in chloroform was much faster, requiring 1 h 30 min. In contrast, dichloromethane and acetonitrile

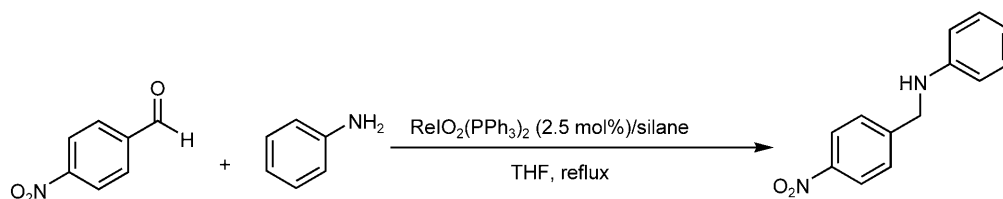
Table 1. Direct reductive amination with phenylsilane catalyzed by oxorhenium complexes.^[a]



Entry	Catalyst	Catalyst [mol%]	Temperature [°C]	Time	Conversion [%] ^[b]
1	$\text{ReIO}_2(\text{PPh}_3)_2$	2.5	reflux	10 min	96
2	$\text{ReIO}_2(\text{PPh}_3)_2$	1.0	reflux	5 h 10 min	91
3	$\text{ReIO}_2(\text{PPh}_3)_2$	2.5	r.t	15 h	95
4	$\text{ReOCl}_3(\text{PPh}_3)_2$	2.5	reflux	1 h	100
5	$\text{ReOCl}_3(\text{dppm})$	2.5	reflux	1 h 10 min	96
6	Re_2O_7	2.5	reflux	1 h 30 min	94
7	MTO	2.5	reflux	2 h 20 min	92
8	without catalyst	–	reflux	6 h 30 min	no reaction

^[a] All reactions were carried out with 1.0 mmol of aldehyde, 1.0 mmol of aniline, and 120 mol% of PhSiH_3 .

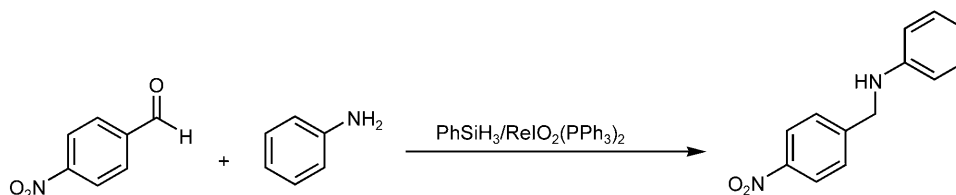
^[b] Conversion was determined by ^1H NMR.

Table 2. Direct reductive amination with different silanes catalyzed by $\text{ReIO}_2(\text{PPh}_3)_2$.^[a]

Entry	Silane	Silane [mol%]	Time	Conversion [%] ^[b]
1	PhSiH_3	120	10 min	96
2	DMPHS	250	30 min	100
3	Et_3SiH	300	24 h	65
4	PMHS	200	24 h	51
5	Ph_3SiH	250	18 h	no reaction
6	without silane	–	6 h 30 min	no reaction

^[a] All reactions were carried out with 1.0 mmol of aldehyde, 1.0 mmol of aniline, and 2.5 mol% of $\text{ReIO}_2(\text{PPh}_3)_2$.

^[b] Conversion was determined by ^1H NMR.

Table 3. Direct reductive amination with phenylsilane and $\text{ReIO}_2(\text{PPh}_3)_2$ in different solvents.^[a]

Entry	Solvent	Temperature [°C]	Time	Conversion [%] ^[b]
1	THF	reflux	10 min	96
2	THF	r.t.	15 h	95
3	CHCl_3	reflux	1 h 30 min	92
4	toluene	reflux	9 h	87
5	benzene	reflux	9 h	85
6	CH_2Cl_2	reflux	1 h	60
7	CH_3CN	reflux	24 h	47

^[a] All reactions were carried out with 1.0 mmol of aldehyde, 1.0 mmol of aniline, 120 mol% of PhSiH_3 , and 2.5 mol% of $\text{ReIO}_2(\text{PPh}_3)_2$.

^[b] Conversion was determined by ^1H NMR.

only afforded the amine in moderate conversions (Table 3, entries 6 and 7).

To evaluate the general applicability of the catalytic system $\text{PhSiH}_3/\text{ReIO}_2(\text{PPh}_3)_2$ (2.5 mol%), the direct reductive amination was explored with a variety of aldehydes and aniline (Table 4). Generally, good to excellent yields of secondary amines were obtained under the optimized reaction conditions, including aldehydes bearing electron-withdrawing or electron-donating groups. The reactions were very fast (10–40 min), except the reductive amination of 4-cyanobenzaldehyde that required 7 h (Table 4, entry 6).

Reductive amination of aldehydes containing several functional groups such as $-\text{NO}_2$, $-\text{CF}_3$, $-\text{SO}_2\text{R}$, $-\text{CO}_2\text{R}$, $-\text{Br}$, $-\text{CN}$, $-\text{OCH}_3$, $-\text{SCH}_3$, $-\text{NCOR}$ were

successfully accomplished with the catalytic system $\text{PhSiH}_3/\text{ReIO}_2(\text{PPh}_3)_2$ (2.5 mol%) (Table 4, entries 1–6 and 8–10), showing the high chemoselectivity of this novel methodology.

The substrate versatility of this novel method was further demonstrated by the chemoselective reductive amination of cinnamaldehyde with aniline in 79% yield (Table 4, entry 11). Another interesting result was the reductive amination of ferrocenecarboxaldehyde with aniline in 72% yield (Table 4, entry 12).

Reductive amination of 4-methoxybenzaldehyde was also explored using different anilines with the system $\text{PhSiH}_3/\text{ReIO}_2(\text{PPh}_3)_2$ (2.5 mol%) (Table 5). All these reactions gave good to excellent yields of the corresponding amine. The reactions carried out

Table 4. Direct reductive amination of aldehydes with the catalytic system $\text{PhSiH}_3/\text{ReIO}_2(\text{PPh}_3)_2$.^[a]

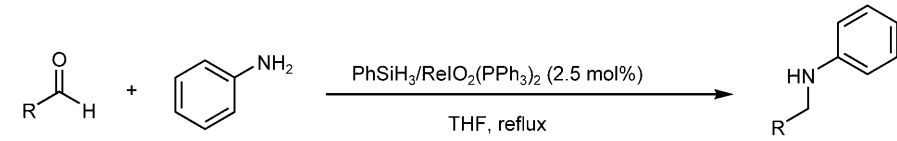
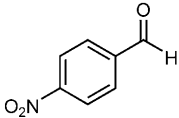
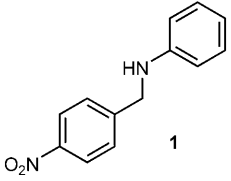
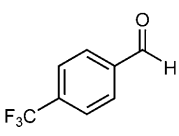
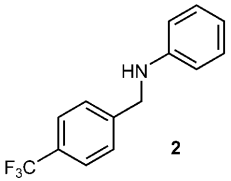
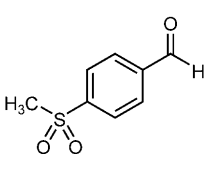
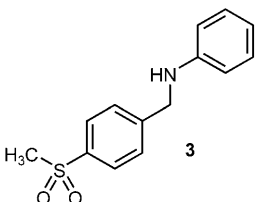
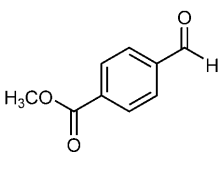
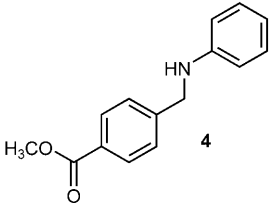
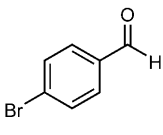
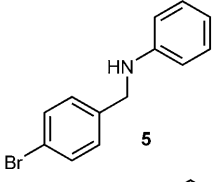
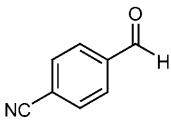
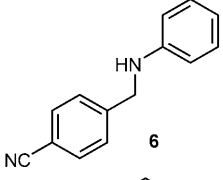
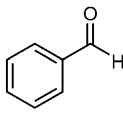
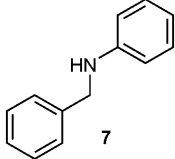
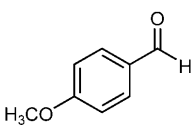
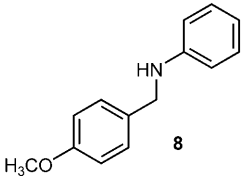
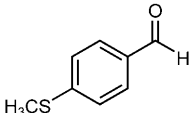
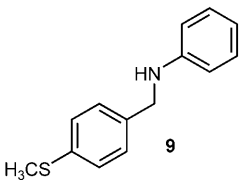
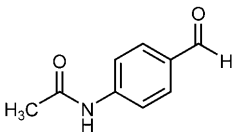
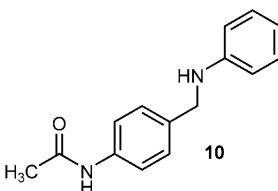
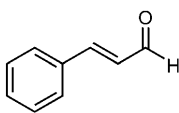
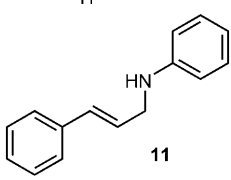
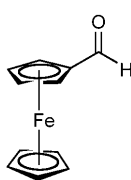
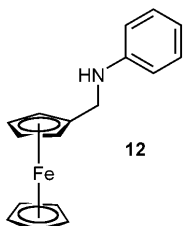
				
Entry	Aldehyde	Product	Time	Yield [%] ^[b]
1			10 min	90
2			20 min	89
3			5 min	83
4			15 min	84
5			40 min	82
6			7 h	90
7			10 min	87
8			5 min	87

Table 4. (Continued)

Entry	Aldehyde	Product	Time	Yield [%] ^[b]
9			10 min	82
10			10 min	73
11			30 min	79
12			30 min	72

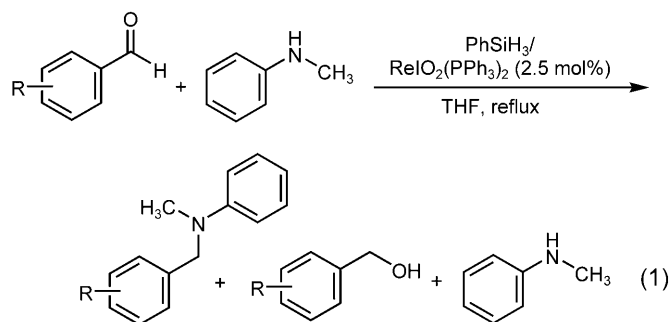
^[a] All reactions were carried out with 1.0 mmol of aldehyde, 1.0 mmol of aniline, 120 mol% of PhSiH₃, and 2.5 mol% of ReIO₂(PPh₃)₂.

^[b] Isolated yield.

with anilines containing electron-withdrawing groups were much faster (Table 5, entries 2–5) than the reactions with anilines containing electron-donating groups (Table 5, entries 6–8).

Finally, we investigated the reaction of *N*-methylaniline with several aldehydes in order to test the efficiency of the catalytic system PhSiH₃/ReIO₂(PPh₃)₂ in the synthesis of tertiary amines by direct reductive amination (Table 6). The reactions were carried out with different aromatic aldehydes bearing electron-withdrawing or electron-donating groups, affording the corresponding tertiary amines in moderate yields in few minutes (5–20 min). A small amount of *N*-methylaniline and alcohol, resulting of the reduction of aldehyde with the system PhSiH₃/ReIO₂(PPh₃)₂ was also obtained as secondary products [Eq. (1)]. In order to minimize the amount of alcohol formed, the reductive amination of 4-methoxybenzaldehyde and *N*-methylaniline was carried out by slowly addition of the silane. However, similar yields of alcohol were obtained.

Several experiments were carried out in order to ascertain some fundamental mechanism aspects of



this reductive amination. No reaction was observed when 4-nitrobenzaldehyde and aniline was treated with phenylsilane without catalyst (Table 1, entry 8) or when 4-nitrobenzaldehyde and aniline was treated with 2.5 mol% of ReIO₂(PPh₃)₂ without silane (Table 2, entry 6), after 6 h 30 min. These results show that silane and ReIO₂(PPh₃)₂ play an active role in the reduction.

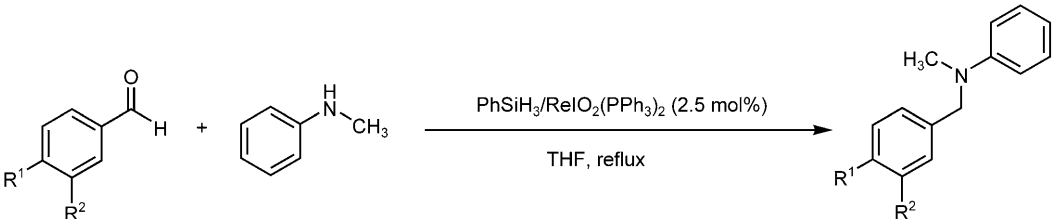
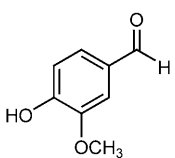
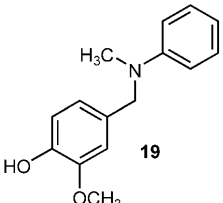
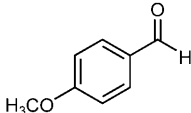
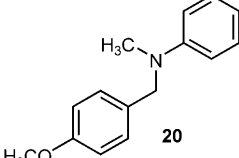
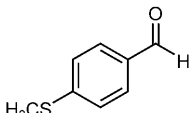
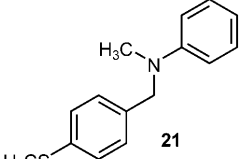
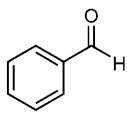
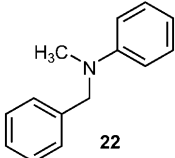
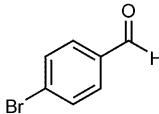
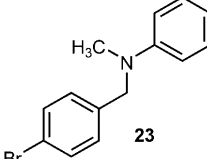
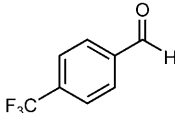
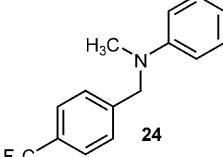
The previous works of Toste^[12] have demonstrated that ReIO₂(PPh₃)₂ activates the Si–H bond of silanes, producing the hydride species

Table 5. Direct reductive amination of 4-methoxybenzaldehyde with different anilines using the catalytic system $\text{PhSiH}_3/\text{ReIO}_2(\text{PPh}_3)_2$.^[a]

Entry	Aniline	Product	Time	Yield [%] ^[b]
1		 8	5 min	87
2		 13	5 min	93
3		 14	5 min	93
4		 15	5 min	94
5		 16	35 min	94
6		 17	1 h 15 min	91
7		 18	2 h 30 min	75

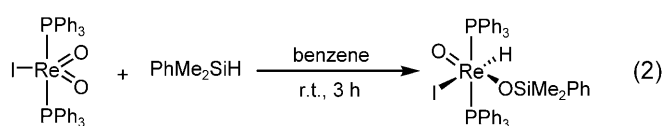
^[a] All reactions were carried out with 1.0 mmol of aldehyde, 1.0 mmol of aniline, 120 mol% of PhSiH_3 , and 2.5 mol% of $\text{ReIO}_2(\text{PPh}_3)_2$.^[b] Isolated yield.

Table 6. Direct reductive amination of aldehydes with *N*-methylaniline using the catalytic system $\text{PhSiH}_3/\text{ReIO}_2(\text{PPh}_3)_2$.^[a]

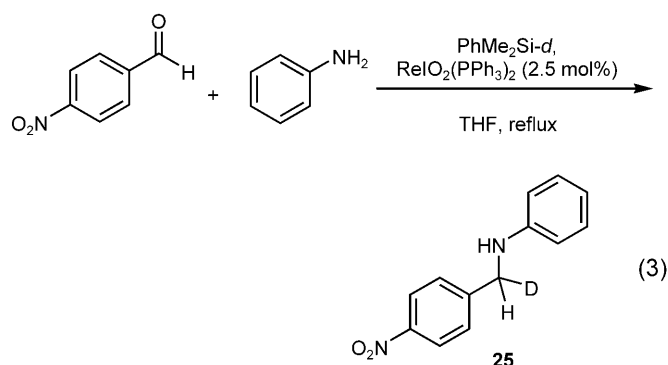
				
Entry	Aldehyde	Product	Time	Yield [%] ^[b]
1		 19	5 min	62
2		 20	10 min	64
3		 21	10 min	65
4		 22	20 min	64
5		 23	10 min	59
6		 24	20 min	65

^[a] All reactions were carried out with 1.0 mmol of aldehyde, 1.0 mmol of *N*-methylaniline, 120 mol% of PhSiH_3 , and 2.5 mol% of $\text{ReIO}_2(\text{PPh}_3)_2$.

^[b] Isolated yield.



$(\text{PPh}_3)_2(\text{O})(\text{I})\text{Re}(\text{H})\text{OSiMe}_2\text{Ph}$ [Eq. (2)]. Based on this result, and to investigate the reduction of the imine intermediate by a hydride species, we carried out the reductive amination of 4-nitrobenzaldehyde with aniline using dimethylphenylsilane-*d* and



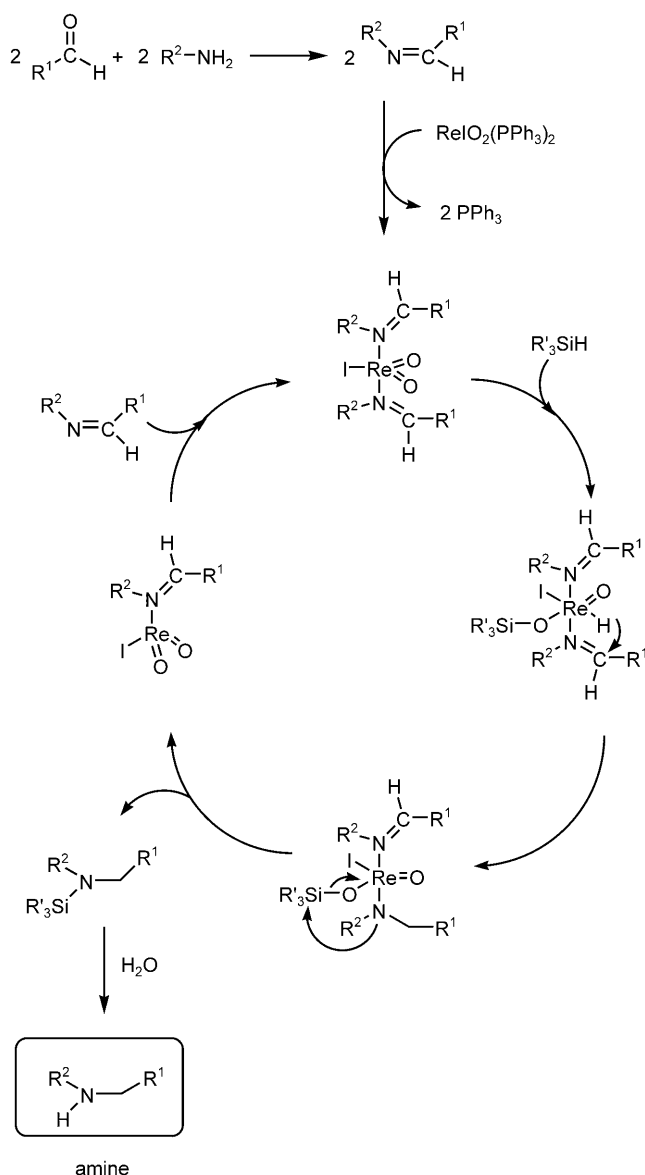
2.5 mol% of $\text{ReIO}_2(\text{PPh}_3)_2$ in refluxing THF [Eq. (3)]. This reaction resulted in the incorporation of the deuterium only in the carbon of the double bond, as confirmed by ^1H NMR. This result is consistent with the hydrosilylation of the imine to give an intermediate *N*-silylamine, followed by a rapid hydrolysis, probably, due to the presence of a trace of water in the reaction mixture.

A plausible mechanism (Scheme 1) for the direct reductive amination of aldehydes with the catalytic system $\text{PhSiH}_3/\text{ReIO}_2(\text{PPh}_3)_2$ should initiate by the formation of the imine, and coordination of this molecule to the catalyst by substitution of the two phosphines, affording the complex $\text{ReIO}_2(\text{imine})_2$. In the second step, the hydride species $(\text{imine})_2(\text{O})\text{IRe}(\text{H})\text{OSiR}_3$ is formed as result of the addition of the Si–H bond of the silane to one of the oxorhenium bonds. This reaction is similar to the formation of the hydride $(\text{PPh}_3)_2(\text{O})\text{IRe}(\text{H})\text{OSiMe}_2\text{Ph}$ reported by Toste,^[12] reacting $\text{ReIO}_2(\text{PPh}_3)_2$ with PhMe_2SiH [Eq. (2)].

In the next step occurs the hydrosilylation of the imine, followed by hydrolysis to the corresponding amine. Finally, the $\text{ReIO}_2(\text{imine})$ species formed will be stabilized by the entry of another molecule of imine, regenerating the dioxorhenium complex $\text{ReIO}_2(\text{imine})_2$.

Conclusions

In conclusion, we have developed a new and efficient method for direct reductive amination of aldehydes to the corresponding secondary amines using the catalytic system silane/oxorhenium(V) and oxorhenium(VII) complexes. This mild and practical method is highly chemoselective, tolerating a large range of functional groups such as $-\text{NO}_2$, $-\text{CF}_3$, $-\text{SO}_2\text{R}$, $-\text{CO}_2\text{R}$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{CN}$, $-\text{OH}$, $-\text{OCH}_3$, $-\text{SCH}_3$, $-\text{NCOR}$, and double bond. This novel methodology was also applied to the synthesis of tertiary amines in moderate yields.



Scheme 1. Proposed catalytic cycle for the direct reductive amination of aldehydes with the system silane/ $\text{ReIO}_2(\text{PPh}_3)_2$.

Other advantages of this procedure include high isolated yields, low catalyst loading (2.5 mol%), fast reactions, simple experimental operation, stability of the catalysts towards air and moisture, allowing the reaction to be carried out under air atmosphere.

In comparison to the other procedures reported in the literature, this method is more chemoselective than some hydrogenation systems in the reductive amination of substrates containing double bonds or nitro, cyano, and halo groups. Furthermore, the reactions carried out with our catalytic system were much faster, using less amount of catalyst and silane, than the method reported in the literature employing the

system $\text{PhSiH}_3/\text{MoO}_2\text{Cl}_2$.^[9] All these features make this method an attractive and useful alternative in organic synthesis.

The results obtained extend the scope of the use of high-valent oxorhenium complexes as effective catalysts for C–N bond formation. Further applications of the catalytic system silane/oxo-rhenium complexes to other organic reductions and C–X bond forming reactions are now in progress in our group.

Experimental Section

General Procedure for Direct Reductive Amination of Aldehydes with $\text{PhSiH}_3/\text{ReIO}_2(\text{PPh}_3)_2$

To a mixture of aldehyde (1.0 mmol), aniline (1.0 mmol) and $\text{ReIO}_2(\text{PPh}_3)_2$ (2.5 mol%) in THF (3 mL) at reflux temperature was added PhSiH_3 (120 mol%). The reaction mixture was stirred under air atmosphere (the reaction times are indicated in Table 4, Table 5, and Table 6) and the progress of the reaction was monitored by TLC and ^1H NMR. Upon completion, the reaction mixture was evaporated and purified by silica gel column chromatography with the appropriate mixture of *n*-hexane and ethyl acetate to afford the amines.

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