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Amine Synthesis through Mild Catalytic Hydrosilylation of Imines using Polymethylhydroxysiloxane and $[RuCl_2(arene)]_2$ Catalysts

Bin Li, Jean-Baptiste Sortais, Christophe Darcel,* and Pierre H. Dixneuf[a]

Dedicated to Prof. Hubert Le Bozec, a pioneer in the field of metal complexes for nonlinear optics, on the occasion of his 60th birthday

The development of synthetic strategies toward amines under mild and green conditions is of interest in many areas, such as the production of natural products, agrochemicals, pharmaceuticals, and medicinal compounds. Reductive amination of carbonyl derivatives in the presence of primary amines, through sequential condensation/catalytic reduction,[1] constitutes a basic method for producing substituted amines, but it often requires drastic reaction conditions. Tremendous progress in amine synthesis has recently been achieved using transition-metal catalyzed C–N bond formation, in particular in the field of Pd-catalyzed Buchwald–Hartwig[2] and Cu-catalyzed Ullman reactions.[3]

An alternative solution arises from the transition-metal catalyzed reduction of imines, easily produced from a variety of aldehydes and ketones, through hydrogenation[4,5] or hydrogen transfer[6] promoted by catalysts such as ruthenium, iridium, and rhodium; this is one of the most ubiquitous protocols in organic synthesis to produce amines. Whereas hydrogenation is the most desired reduction process from an economical and environmental point of view, catalytic hydrosilylation,[7] which does not require autoclave pressure, can be an interesting alternative, mainly when the reaction is performed with polymethylhydroxysiloxane (PMHS) under mild conditions and under air. PMHS is not only an inexpensive and abundant hydrosilane source arising from the silicone industry, but it is stable to air and water, soluble in most organic solvents, and a non-toxic reducing reagent.[8] In addition to the reported hydrosilylation of amides,[9] hydrosilylation of imines has been performed under smooth conditions in the presence of various metal catalysts;[10–16] however, a further desilylation step was required to obtain the amines. There have been only a few reports on imine hydrosilylation using ruthenium-based complexes.[17,18]

We have recently shown that $[RuCl_2(p\text{-cymene})]_2$ is able to efficiently catalyze the hydrosilylation of bulky imines in diethyl ether at room temperature in the presence of Ph_2SiH_2, leading to the corresponding amines following a desilylation step (NaOH/MeOH).[19] The use of an inexpensive, abundantly available, safe, and stable reducing silylating agent, such as PMHS, should make this approach highly attractive for a green catalysis point of view. Notably, PMHS has recently been used in the catalytic reduction of imides into amines.[20]

Herein, we report that: i) the easily available $[RuCl_2(p\text{-cymene})]_2$ complex[21] is an efficient catalyst for the hydrosilylation of imines using the stable and safe hydrosilane reagent PMHS, and ii) the reaction takes place simply in ethanol, under air, at room temperature, and without further basic desilylation step, leading to a variety of functional amines arising from aldimines and ketimines.

The search for a catalytic system allowing the hydrosilylation of imine **1a** directly into amine **2a** with Ph_2SiH_2 and PMHS under mild conditions was undertaken. Our successful results with ruthenium(II)-based catalysts are displayed in Table 1.

Firstly, it was shown that $[Ru(OAc)_2(p\text{-cymene})]$ in the presence of Ph_2SiH_2 was not effective for the hydrosilylation of imine **1a**, whereas $[RuCl_2(p\text{-cymene})]_2$ appeared to be an efficient catalyst in diethyl ether (Table 1, entries 1 and 2); however, desilylation with NaOH/MeOH was still required. When the reaction was performed in methanol, ethanol, or more importantly in ethanol under air using $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol%), the reaction was complete after 0.5 h at room temperature, and directly gave the amine (Table 1, entries 3–5). As PMHS is a less expensive and greener hydrosilylation reagent than Ph_2SiH_2,[8] it was then evaluated under closely related conditions. The reaction required 2 h at room temperature to reach completion (Table 1, entries 6 and 7). The amount of catalyst could be decreased to 1 mol% in ethanol under air to reach complete conversion and amine **2a** was obtained in 90% isolated yield (Table 1, entry 8). However, a shorter reaction time and/or decreasing the amount of catalyst (0.5 mol%) led to lower conversions (Table 1, entries 9–11). Other catalysts, such as $[Ru(OAc)_2(p\text{-cymene})]$ or $[RuCl_2(PMe_3)(p\text{-cymene})]$, were ineffective for this reaction (Table 1, entries 12 and 13) in the presence of PMHS.

The reaction of $[RuCl_2(p\text{-cymene})]_2$ with PMHS under air in ethanol (Table 1, entry 8) offered the best catalytic activity to produce amine **2a** at room temperature. These conditions were applied to a variety of aldimines **1** to directly produce amines **2**. The results are shown in Table 2.

Aldimines **1a** and **1h** were reduced at room temperature for 2 h to give good isolated yields of 90 and 88% for **2a** and **2h**, respectively (Table 2, entries 1 and 8). This hydrosilylation reaction tolerated $sp^2C–X$ (halide) bonds to produce amines **2b**, **2c**, and **2i** in good yields (Table 2, entries 2, 3, and 9). In the presence of cyano and nitro electron-withdrawing groups, the hydrosilylation was more difficult to perform, and 2 mol% of ruthenium(II) catalyst was used with a longer reaction time to reach satisfactory yields for **2d** and **2e** (87 and 69%, respec-

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[a] B. Li, Dr. J.-B. Sortais, Prof. Dr. C. Darcel, Prof. Dr. P. H. Dixneuf
Catalyse et Organométalliques, Institut Sciences Chimiques de Rennes
UMR 6226 CNRS-Université de Rennes 1, Ave Général Leclerc
35042 Rennes Cedex (France)
Fax: (+) 33223236939
E-mail: christophe.darcel@univ-rennes1.fr

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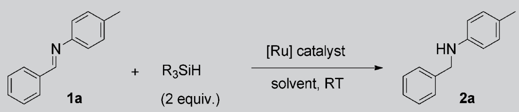
Table 1. Optimization of the ruthenium-catalyzed hydrosilylation of imine **1a** into amine **2a** with Ph_2SiH_2 and PMHS.[a]



Entry	Catalyst	Amount used [mol %]	Silane	Solvent	Time [h]	Conv. [%][b]
1	$Ru(OAc)_2$(*p*-cymene)	5	Ph_2SiH_2	1) Et_2O (1 mL) 2) MeOH + NaOH	16	15
2	[$RuCl_2$(*p*-cymene)]$_2$	2.5	Ph_2SiH_2	1) Et_2O (1 mL) 2) MeOH + NaOH	16	99
3	[$RuCl_2$(*p*-cymene)]$_2$	2.5	Ph_2SiH_2	MeOH (2 mL)	0.5	99
4	[$RuCl_2$(*p*-cymene)]$_2$	2.5	Ph_2SiH_2	EtOH (2 mL)	0.5	99
5	[$RuCl_2$(*p*-cymene)]$_2$	2.5	Ph_2SiH_2	EtOH (2 mL) under air	0.5	99
6	[$RuCl_2$(*p*-cymene)]$_2$	2.5	PMHS	EtOH (2 mL)	2	99
7	[$RuCl_2$(*p*-cymene)]$_2$	2.5	PMHS	EtOH (2 mL) under air	2	99
8	[$RuCl_2$(*p*-cymene)]$_2$	1	PMHS	EtOH (2 mL) under air	2	99 (90)[c]
9	[$RuCl_2$(*p*-cymene)]$_2$	0.5	PMHS	EtOH (2 mL) under air	2	62[d]
10	[$RuCl_2$(*p*-cymene)]$_2$	1	PMHS	EtOH (2 mL) under air	1.5	94
11	[$RuCl_2$(*p*-cymene)]$_2$	1	PMHS	EtOH (2 mL) under air	1	85
12	$Ru(OAc)_2$(*p*-cymene)	2	PMHS	EtOH (2 mL) under air	2	0
13	$RuCl_2(PMe_3)$(*p*-cymene)	2	PMHS	EtOH (2 mL) under air	2	0

[a] Imine substrate (0.25 mmol), [Ru] catalyst, silane (0.5 mmol), solvent. [b] Determined by using ^1H NMR spectroscopy and GC. [c] Isolated yield. [d] Imine substrate (0.5 mmol), silane (1 mmol).

tively, Table 2, entries 4 and 5). The overall reduction was favored by electron-donating groups (Table 2, entries 6 and 7). When the reaction was performed with the imine functionality bearing a methyl group in the *ortho*-position of the *N*-aryl substituent, the corresponding amine was obtained in 94 % yield, which shows that *ortho* substituents do not hamper the reaction (Table 2, entry 10). This hydrosilylation reaction could also be applied to an imine containing a functional group, such as a furan or bulky ferrocenyl group, to afford amines **2k** and **2l**, which were isolated in 78 and 93 % yields, respectively. By contrast, with 4-methoxy-*N*-(pyridin-2-ylmethylidene)aniline (**1m**), no reaction occurred, which is likely due to the coordination of the pyridine-imine as a bidentate ligand to the ruthenium center poisoning the ruthenium(II) catalyst (Table 2, entry 13).

Interestingly, the hydrosilylation reaction tolerates functional ketone and ester groups of imines **1n** and **1o**, and the corresponding amines, **2n** (86 %) and **2o** (90 %), were directly obtained without alteration of the carbonyl moieties (Table 2, entries 14 and 15)

More importantly, whereas ruthenium(II) catalysts have been use for the hydrosilylation of alkenes,[17f] this ruthenium(II) hydrosilylation of imines appeared to be very chemoselective in the presence of a C=C bond, as demonstrated in the hydrosilylation of the unsaturated imine **1p**, which led to the corresponding unsaturated amine **2p** with good conversion and yield, retaining the non-reduced double bond (Table 2, entry 16).

The above described catalytic system has been evaluated for the PMHS hydrosilylation of ketimine **3a**, which is expected to be more difficult to hydrosilylate than the corresponding aldimines. The use of catalyst [$RuCl_2$(*p*-cymene)]$_2$ (1 mol %) with PMHS at room temperature for 4 h led only to 60 % of conversion of **3a**, but a simple increase of the catalyst amount to 2 mol % at room temperature for 4 h, in ethanol and under air, allowed complete conversion of the imine **3a**, and amine **4a** was isolated in 97 % yield, (Table 3, entry 1).

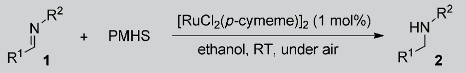
The hydrosilylation of a variety of ketimines **3** with catalyst [$RuCl_2$(*p*-cymene)]$_2$ (2 mol %) with PMHS (2 equiv.) in ethanol under air, was performed and the results are shown in Table 3. After 4 h at room temperature, the amines **4b**–**d**, and **4f** were directly obtained in 91–97 % yields (Table 3, entries 2–4 and 6). The formation of amines **4e** and **4g** containing an electron-donating group required a longer reaction time (10–20 h) to reach good yields (Table 3, entries 5 and 7). However, naphthyl amine **4h** was easily obtained in good yield (99 %) after only 4 h (Table 3, entry 8). The ferrocenyl ketimine **3i** was quantitatively hydrosilylated after 20 h, and amine **4i** was isolated in 87 % yield. The imines **3j** and **3k**, arising from the dialkylketones pentan-3-one and α-tetralone, also required longer reaction times, but the corresponding amines **4j** and **4k** were isolated in good yields (85 and 87 %, respectively) (Table 3, entries 10 and 11).

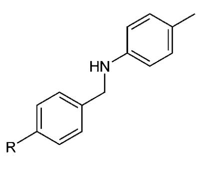
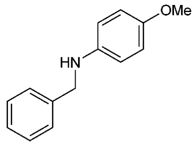
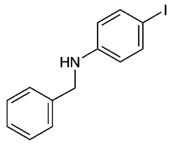
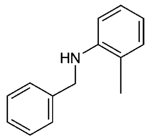
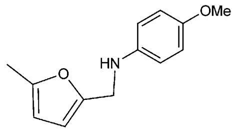
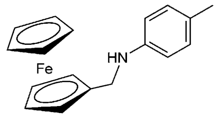
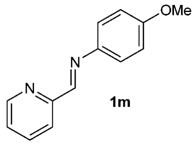
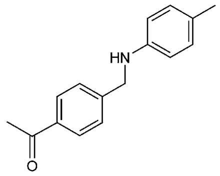
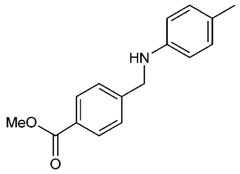
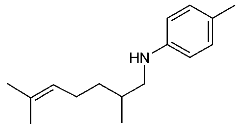
The above results show that the easily available and stable [$RuCl_2$(*p*-cymene)]$_2$ complex is an excellent catalyst for the direct hydrosilylation of aldimines and ketimines into secondary amines using PMHS as the hydrosilane source. The conditions are compatible with green processes because of the use of ethanol as the solvent, under air, at room temperature, and PMHS as one of the greenest hydrosilylation reagents. Interestingly, the reaction is compatible with a wide range of functional groups, such as nitro, cyano, and halide; the easy-to-reduce ketone, ester, and alkene functions are tolerated; and amines arising from dialkyl ketones can be easily obtained.

Experimental Section

A typical procedure for ruthenium-catalyzed hydrosilylation of imines was as follows: [$RuCl_2$(*p*-cymene)]$_2$ (0.005 mmol, 3.1 mg, 1 mol %), *N*-benzylidenetoluidine (0.5 mmol, 98 mg), PMHS (1 mmol, 60 μL), and HPLC-grade ethanol (2 mL) were introduced in a Schlenk tube equipped with magnetic stirring bar under air. The reaction mixture was stirred at room temperature for 2 h. The conversion of the reaction was then analyzed by using gas chromatography. The solvent was evaporated under vacuum, and the desired product was purified by using column chromatography.

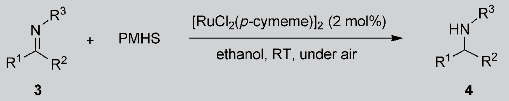
Table 2. $[RuCl_2(p\text{-cymene})]_2$-catalyzed hydrosilylation of aldimines with PMHS.[a]

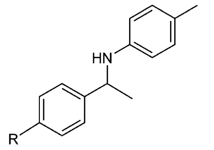
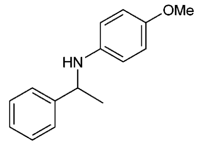
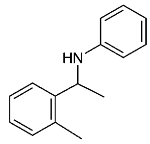
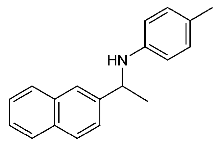
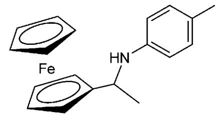
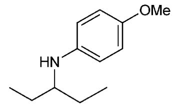
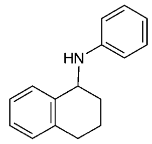


Entry	Product		Time [h]	Conv. [%][b]	Yield [%][c]
1		**2a**, R=H	2	99	90
2		**2b**, R=Cl	2	99	97
3		**2c**, R=Br	2	96	88
4		**2d**, R=CN	6	92	87[d]
5		**2e**, R=NO_2	20	70	69[e]
6		**2f**, R=OMe	2	99	96
7		**2g**, R=Me	2	99	96
8		**2h**	2	99	88
9		**2i**	2	99	97
10		**2j**	4	95	94
11		**2k**	4	97	78
12		**2l**	2	95	93[d]
13	 **1m**	–	20	0	0[e]
14		**2n**	2	90	86[d]
15		**2o**	10	92	90
16		**2p**	16	97	80[d]

[a] Typical conditions: $[RuCl_2(p\text{-cymene})]_2$ (1 mol%), aldimine (0.5 mmol), PMHS (1 mmol), ethanol (2 mL), RT, under air. [b] Conversion determined by using GC. [c] Isolated yield. [d] $[RuCl_2(p\text{-cymene})]_2$ (2 mol%) was used. [e] The reaction was performed at 50 °C with $[RuCl_2(p\text{-cymene})]_2$ (2 mol%).

Table 3. $[RuCl_2(p\text{-cymene})]_2$-catalyzed hydrosilylation of ketimines with PMHS.[a]



Entry	Product		Time [h]	Conv. [%][b]	Yield [%][c]
1		**4a**, R=H	4	99	97
2		**4b**, R=F	4	96	91
3		**4c**, R=Br	4	99	97
4		**4d**, R=CF_3	4	99	97
5		**4e**, R=OMe	10	97	85[d]
6		**4f**	4	97	95
7		**4g**	20	95	93
8		**4h**	4	99	98
9		**4i**	20	99	87
10		**4j**	20	98	85[d]
11		**4k**	20	99	67

[a] Typical conditions: $[RuCl_2(p\text{-cymene})]_2$ (2 mol%), ketimine (0.5 mmol), PMHS (1 mmol), ethanol (2 mL), RT, under air. [b] Conversion determined by using GC. [c] Isolated yield. [d] The reaction was performed at 50 °C.

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Keywords: amine · catalysis · hydrosilylation · imine · ruthenium

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