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ARTICLE TYPE

Cyclopentadienyl N-heterocyclic carbene-nickel complexes as efficient pre-catalysts for the hydrosilylation of imines

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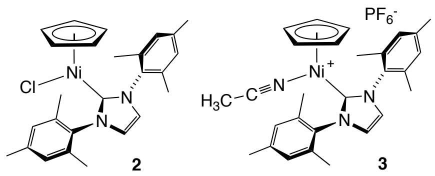
The *in situ* generated nickel hydride complex, [Ni(Mes_2NHC)HCp], and its cationic analogue, [Ni(Mes_2NHC)(NCMe)Cp](PF_6), are efficient and chemoselective pre-catalysts for the hydrosilylation of both aldimines and ketimines under mild conditions.

During the last decade, the development of catalytic reactions based on inexpensive earth-abundant transition metals has become an important area of research as the natural reserves of precious metals decline and their prices increase tremendously. In particular, considerable attention has been devoted to the use of metals such as iron,[1,2] zinc,[3] titanium[4] or copper[5,6] for the reduction of carbonyl derivatives via hydrosilylation. In contrast, nickel, which is another attractive surrogate for precious metals in terms of its abundance and low cost, has been much less studied in this area.[7] Therefore, the interest of some of us in the reactivity of half-sandwich N-heterocyclic carbene (NHC) nickel complexes,[8-10] coupled with the complementary research of other co-authors on iron-catalyzed hydrosilylation,[11] notably with analogous half-sandwich NHC-iron complexes,[12] led us all to demonstrate recently that the nickel hydride complex, [Ni(Mes_2NHC)HCp] **1** (Mes_2NHC = 1,3-dimesitylimidazol-2-ylidene, Cp = cyclopentadienyl) – generated *in situ* by reaction of [Ni(Mes_2NHC)ClCp] **2** and $NaHBEt_3$ – is an efficient catalyst for the hydrosilylation of both aldehydes and ketones at room temperature.[13,14]

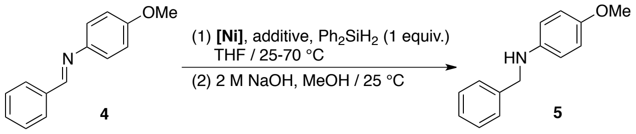
Transition-metal catalyzed hydrosilylation of aldimines and ketimines is also an interesting target due to the significance and omnipresence of the resulting amines in the field of natural products, pharmaceutical and agronomical compounds.[15] Compared to both the noble[16-18] and most of the first-row metals,[19-24] nickel has again been very rarely employed for this reduction reaction. We are indeed aware of only one example, where 1:1 complexes formed *in situ* from [Ni(OAc)$_2$] and O,N,S-pincer type ligands were shown to reduce a small array of imines *via* hydrosilylation.[25,26] This scarcity, coupled with the recent finding that, in addition of being an efficient pre-catalyst for the hydrosilylation of carbonyl derivatives[12a,b,d] (as its nickel analogues[13,14]), the cationic half-sandwich iron-NHC complex [Fe(Mes_2NHC)(CO)$_2$Cp]I was also an efficient pre-catalyst for the hydrosilylation of both aldimines and ketimines,[12c] prompted us to investigate the catalytic activity of [Ni(Mes_2NHC)ClCp] **2**[26] and its cationic derivative [Ni(Mes_2NHC)(NCMe)Cp](PF_6) **3**[10a] in these reactions (Scheme 1).



Scheme 1 Selected cyclopentadienyl NHC-nickel(II) pre-catalysts.

Initial studies focused on the hydrosilylation of *N*-benzylidene-4-methoxyaniline **4** with one equivalent of Ph_2SiH_2 in THF in the presence of catalytic amounts of complexes **2** and **3** under various conditions, in order to optimize the reaction parameters (Table 1). In the sole presence of the neutral complex **2** (5 mol%)**,** 70 °C were required to observe 50% conversion of the aldimine **4** to the corresponding amine **5** after 24 h of reaction and a basic quench (entries 1 and 2). Addition of 10 mol% of KPF_6 as a chloride scavenger led to full conversion under otherwise unchanged

Table 1 Optimization for the reduction of aldimines with **2** and **3**[a]



Entry	Pre-catalyst (mol%)	Additive (mol%)	Temp. (°C)	Time (h)	Conversion (%)[b]
1	**2** (5)	-	25	18	0
2	**2** (5)	-	70	24	50
3	**2** (5)	KPF_6 (10)	70	24	> 98
4	**3** (5)	-	70	24	> 98
5	**2** (1)	KPF_6 (2)	70	24	40
6	**3** (1)	-	70	24	> 98
7	**3** (1)	-	50	24	> 98
8	**3** (1)	-	25	17	10
9	**2** (1)	$NaHBEt_3$ (2)	25	17	> 98
10	-	$NaHBEt_3$ (2)	25	17	0
11	**2** (1)	$NaHBEt_3$ (2)	25	8	90
12	**2** (0.5)	$NaHBEt_3$ (1)	25	24	90

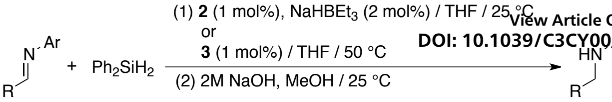
[a] Typical procedure: activation of **2** with the additive in THF (4 mL) at RT for 5 min or dissolution of **3** in THF (4 mL) at RT was followed by the addition of **4** (1 mmol) and Ph_2SiH_2 (1 mmol), and the reaction mixture was stirred at 25, 50 or 70 °C for 8 to 24 h. [b] Conversions determined by ^{1}H NMR spectroscopy after methanolysis: 2M NaOH (2 mL), MeOH (2 mL), RT, 2 h.

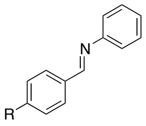
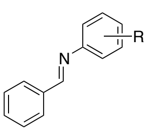
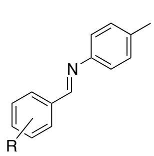
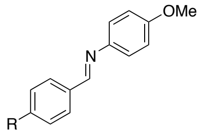
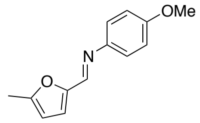
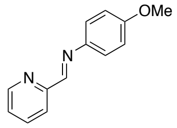
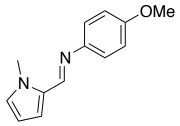
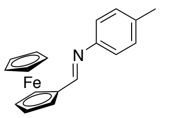
conditions (entry 3). This promising result led us to use the well-defined cationic complex **3** (5 mol%), and complete reduction was also observed (entry 4). Reducing the catalytic loading to 1 mol% of **3** also permitted the reaction to reach full conversion (entry 6), which contrasts with the result obtained with 1 mol% of the *in situ* generated cationic complex from **2** and KPF_6 (40% conversion, entry 5).[27] Interestingly, the temperature can be decreased to 50 °C without loss of catalytic activity (entry 7). However, further lowering of the reaction temperature to 25 °C led to a dramatic drop in activity, as only 10% conversion was detected after 17 h (entry 8). Nevertheless as stated above, we have shown in a previous contribution that the nickel hydride complex **1** generated by reaction of 2 equiv. of $NaHBEt_3$ with the neutral complex **2** was a particularly active catalyst for hydrosilylation of both aldehydes and ketones *at room temperature*.[13] Using 1 mol% of this *in situ* generated hydride species allowed to observe a full conversion when performing the reaction at 25 °C for 17 h (entry 9). Decreasing either the reaction time to 8 h or else the catalytic loading to 0.5 mol% allowed us to obtain 90% conversion (entries 11 and 12). Various other silanes and solvents were also screened (see the Supporting Information), but the combination of Ph_2SiH_2 and THF was found to be optimal.

With these optimized conditions in hand (1 equiv. of Ph_2SiH_2, 1 mol% of **2**, 2 mol% of $NaHBEt_3$, THF, 25 °C, 17 h or 1 equiv. of Ph_2SiH_2, 1 mol% of **3**, *no additive*, THF, 50 °C, 24 h), we then explored the scope of the hydrosilylation of aldimines (Table 2). Electronic effects at the *para*-position of the benzylidene or aniline moiety were generally minor (entries 1-3, 5-6, and 10-20). Thus, aldimines bearing an electron-donating group gave the corresponding amines with good to excellent conversions (entries 1-3, 5-6, and 10-12). Interestingly, no dehalogenation occurred with a chloro-substituted aldimine irrespective of the catalytic system used, **2**-$NaHBEt_3$ or **3**-*no additive* (entries 13 and 14), and the corresponding amine was isolated in good yield (80%, entry 13). However, with bromo- and iodo-substituted aldimines, low conversions were obtained, probably due to a rapid catalyst deactivation, as previously observed for the hydrosilylation of aldehydes and ketones (entries 4 and 7).[13] Strikingly, functional carbonyl groups such as esters and amides were not affected under these catalytic conditions irrespective of the catalytic system used, **2**-$NaHBEt_3$ or **3**-*no additive* (entries 15-16 and 19-20), and the corresponding secondary amines were isolated in good yields (76 and 72%, entries 15 and 20). Moreover, although 5% of the fully reduced compound was detected in the crude reaction mixture, the cyano functional group was also well tolerated and the *N*-(4-cyanobenzyl)-*p*-toluidine resulting from the selective reduction of the 4-cyanobenzylidene derivative was isolated in 74% yield (entry 17). In contrast, only moderate conversion was observed for the hydrosilylation of the 4-methoxy-*N*-(4-nitrobenzilidene)aniline under forcing conditions, and a mixture of products resulting from the reduction of the nitro group was observed (entries 21 and 22).

Substitution in *ortho*-position of the aniline moiety seems to have an inhibiting effect, most probably for steric reasons, as shown by the moderate conversion observed for the reduction of benzylidene-*o*-methylaniline, even at 50 °C (entries 8 and 9). Substitution at the *meta*-position of the benzylidene moiety seems in contrast to have no notable effect (entry 18).

Table 2 Scope of the reduction of adimines with **2**-$NaHBEt_3$ and **3**[a]



Entry	Substrate		Pre-cat.	Conv. (%)[b]	Yield (%)[c]
1		R = Me	**2**	> 98	83
2		R = Me	**3**	> 98	-
3		R = OMe	**2**	> 98	90
4		R = Br	**2**	20	-
5		R = *p*-OMe	**2**	> 98	89
6		R = *p*-OMe	**3**	> 98	-
7		R = *p*-I	**2**	27	-
8		R = *o*-Me	**2**	28	-
9		R = *o*-Me	**2**	48[d]	39
10		R = *p*-OMe	**2**	> 98	84
11		R = *p*-OMe	**3**	> 98	-
12		R = *p*-NMe_2	**2**	77	57
13		R = *p*-Cl	**2**	> 98	80
14		R = *p*-Cl	**3**	71	-
15		R = *p*-CO_2Me	**2**	95	76
16		R = *p*-CO_2Me	**3**	> 98	83
17		R = *p*-CN	**2**	94[e]	74
18		R = 3,4,5-OMe	**2**	93	81
19		R = NHAc	**2**	70	-
20		R = NHAc	**2**	90[d]	72
21		R = NO_2	**2**	0	-
22		R = NO_2	**2**	40[f]	-
23			**2**	20	-
24			**2**	80[f]	57
25			**2**	43	-
26			**2**	70[f]	61
27			**2**	20	-
28			**2**	60[f]	-
29			**2**	87[f,g]	70
30			**2**	> 98	85

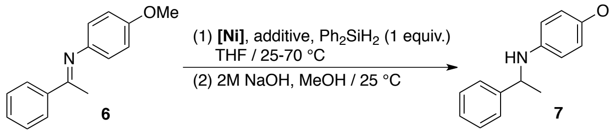
[a] Typical procedure: activation of **2** (1 mol%) with $NaHBEt_2$ (2 mol%) in THF (4 mL) at RT for 5 min or dissolution of **3** (1 mol%) in THF (4 mL) at RT was followed by the addition of aldimine (1 mmol) and Ph_2SiH_2 (1 mmol), and the reaction mixture was stirred at 25 °C for 17 h (**2**) or at 50 °C for 24 h (**3**). [b] Conversions determined by ^1H NMR spectroscopy after methanolysis: 2M NaOH (2 mL), MeOH (2 mL), RT, 2 h. [c] Isolated yields. [d] 50 °C. [e] 5% reduction of both the aldimine and the cyano group was also observed. [f] 70 °C. [g] **2** (5 mol%), $NaHBEt_3$ (10 mol%).

This reduction can also be conducted with heteroaromatic aldimines such as 5-methylfur-2-yl-, pyridin-2-yl- and *N*-methylpyrrol-2-yl-4-methoxyaniline, but at higher temperature

(50 °C or 70 °C), and the corresponding amines were isolated in moderate yields (57-70%, entries 23-29). Finally, 4-methyl-*N*-(ferrocenylmethylidene)aniline was totally reduced and led to the corresponding amine in good yield (85%, entry 30).

Given the high activity of both catalytic systems for aldimines, we then investigated their potential for the hydrosilylation of ketimines, with *N*-[1-phenylethylidene]-4-methoxyaniline **6** as the model substrate (Table 3). To obtain similar activities, slightly harsher conditions had to be used, by either performing the reaction at higher temperature (with **2**-NaHBEt$_3$, entries 5-9) or with higher pre-catalyst and Ph$_2$SiH$_2$ loadings (with **3**, entries 3 and 4). Thus, to observe full conversion of **6** to the corresponding amine **7** after a methanolysis step, 50 °C for 17 h were required in the presence of 1 mol% of **2** and 2 mol% of NaHBEt$_3$ (entry 7), and 2 equiv. of Ph$_2$SiH$_2$ were required in the presence of 5 mol% of **3** (entry 4). Notably, in the case of **2**-NaHBEt$_3$, when the reaction was performed at a lower temperature or with a lower catalyst loading, the conversion significantly decreased (entries 6 and 9).

Table 3 Optimization for the reduction of ketimines with **2** and **3**[a]

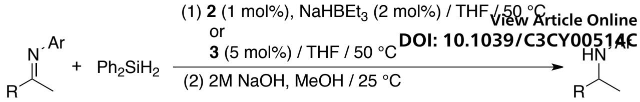


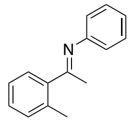
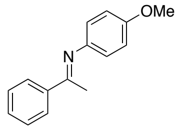
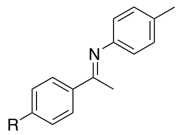
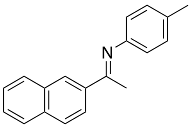
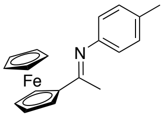
Entry	Pre-catalyst (mol%)	Additive (mol%)	Temp. (°C)	Time (h)	Conversion (%)[b]
1	**2** (5)	-	70	24	10
2	**2** (5)	KPF$_6$ (10)	70	24	60
3	**3** (5)	-	50	17	70
4[c]	**3** (5)	-	50	24	> 98
5	**2** (5)	NaHBEt$_3$ (10)	50	17	> 98
6	**2** (5)	NaHBEt$_3$ (10)	25	17	50
7	**2** (1)	NaHBEt$_3$ (2)	50	17	> 98
8	**2** (1)	NaHBEt$_3$ (2)	50	3	80
9	**2** (0.5)	NaHBEt$_3$ (1)	50	17	65

[a] Typical procedure: activation of **2** with the additive in THF (4 mL) at RT for 5 min or dissolution of **3** in THF (4 mL) at RT was followed by the addition of **6** (1 mmol) and Ph$_2$SiH$_2$ (1 mmol), and the reaction mixture was stirred at 25, 50 or 70 °C for 3 to 24 h. [b] Conversions determined by ^{1}H NMR spectroscopy after methanolysis: 2M NaOH (2 mL), MeOH (2 mL), RT, 2 h. [c] Reaction run with 2 equiv. of Ph$_2$SiH$_2$.

With these optimized conditions in hand (1 equiv. of Ph$_2$SiH$_2$, 1 mol% of **2**, 2 mol% of NaHBEt$_3$, THF, 50 °C, 17 h or 2 equiv. of Ph$_2$SiH$_2$, 5 mol% of **3**, *no additive*, THF, 50 °C, 24 h), the scope of the hydrosilylation of ketimines was then explored. With several ketimines derived from (substituted) acetophenones and (4-substituted) anilines, the corresponding amines were obtained with high conversions and good isolated yields (Table 4, entries 1-10). Notably, full conversion and good isolated yield were obtained with *N*-(2-methylphenyl)ethylidene-aniline (entry 1), which demonstrates that steric hindrance at the phenylethylidene moiety does not inhibit the reaction. Similarly, good conversion was obtained for the reduction of naphtylethylidene toluidine (entry 14). As observed with aldimines, in the presence of a strong electron withdrawing group such as a trifluoromethyl group, the reaction was more difficult to carry out and harsher conditions (5 mol% of **2**, 10 mol% of NaHBEt$_3$, 70 °C, 17 h) were necessary to reach 85% conversion and 69% isolated yield (entries 11-13). Finally, the ferrocenyl imine derivative could also be reduced to the corresponding amine with 80% conversion and 66% isolated yield by using the latter conditions (entry 17).

Table 4 Scope of the reduction of ketimines with **2**-NaHBEt$_3$ and **3**[a]

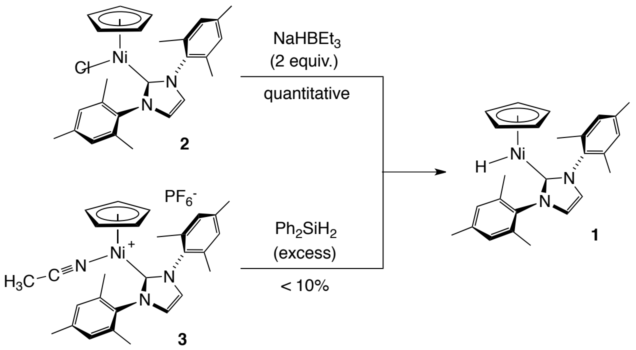


Entry	Substrate	Pre-cat.	Conv. (%)[b]	Yield (%)[c]
1		**2**	> 98	77
2		**2**	> 98	78
3		**3**	> 98	-
4	 R = H	**2**	79	63
5	R = Me	**2**	86	73
6	R = OMe	**2**	> 98	84
7	R = OMe	**3**	> 98	-
8	R = Cl	**2**	90	77
9	R = F	**2**	90	75
10	R = F	**3**	> 98	80
11	R = CF$_3$	**2**	30	-
12	R = CF$_3$	**2**	52[d]	-
13	R = CF$_3$	**2**	85[d,e]	69
14		**2**	90	59
15		**2**	20	-
16		**2**	48[d]	-
17		**2**	80[d,e]	66

[a] Typical procedure: activation of **2** (1 mol%) with NaHBEt$_2$ (2 mol%) in THF (4 mL) at RT for 5 min or dissolution of **3** (5 mol%) in THF (4 mL) at RT was followed by the addition of aldimine (1 mmol) and Ph$_2$SiH$_2$ (1 mmol (**2**) or 2 mmol (**3**)), and the reaction mixture was stirred at 50 °C for 17 h (**2**) or 24 h (**3**). [b] Conversions determined by ^{1}H NMR spectroscopy after methanolysis: 2M NaOH (2 mL), MeOH (2 mL), RT, 2 h. [c] Isolated yields. [d] 70 °C. [e] **2** (5 mol%), NaHBEt$_3$ (10 mol%).

We demonstrated in our previous contribution which targeted the hydrosilylation of carbonyl derivatives,[13] that the nickel hydride complex **1** resulting from the reaction of **2** and NaHBEt$_3$ is most probably the *true* pre-catalyst with this catalytic system. Simultaneously, Royo et al. demonstrated that an analogous Cp-NHC tethered nickel hydride complex generated *in situ* by the reaction of the corresponding alkoxide complex with PhSiH$_3$ was most probably the active species in a very similar hydrosilylation process.[14] We thus wondered if such hydride species was also generated with the catalytic system composed of the sole cationic complex **3** and Ph$_2$SiH$_2$.[28]

For that purpose, we reacted **3** with 0.5 or 1 equivalent of Ph$_2$SiH$_2$ in THF-d_8 at RT and 50 °C, and monitored the reactions by ^{1}H NMR spectroscopy. In all cases, we observed, after 5 min



Scheme 2 Generation of the nickel hydride complex **1** from the neutral and cationic complexes **2** and **3**.

of reaction, the formation of a small amount (generally less than 10% with respect to the remaining amount of **3**) of a nickel hydride species, which we unambiguously identified as being **1** by comparison with the ^{1}H NMR spectrum of a pure sample in THF-d_8. Concomitantly, new signals started to appear in the aromatic area (probably resulting from the oligomerization and/or polymerization of Ph_2SiH_2), as well as a singlet at 1.94 ppm, which we attribute to free CH_3CN. The rest of the reaction mixture mostly consisted in non-reacted **3** and Ph_2SiH_2 (see the Supporting Information). It is noteworthy that in all cases we also observed the immediate and steady evolution of a gas, which we think is H_2, as observed by Zargarian et al. in the reactions of analogous nickel complexes of the type [Ni(PR$_3$)Me(1-Me-indenyl)] with $PhSiH_3$.[29] Finally, after a reaction time varying from 20 min for the reactions conducted at 50 °C to 6-22 h for the reactions conducted at RT (with 0.5 or 1 equiv. of Ph_2SiH_2), all Ph_2SiH_2 was consumed, and the reaction medium consisted in a complicated mixture of products with small remaining amounts of complexes **1** and **3**. In contrast, the neutral complex **2** gave strictly no reaction with Ph_2SiH_2 (0.5 equiv.) in THF-d_8 at RT, even after 6 h, and required 70°C to produce traces amount of **1**.

These results may explain the total absence of reduction of the aldimine **4** when the reaction was performed in the sole presence of 5 mol% of **2** at RT (Table 1, entry 1), as well as the moderate conversion observed in the sole presence of 5 mol% of **2** at 70°C (Table 1, entry 2) and the slightly harder conditions (50°C) required with **3** to observe full reduction (Table 1, entries 7 and 8); only small amounts of **2** or **3** are converted to **1** by reaction with Ph_2SiH_2,[30] whereas all **2** is converted to **1** by reaction with 2 equiv. of NaHBEt$_3$ (Scheme 2). Additionally, although another true pre-catalyst (or active species) cannot be ruled out in the absence of NaHBEt$_3$, these results tend to confirm the necessity to generate the nickel hydride complex **1** to observe a catalytic activity.[13]

In summary, using the nickel hydride complex **1**, generated *in situ* from the neutral complex **2** and 2 equiv. of NaHBEt$_3$, or the cationic complex **3**, an efficient and chemoselective hydrosilylation of both aldimines and ketimines was carried out at RT or 50 °C, leading the corresponding amines with moderate to good yields.

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Notes and references

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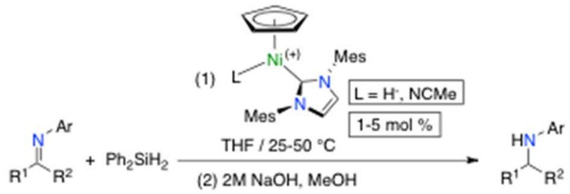

The *in situ* generated nickel hydride complex, [Ni(Mes$_2$NHC)HCp], and its cationic analogue, [Ni(Mes$_2$NHC)(NCMe)Cp](PF$_6$), are efficient and chemoselective pre-catalysts for the hydrosilylation of imines under mild conditions.