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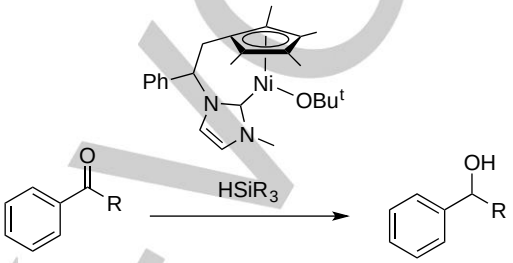
Selective Reduction of Nitroarenes with Silanes Catalysed by Nickel N-Heterocyclic Carbenes

Rita Lopes,[a] Mariette M. Pereira,[b] Beatriz Royo*[a]

Abstract: An efficient catalytic system for the reduction of nitroarenes to amines was developed using a well-defined nickel-NHC complex as catalyst and phenylsilane as reducing agent. The excellent activity of the catalyst provides access to anilines containing a wide array of reactive functionalities at 20 °C, and without using any base or additive. Notably, the catalytic system allows the reduction of 5,10,15,20-tetra-(nitrophenyl)porphyrin (TNPP) and Cu(II) β-nitroporphyrin to the corresponding aminoporphyrins.

Introduction

During the last decade, there has been much interest in the development of new catalysts based on inexpensive, non-toxic and abundant first-row transition metals.[1] Among them, nickel is an attractive metal for catalysis, since it can adopt flexible number of oxidation states, Ni(0), Ni(I), Ni(II), Ni(III), Ni(IV) offering unique reactivity pathways.[2] In particular, organometallic nickel complexes bearing N-heterocyclic carbene ligands (NHCs) have become a fascinating class of compounds for homogeneous catalysis. The rapid evolution of the Ni-NHC chemistry has led to a large number of applications in the field of catalysis, including C-C, C-N, C-S bond forming reactions, and also oxidation reactions.[3,4] In contrast, reduction of functional groups catalysed by well-defined Ni-NHC complexes is poorly developed. Recently, we[5a] and Chetcuti´s group[6] independently disclosed two closely related half-sandwich Ni(II)-NHC complexes capable to perform the reduction of carbonyl compounds using silane as the stoichiometric reductant (Scheme 1). More recently, the group of Montgomery[7] developed an interesting system for the hydrosilylation of carbonyl groups, and Sortais, Ritleng and co-workers extended the use of half-sandwich Ni(II)-NHC complexes to the reduction of imines.[8] Apart from hydrosilylation reactions, reduction of imines through hydrogen transfer processes has been achieved in good yields by using a combination of Ni(0)/IMes.HCl/Et_2CHONa,[9] and electrocatalytic conversion of CO_2 to CO was performed using a NHC-isoquinoline nickel complex.[10] Pursuing our interest in developing catalytic systems with iron[11] and nickel NHCs,[5] we became interested in exploring the activity of half-sandwich Ni-NHC complexes in the selective reduction of nitroarenes with silanes.



Scheme 1. Half-sandwich nickel-NHC complex catalysing the reduction of carbonyl groups reported by our group.[5a]

Functionalised anilines are valuable building blocks for the synthesis of dyes, pigments, pharmaceutical and agrochemicals.[12] One of the most general methods for the synthesis of anilines is by catalytic hydrogenation of nitroarenes. Well-established hydrogenation methods for industrial–scale production are based on the use of heterogeneous catalysts, generally based on precious metals, under high temperature and high pressure of H_2 gas.[13] However, selective hydrogenation of the nitro group in the presence of other reducible groups under mild conditions remains a challenging task. An alternative method to direct hydrogenation is the use of hydrosilanes as reducing agents, which avoids the use of hazardous pressurized H_2 gas. At laboratory scale, the catalytic reduction of nitroarenes through hydrosilylation processes is an interesting approach since hydrosilanes are readily available and easy to handle.[14] Currently, methods for hydrosilylation of nitroarenes have mainly developed using precious metals as catalysts,[15] and few catalytic systems using cheap metals are described in the literature.[16,17]

Herein, we present the use of well-defined Ni-NHC complexes as catalysts for the reduction of a set of nitroarenes, including the value added nitroporphyrins, using phenylsilane as reducing agent under mild conditions.

Results and Discussion

The catalytic activity of half-sandwich Ni-NHC complexes **1**[5a] and **2**[5b] (Scheme 2) in the reduction of nitroarenes was tested using the primary silane $PhSiH_3$ as reducing agent and 1-chloro-4-nitrobenzene as a model substrate. Initially, the reaction was carried out in toluene at 60 °C in the presence of 2 mol% of catalyst and using a $PhSiH_3$:substrate ratio of 5:1. Under these

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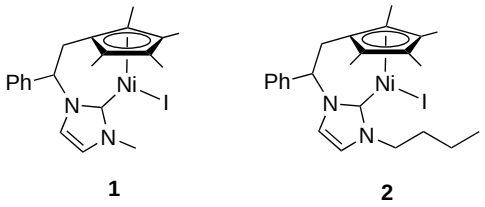
conditions, a remarkable effect of the wingtips substituents of the NHC ligands in complexes **1** and **2**, [5] was observed (Table 1, entries 1 and 3).



1 **2**

Scheme 2. Nickel NHC complexes **1** and **2**.[5]

Complex **2**, possessing a larger N-chain, is more active than **1**, affording 95% yield of 4-chloro-aniline in just 3 h. The reaction profile is depicted in Figure 1. As shown in this profile, complex **2** displayed higher reaction rate than **1**. Progressively, the reaction rate increases to reach selective conversion to 4-chloroaniline in 3 h, while the reaction catalysed by complex **1** reached just 62% of aniline in 3 h.

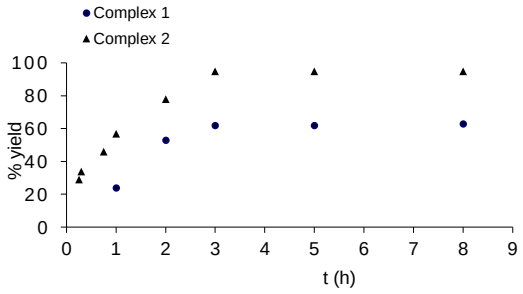
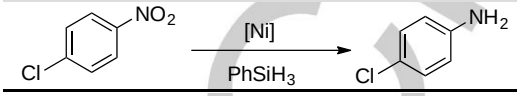


Figure 1. Time-dependent profile of the reaction of 1-chloro-4-nitrobenzene with phenylsilane using complexes **1** and **2**. Reaction conditions: 1-chloro-4-nitrobenzene (1 mmol), catalyst (2 mol%), $PhSiH_3$ (5 mmol), toluene (0.4 mL), 60 °C.

We observed that the catalytic reduction of 1-chloro-4-nitrobenzene could be conducted at 20 °C by increasing the catalyst loading to 10 mol%. High yield (83%) of 4-chloroaniline was obtained in 15 h using 10 mol% of **2** (Table 1, entry 4). When the amount of **2** is reduced to 5 mol%, a 69 % yield of 4-chloroaniline was obtained under those conditions (Table 1, entry 5). Solvent had a significant influence on the reaction in terms of reactivity. Replacing toluene with acetonitrile, THF or CH_2Cl_2 produced a significant drop in conversion (Table 1, entries 6-8). The reaction can be performed under neat conditions affording high yield (85%) of the corresponding amine (Table 1, entry 9). Full conversion of 1-chloro-4-nitrobenzene to 4-chloroaniline was obtained with a primary silane ($PhSiH_3$) at 60 °C using **2** as catalyst (Table 1, entry 3). However, secondary silanes (Ph_2SiH_2), alkyl silanes and alkoxysilanes, such as Et_3SiH and $(EtO)_3SiH$ showed no reactivity. As expected, no reaction took place in the absence of catalyst (Table 1, entries 10 and 11). Complex **2** displayed slightly higher activity than the nickel complex Ni(*a*NHC)$_2$Cl$_2$ bearing an abnormal NHC ligand recently reported by Mandal and co-workers, which needed higher temperature (90 °C) to afford 78% yield of the corresponding amine.[17]

Table 1. Reduction of 1-chloro-4-nitrobenzene with $PhSiH_3$ using **1** and **2**[a]

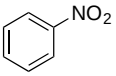
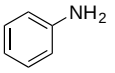
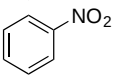
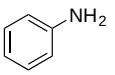


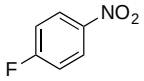
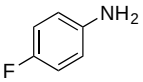
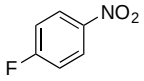
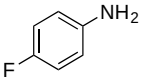
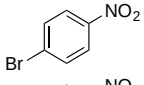
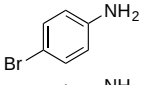
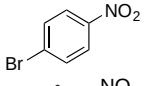
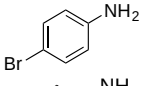
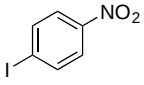
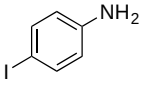
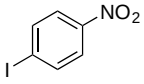
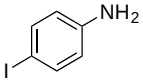
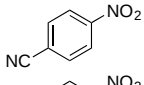
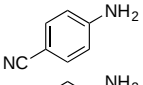
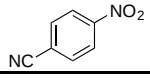
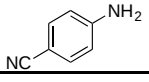
Entry	Catalyst	Loading	Solvent	T (°C)	T (h)	Yield (%)[b]
1	**1**	2	toluene	60	3	62
2	**1**	10	toluene	20	15	72
3	**2**	2	toluene	60	3	95
4	**2**	10	toluene	20	15	83
5	**2**	5	toluene	20	15	69
6	**2**	2	MeCN	60	3	25
7	**2**	2	THF	60	3	34
8	**2**	2	CH_2Cl_2	60	3	27
9	**2**	2	neat	60	3	85
10	none	-----	toluene	60	3	0
11	none	-----	toluene	20	15	0

[a] Reaction conditions: substrate (1 mmol), catalyst, $PhSiH_3$ (5 mmol), solvent (0.4 mL). [b] Isolated yield after column chromatography.

Then, we decided to investigate the catalytic activity of **2** with various nitroarenes, and we found that the reductions proceed with high yields and selectivities when other functional groups such as halogen and cyano are present. Notably, halogenated nitroarenes (Br, F, I) were chemoselectively reduced to the corresponding anilines; no dehalogenated product was observed in any case. When the reactions are performed at 60 °C using 2 mol% of **2**, high yields are obtained in 3 h (Method A). The reactions can be performed at 20 °C using higher catalyst loading (10 mol%) and longer reaction times (15 h), Method B. Results are summarised in Table 2.

Table 2. Reduction of nitrobenzenes to amines with $PhSiH_3$ using **2**.[a]

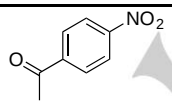
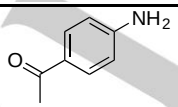
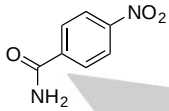
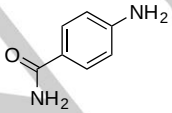
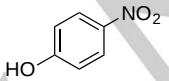
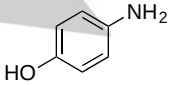
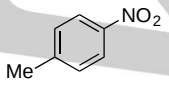
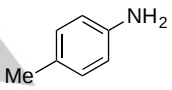
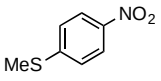
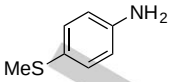
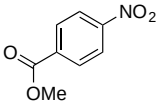
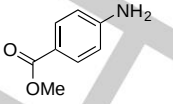
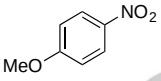
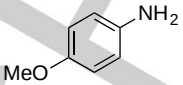
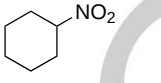
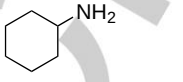
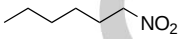
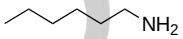
Entry	Substrate	Product	Method	Yield (%)[b]
1			A	87
2			B	91

3			A	79
4			B	91
5			A	70
6			B	80
7			A	88
8			B	90
9			A	74
10			B	82

[a] Reaction conditions: Method A: substrate (1 mmol), **2** (2 mol%), $PhSiH_3$ (5 mmol), toluene (0.4 mL), 60 °C, 3 h; Method B: substrate (1 mmol), **2** (10 mol%), $PhSiH_3$ (5 mmol), toluene (0.4 mL), 20 °C, 15 h. [b] Isolated yield.

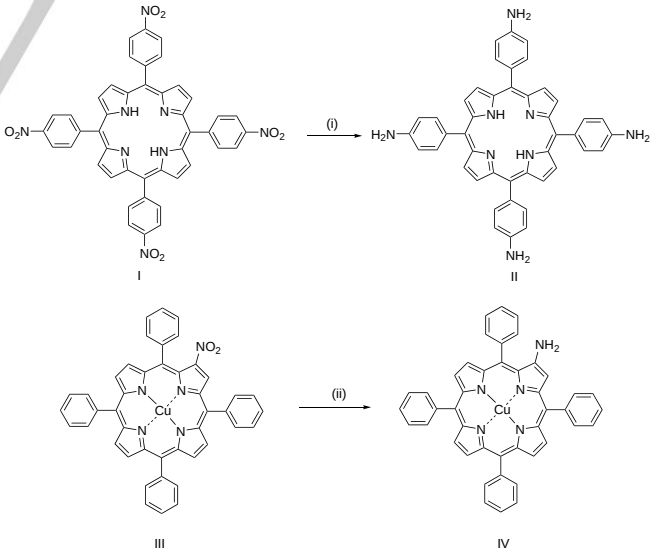
Moreover, the present catalytic system also showed remarkable chemoselectivity in the reduction of a variety of substrates bearing other easily reducible functional groups such as ketone (Table 3, entry 1), amide (Table 3, entry 2), hydroxyl (Table 3, entry 3), methyl (Table 3, entry 4), methylthio (Table 3, entry 5), ester (Table 3, entry 6), and methoxy (Table 3, entry 7). In all cases high yields (up to 81%) have been obtained. Exceptions are the reduction of nitrobenzenes substituted by amide and methylthio groups, where moderate yields were obtained (entries 2 and 5, Table 3). Furthermore, the reduction of nitrobenzene substituted with an aldehyde or alkene gave, in both cases, a mixture of compounds attributed to the reducing of both functionalities. In addition, nitrocyclohexane and 1-nitrohexane were reduced to corresponding amines in good yield (entries 8 and 9, Table 3).

Table 3. Reduction of nitrobenzenes to amines with $PhSiH_3$ using **2**[a]

Entry	Nitroarene	Amine	Yield (%)[b]
1			96
2			59
3			97
4			94
5			67
6			88
7			81
8			81
9			77

[a] Reaction conditions: Method B: substrate (1 mmol), **2** (10 mol%), $PhSiH_3$ (5 mmol), toluene (0.4 mL), 20 °C, 15 h [b] Isolated yield.

Finally, another relevant example to demonstrate the scope of this new catalytic system, is the highly efficient reduction of 5,10,15,20-tetra-(nitrophenyl)porphyrin (TNPP, **I**) and Cu(II) β-nitroporphyrin (**III**), Scheme 3. In a typical reaction, to a toluene solution of nitro-porphyrins **I** or **III**, the catalyst **2** and phenylsilane were added, and the reaction was maintained along 15 hours at 20 °C. After easy work-up and chromatographic purification, the desired porphyrinic amino compounds **II** and **IV** have been obtained with isolated yields of 86 and 94%, respectively. This is a quite remarkable result that opens the way for the large scale preparation on amino-porphyrins, very important for the preparation of new functionalized materials,[18] without the use of highly toxic Sn/HCl approaches.[18,19,20]



Scheme 3. Reduction of 5,10,15,20-tetra-(nitrophenyl)porphyrin, TNPP (**I**) and Cu(II) β-nitroporphyrin (**III**). Reaction conditions: (i) catalyst **2** (10 mol%), $PhSiH_3$ (20 mmol), toluene (0.4 mL), 20 °C, 15 h; (ii) catalyst **2** (10 mol%), $PhSiH_3$ (5 mmol), toluene (0.4 mL), 20 °C, 15 h.

In order to get an insight into the reaction mechanism, we performed the stoichiometric reaction of complex **2** with one equivalent of 1-chloro-4-nitrobenzene in C_6D_6. The reaction mixture was heated at 60 °C and monitored by ^{1}H NMR. Complex **2** did not react with the substrate after being heated for 6 h. We also explored the stoichiometric reaction of **2** with $PhSiH_3$. The reaction was performed in a J Young valve NMR tube. Phenylsilane was added to a solution of **2** in deuterated benzene, and the reaction was heated to 60 °C and monitored by ^{1}H NMR and ^{29}Si NMR during 24 h. Complex **2** did not react with phenylsilane. This result contrast with those reported by Mandal, which reported that a Ni complex bearing an abnormal NHC reacted with an stoichiometric amount of $PhSiH_3$ forming a Ni-silyl complex.[17] Similar result was observed by Shimada when reacted a (salicylaldiminato)Ni(II) complex with an stoichiometric amount of Ph_2SiH_2.[16i] They proposed the formation of an intermediary silyl complex based on ^{29}Si NMR experiments. In 2012, we reported the formation of the silyl Ni complex (Cp*-NHC^{Me})Ni-SiH_2Ph formed by stoichiometric reaction of the Ni alkoxide (Cp*-NHC^{Me})Ni-OBu^t with $PhSiH_3$.[5a] The silyl complex displayed a resonance at δ -18.7 ppm in its ^{29}Si NMR spectrum, and the silyl hydrogen resonances at δ 4.67 and δ 4.44 ppm in its ^{1}H NMR spectrum. Therefore, if complex **2** were reacted with $PhSiH_3$ forming the expected silyl complex (Cp*-NHC^{nBu})Ni-SiH_2Ph, a resonance close to δ -18 ppm would be observed in the ^{29}Si NMR spectrum. Nevertheless, we only observed a resonance at δ -59.5 ppm, which corresponds to free $PhSiH_3$. We believe that complex **2** reacts with phenylsilane under catalytic conditions in which a large excess of silane is present. We have attempted to explore the nature of the Ni species that remained after catalysis. We isolated a brown residue, which corresponds to a complex mixture as showed by its ^{1}H NMR. The ^{29}Si NMR of the residue did not displayed any resonance characteristic of a Ni-silyl species. The kinetic profile of complex **2** indicates the rapid formation of the active species, since 29% yield of the corresponding product is formed after 15 min of reaction (Figure 1).

Conclusions

A new catalytic system capable to perform the selective reduction of functionalised nitroarenes at 20 °C was developed. The half-sandwich Ni-NHC complex **2** catalysed the reduction of nitroarenes to anilines with phenylsilane without adding any base or additives. Under the optimised conditions, the reduction of nitroarenes was chemoselective, displaying tolerance to a wide variety of fuctional groups including halogens, cyano, hydroxyl, ketone, amide, methoxy, and ester groups. Notable, nitroporphyrins were selectively reduced to the corresponding aminoporphyrins. The described catalytic system represents a synthetically useful method for the reduction of nitroarenes.

Experimental Section

Typical procedure for catalytic reduction of nitroarenes

Method A: In a closed vessel, under nitrogen atmosphere, a mixture of catalyst (2 mol%), nitroarene (1 mmol), phenylsilane (5 mmol), and toluene (0.4 mL) was heated to 60 ºC for 3 h. All volatiles were removed under vacuo and the remaining residue was purified by column chromatograpy (with a mixture ethyl acetate:hexane and MeOH). The NMR spectra produced was compared with the reported data for identification of products.[21]

Method B: In a closed vessel, under nitrogen atmosphere, a mixture of catalyst (10 mol%), nitroarene (1 mmol), phenylsilane (5 mmol), and toluene (0.4 mL) was stirred for 15 h at 20 ºC. All volatiles were removed under vacuo and the remaining residue was purified by column chromatograpy (with a mixture ethyl acetate:hexane and MeOH). The NMR spectra produced was compared with the reported data for identification of products.[21]

Catalytic reduction of 5,10,15,20-tetra-(amino-phenyl)porphyrin (I)

Under nitrogen atmosphere, a 5 mL screw-capped vial was charged with compound **I** (1.0 mmol), $PhSiH_3$ (20.0 mmol), catalyst **2** (10 mol%), and toluene (0.4 mL). After being stirred for 15 h at room temperature, all volatiles were evaporated, and the remaining residue was purified by column chromatography (with a mixture of MeOH/ACN/Acetone/Et_3N) to yield 5,10,15,20-tetra-(amino-phenyl)porphyrin.[19]

Catalytic reduction of Cu(II) β-nitroporphyrin (III)

Under nitrogen atmosphere, a 5 mL screw-capped vial was charged with compound **II** (1.0 mmol), $PhSiH_3$ (5.0 mmol), catalyst **2** (10 mol%),, and toluene (0.4 mL). After being stirred for 15 h at room temperature, all volatiles were evaporated, and the remaining residue was purified by column chromatography (with a mixture of MeOH/ACN/Acetone/Et_3N) to yield 5,10,15,20-tetra-(amino-phenyl)porphyrin.[20]

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Keywords: nickel• N-heterocyclic carbenes • hydrosilylation • reduction nitroarenes • porphyrins

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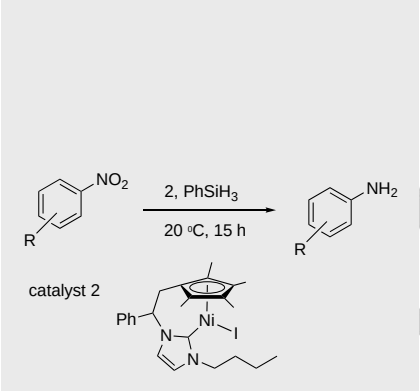
Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Well-defined Ni(II)-NHC complexes were used as catalysts for the reduction of nitroarenes to amines with silanes at 20 °C. Excellent yields and chemoselectivities were obtained for a wide range of nitroarenes, including nitroporphyrines.



*Rita Lopes, Mariette M. Pereira, Beatriz Royo**

Page No. – Page No.

Selective reduction of nitroarenes with silanes catalysed by nickel N-heterocyclic carbenes