The $NiCl_2$-Li-Arene (cat.) Combination as Reducing System, Part 9: Catalytic Hydrogenation of Organic Compounds using the $NiCl_2$-Li-(Naphthalene or Polymer-Supported Naphthalene) (cat.) Combination

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Received: July 30, 2002; Accepted: October 7, 2002

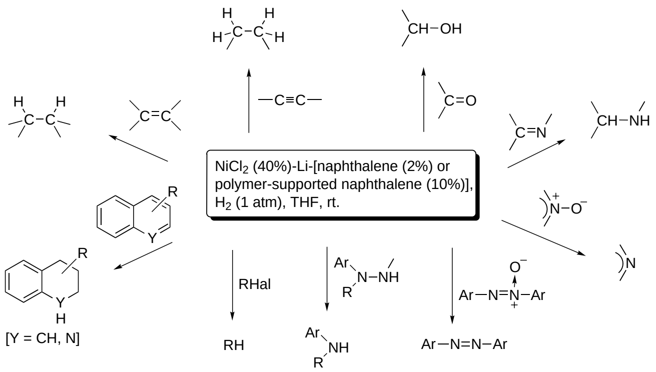
Abstract: The reaction of lithium powder, a catalytic amount of naphthalene or polymer-supported naphthalene, and anhydrous nickel(II) chloride, in THF at room temperature, generates a finely divided and very reactive nickel(0) which has been efficiently applied to the catalytic hydrogenation of different organic compounds such as alkenes, alkynes, carbonyl compounds, imines, organic halides, aromatic compounds, hydrazines, azoxy compounds, and *N*-oxides.

Keywords: catalytic hydrogenation; lithium; naphthalene; nickel; polymer-supported naphthalene

Introduction

Catalytic hydrogenation is one of the most frequently applied reactions in organic synthesis which allows the reduction of many functional groups often with high control of the chemo-, regio-, and stereoselectivity.[1] In general, heterogeneous catalytic hydrogenation[2] is preferred due to the mild reaction conditions mostly required and to the easy separation of the catalyst. Among the many catalysts available, nickel catalysts[3] are universal and widely used both in the laboratory and in industry. They can be found in a supported form (nickel on kieselguhr,[3] alumina,[4] or carbon[5]), as a nickel-aluminium alloy powder,[6] or obtained by reduction of nickel salts such as nickel aluminides and nickel borides,[7] nickel precipitated from a nickel halide and zinc,[8] or the Nic catalysts [NaH-NaOR-Ni(II) salts], which generate nickel hydride species.[9] Especially reactive are those nickel catalysts in the form of colloids[10] or as solvated metal atom dispersed powders.[11] However, Raney nickel is probably by far the most used nickel catalyst because of its high activity, being able to reduce practically any function.[3,12] Its main disadvantages are: (a) the difficulty in calculating the dosage (it is usually measured as a suspension rather than weighed); (b) ferromagnetic properties that preclude the use of magnetic stirring; (c) it is potentially hazardous (pyrophoric); and (d) it becomes inactive after prolonged storage, presumably because it loses hydrogen slowly. On the other hand, in the last years we have developed a reduction methodology based on the use of dihydrated nickel(II) chloride, lithium, and a catalytic amount of an arene, which showed to be very efficient in the reduction of a wide variety of organic substrates such as alkenes,[13a, h] alkynes,[13b] carbonyl compounds and imines,[13c] organic halides,[13d] sulfonates, aromatic and heteroaromatic compounds,[13e] hydrazines, azo compounds, azoxy compounds, and *N*-oxides,[13f] and nitrones.[13g] The main advantages of this methodology are: (a) the source of hydrogen is the water contained in the nickel salt; (b) the grade of hydrogenation can be controlled by the stoichiometry of the reaction; and (c) deuterated products are easily obtained by utilizing a nickel salt containing two molecules of deuterium oxide instead of water.

However, by applying this methodology stoichiometric amounts of the nickel salt are needed in order to get good reaction conversions. In a preliminary communication,[14] we reported a nickel-catalyzed hydrogenation reaction involving external molecular hydrogen and very reactive catalytic nickel(0), which was prepared from anhydrous nickel(II) chloride, lithium, and a catalytic amount of naphthalene. This reducing system found successful application in the reduction of a wide range of organic compounds including alkenes, alkynes, halogenated materials, aromatic and heteroaromatic compounds, hydrazines, azoxy compounds, and *N*-oxides. In all these reactions, lithium powder was activated by catalytic naphthalene as electron carrier, which though present in negligible amounts, is incorporated in the crude reaction product unless some purification technique is applied. On the other hand, polymer-supported arenes have found recent applications as electron transfer reagents in lithiation processes,



Scheme 1.

their easy recovery and reuse being their major advantages.[15]

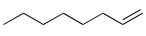
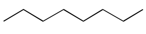
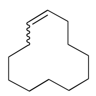
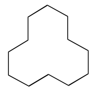
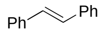
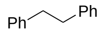
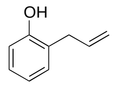
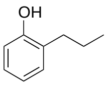
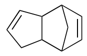
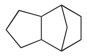
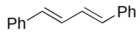
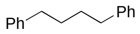
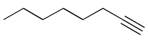
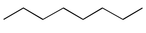
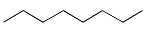
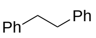
In the present paper we report the scope of the use of a naphthalene-supported polymer, as an alternative electron transfer catalyst to naphthalene, in the nickel-catalyzed hydrogenation of the above-mentioned types of organic substrates. In addition, both systems, NiCl$_2$-Li-naphthalene (cat.) and NiCl$_2$-Li-(polymer-supported naphthalene) (cat.), were also applied to the catalytic hydrogenation of carbonyl compounds and imines (Scheme 1).

Results and Discussion

Initially, we prepared a solid mixture composed of nickel(II) chloride, lithium powder, and a catalytic amount of naphthalene in the molar ratio 1:5:0.05, respectively. Some preliminary experiments[14] revealed that a 20 mol % of nickel led to partial reduction of the substrates, and long reaction times were needed in some cases to complete the reaction, whereas *ca*. 40 mol % of nickel had an ideal behaviour in most of the starting materials studied. The polymer-supported naphthalene was prepared by radical copolymerization of 2-vinylnaphthalene and divinylbenzene (mixture of isomers) in a 19 to 1 molar ratio, respectively.[15b, c] Thus, the reaction of the above mixture (40 mol % Ni) in the presence of naphthalene or polymer-supported naphthalene, with a variety of organic substrates in THF at room temperature, and under an atmosphere of molecular hydrogen (1 atm), led to the corresponding reduced products in moderate to excellent yields (Tables 1–4).

This methodology was initially applied to the hydrogenation of alkenes and alkynes (Table 1). Thus, alkyl chain, cyclic, conjugated, and functionalized alkenes, as well as dienes gave the expected reduced products in very high yields, independently of the electron transfer reagent used (Table 1, entries 1–6). A representative group of alkynes including terminal, internal, and conjugated alkynes was also transformed into the corresponding alkanes (Table 1, entries 7–9).

Table 1. Hydrogenation of alkenes and alkynes.

Entry	Starting Material	t [h]		Product	Yield [%][c]	
		A[a]	B[b]		A[a]	B[b]
1		0.5	0.5		97[d]	97[d]
2		1.0	1.0		95	99
3		1.0	6.0		96	99
4		1.5	1.5		98	98
5		3.0	1.0		95	96
6		2.0	1.5		94	96
7		4.0	2.5		80[d]	93[d-f]
8		12.0	0.5		97[d]	98[d]
9	Ph—≡—Ph	2.0	12.0		96	93[e]

[a] Method A: NiCl$_2$-Li-naphthalene, THF, rt.

[b] Method B: NiCl$_2$-Li-(polymer-supported naphthalene), THF, rt.

[c] Isolated yield of the reaction crude after filtration and evaporation of solvents, unless otherwise is stated.

[d] GLC yield.

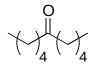
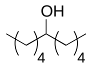
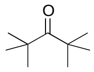
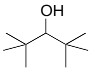
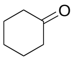
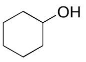
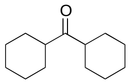
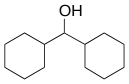
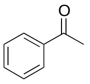
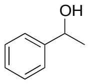
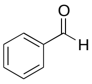
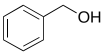
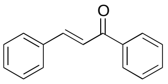
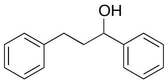
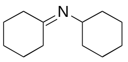
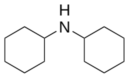
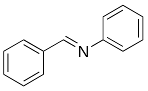
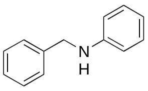
[e] Reaction performed at –78 °C → rt.

[f] 81 and 86% yields were obtained when the reaction was performed for 0.5 h at rt and 0 °C, respectively.

Concerning carbonyl compounds, a series of dialkyl, cycloalkyl, dicycloalkyl, and aromatic ketones could be hydrogenated to the corresponding secondary alcohols (Table 2, entries 1–5), although heating at 50 °C was required in two cases for improving the yields (Table 2, entries 2 and 4). Hydrogenation of benzaldehyde proceeded with moderate yields (Table 2, entry 6), due to the fact that side reactions such as coupling compete with the main reduction pathway, whereas reduction of the α,β-unsaturated ketone chalcone furnished the corresponding saturated alcohol, no chemoselectivity being observed (Table 2, entry 7). A ketimine and an aldimine were also reduced to the expected secondary amines, the latter being obtained in better isolated yields than the former (Table 2, entries 8 and 9, respectively).

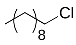
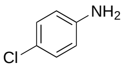
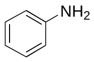
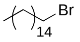
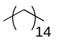
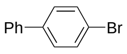
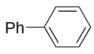
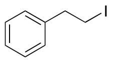
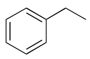
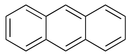
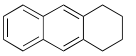
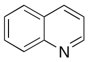
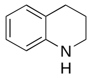
This methodology allowed the hydrodehalogenation reaction of various organic halides. Thus, alkyl, benzylic, and aromatic chlorides, as well as alkyl and aromatic bromides, and an alkyl iodide were reduced to the corresponding hydrocarbons in moderate to excellent yields (Table 3, entries 1–6). As regards aromatic compounds, it is worthy of note that the hydrogenation of anthracene under the above mentioned conditions

Table 2. Hydrogenation of carbonyl compounds and imines.

Entry	Starting Material	t [h] A[a]	t [h] B[b]	Product	Yield [%][c] A[a]	Yield [%][c] B[b]
1		12.0	12.0		64	71
2		2.0	2.0		68[d]	65[d]
3		2.0	2.0		90	82
4		2.0	2.5		84[d]	72[d]
5		12.0	12.0		58	62
6		12.0	12.0		63	60
7		12.0	12.0		67	62
8		6.0	6.0		62	57
9		12.0	12.0		88	69

[a] Method A: NiCl$_2$-Li-naphthalene, THF, rt.
[b] Method B: NiCl$_2$-Li-(polymer-supported naphthalene), THF, rt.
[c] Isolated yield of the reaction crude after filtration and evaporation of solvents, unless otherwise is stated.
[d] Reaction performed at 50 °C.

Table 3. Hydrogenation of organic halides and aromatic compounds.

Entry	Starting Material	t [h] A[a]	t [h] B[b]	Product	Yield [%][c] A[a]	Yield [%][c] B[b]
1		2.0	2.5		68[d]	89
2	Ph_3CCl	2.0	2.0	Ph_3CH	90	95
3		12.0	2.0		50[d]	98
4		2.0	2.0		98	94
5		2.0	2.0		84	93
6		2.0	2.0		86	57
7		2.0	12.0		68[d,e]	65[d,e]
8		12.0	12.0		98	99

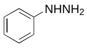
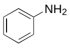
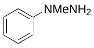
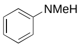
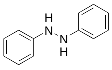
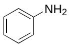
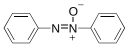
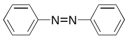
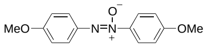
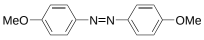
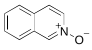
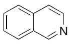
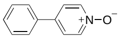
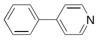
[a] Method A: NiCl$_2$-Li-naphthalene, THF, rt.
[b] Method B: NiCl$_2$-Li-(polymer-supported naphthalene), THF, rt.
[c] Isolated yield of the reaction crude after filtration and evaporation of solvents, unless otherwise is stated.
[d] Isolated yield after column chromatography (silica gel, hexane or hexane/diethyl ether).
[e] Approx. 10% yield of 9,10-dihydroanthracene was obtained as by-product.

furnished mainly 1,2,3,4-tetrahydroanthracene (Table 3, entry 7), whereas using the combination NiCl$_2$ · 2 H$_2$O-Li-DTBB (cat.),[13e] 9,10-dihydroanthracene was the only reaction product, thus indicating the different nature of the mechanisms involved.[16] Quinoline was converted efficiently into 1,2,3,4-tetrahydroquinoline (Table 3, entry 8). In general, similar yield pattern was observed for the naphthalene and polymer-supported naphthalene-catalyzed reactions, though 1-chlorodecane and 4-chloroaniline were better reduced using the polymer-supported naphthalene (Table 3, entries 1 and 3), whereas phenethyl iodide was better reduced with naphthalene (Table 3, entry 6).

The hydrogenation of nitrogen-nitrogen bonds was also achieved by any of the two methods in good yields. Thus, phenylhydrazine, 1-methyl-1-phenylhydrazine, and 1,2-diphenylhydrazine were reduced to the corresponding anilines (Table 4, entries 1–3). Finally, this methodology found application in the deoxygenation reaction of azoxy compounds and *N*-oxides, which proceeded in moderate yields. Thus, starting from azoxybenzene and 4,4′-dimethoxyazoxybenzene, the corresponding azobenzenes were obtained, which did not suffer overreduction to hydrazines or anilines (Table 4, entries 4 and 5). On the other hand, the *N*-oxides isoquinoline *N*-oxide and 4-phenylpyridine *N*-oxide were transformed into the expected deoxygenated heteroaromatic compounds (Table 4, entries 6 and 7).

The nickel(0) prepared in the mentioned manner was very finely divided, standing as a suspension even after several days, and showed to be highly reactive as any attempt to support it failed, resulting in deactivation. In general, the reactivity of this catalyst is comparable to that of Raney nickel as regards the hydrogenation of alkenes,[17] alkynes,[17] ketones,[18] and hydrazines,[19] which is also accomplished under soft reaction conditions. However, the reduction of aromatic compounds,[17] alkyl chlorides,[20] azoxy compounds,[21] and *N*-oxides[22] by Raney nickel does not take place or harsh reaction conditions are required. Our catalyst also showed to be superior to the nickel boride obtained with the NiCl$_2$-NaBH$_4$-DMF combination in the reduction of alkyl chlorides,[7b] and milder reaction conditions

Table 4. Hydrogenation of hydrazines, azoxy compounds, and *N*-oxides.

Entry	Starting Material	t [h]		Product	Yield [%][c]	
		A[a]	B[b]		A[a]	B[b]
1		1.0	1.0		88	89
2		1.0	1.0		98	93
3		12.0	12.0		90	93
4		4.0	12.0		58	61
5		12.0	12.0		57	51
6		1.0	2.0		60	45
7		1.0	2.0		67	58

[a] Method A: $NiCl_2$-Li-naphthalene, THF, rt.

[b] Method B: $NiCl_2$-Li-(polymer-supported naphthalene), THF, rt.

[c] Isolated yield of the reaction crude after filtration an evaporation of solvents, unless otherwise is stated.

were required in the hydrogenations of ketones[18] and of aromatic and heteroaromatic compounds[23] in comparison with other nickel catalysts (H_2-Ni-EtOH, $NiCl_2$-Zn-MeOH). Better behaviour of our catalyst was observed in the reduction of carbon-carbon double and triple bonds in comparison with the nickel-aluminium alloy, the latter being used in large excess in a basic medium and which only affects these functions when they are benzylic or conjugated with a carbonyl group.[6a] Finally, and as an example of the reactivity of our catalyst, the hydrogenation of anthracene to furnish 1,2,3,4-tetrahydroanthracene was carried out in 2 h at room temperature with $NiCl_2$-Li-naphthalene (Table 3, entry 7), whereas hydrogenation over the widely used palladium on charcoal required the use of tetralin as solvent in a sealed tube at 340 °C.[24]

Conclusion

In this paper we have introduced the catalytic hydrogenation of a series of organic compounds by using the system $NiCl_2$-Li-naphthalene (cat.). This combination, which generates a very reactive nickel, has been applied to the reduction of a variety of substrates such as alkenes, alkynes, carbonyl compounds, imines, organic halides, aromatic compounds, hydrazines, azoxy compounds, and *N*-oxides, under very mild reaction conditions (room temperature in most cases and atmospheric pressure). Alternatively, a polymer-supported naphthalene has been used as electron transfer agent instead of naphthalene. Although the results obtained with naphthalene and the polymer-supported naphthalene are comparable, the easy recovery by filtration and reusability of the latter makes it the reagent of choice to carry out the herein reported transformations. In general, these catalysts showed a reactivity superior to other nickel catalysts, and compared to Raney nickel the behaviour was similar in the reduction of alkenes, alkynes, ketones and hydrazines, but better results were obtained in the reduction of aromatic compounds, alkyl chlorides, azoxy compounds and *N*-oxides.

Experimental Section

General Remarks and Starting Materials

For general information see Ref.[25] Anhydrous THF was purchased from Acros (99.9%, stabilized). All starting materials (except benzylideneaniline, azoxybenzene, 4,4′-dimethoxyazoxybenzene) were commercially available (Aldrich, Fluka) of the best grade and were used without further purification. For the preparation of benzylideneaniline, see Ref.[26] Azoxybenzene and 4,4′-dimethoxyazoxybenzene were prepared according to Ref.[13f] For the preparation of the polymer-supported naphthalene, see Ref.[15b, c] All reaction products gave satisfactory physical, chromatographic, and spectroscopic data by comparison with authentic samples which were commercially available or previously prepared by us following other methodologies.[13]

Preparation of the Catalytic Mixture

The catalytic mixture was composed of lithium powder (175 mg, 25 mmol), anhydrous nickel(II) chloride (650 mg, 5.0 mmol), and ground naphthalene (32 mg, 0.25 mmol) or polymer-supported naphthalene (160 mg, 1.0 mmol), which was always kept under nitrogen. Within several weeks, no apparent loss of activity was observed for this catalytic mixture.

General Procedure for the Catalytic Hydrogenation

The catalytic mixture [(75 mg for naphthalene), (88 mg for polymer-supported naphthalene), 40 mol % Ni] was introduced into a Shlenck tube together with THF (3 mL) and the starting material (1 mmol) under a hydrogen atmosphere (1 atm) at room temperature. The reaction mixture, which was initially green, changed to black indicating the formation of Ni(0). We observed that Ni(0) was generated faster when only a small amount (< 0.5 mL) of the total THF was first added, followed by successive addition of the rest of THF and the corresponding starting material. The course of the reaction was followed by GLC and/or TLC, and after the reaction time specified in Tables 1–4, the resulting black suspension was diluted with diethyl ether (20 mL) and filtered through a pad containing silica gel and celite (*ca.* 3:1). After drying the filtrate over anhydrous Na_2SO_4, it was evaporated (15 torr) and the resulting residue analyzed without any purification or purified by column chromatography (silica gel, hexane or hexane/diethyl ether) (see footnotes in Tables 1–4).

Acknowledgements

This work was generously supported by the Dirección General de Enseñanza Superior (DGES) of the Spanish Ministerio de Educación y Cultura (MEC; grants no. PB97-0133 and BQU2001-0538). We are very grateful to Dr. G. Radivoy for providing samples of the starting materials azoxybenzene and 4,4′-dimethoxyazoxybenzene.

References and Notes

† For Part 8, see Ref.[14]

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[16] It is well known that the reduction of anthracene with dissolving metals yields mainly 9,10-dihydroanthracene, with partial destruction of aromaticity by reaction at the less aromatic central ring. However, in the catalytic hydrogenation of anthracene, the most thermodynamically stable product, 1,2,3,4-tetrahydroanthracene, maintaining the most π-delocalized aromatic system is obtained (see Ref.[3], p. 67).

[17] Ref.[3], Chapter 6.

[18] Ref.[3], Chapter 13.

[19] Ref.[3], p. 133.

[20] Ref.[3], p. 81.

[21] Ref.[3], p. 134.

[22] Ref.[3], p. 131.

[23] Ref.[3], pp. 72–73.

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