

Letter

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NHC-based Iridium Catalysts for Hydrogenation and Dehydrogenation of N-Heteroarenes in Water under Mild Conditions

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ABSTRACT:

We present a set of iridium complexes containing triazolylidene ligands that are highly active for the reduction of quinoline under 5 atm of H_2 pressure and using water as a solvent. This reduction is effective also with a wide variety of quinolines having functionalities at the 2-, 3-, 6-, and 8positions. One complex is active as well in catalyzing the reverse, *viz* the dehydrogenation of tetrahydroquinoline in high yields and in the same medium without the need of an external hydrogen scavenger. The use of a single catalyst for both hydrogenation and dehydrogenation processes is highly attractive for reversible hydrogen storage in liquid organic hydrogen carriers.



KEYWORDS: NHC carbenes, iridium, hydrogenation, quinoline, dehydrogenation

Catalytic dehydrogenation and hydrogenation reactions of organic molecules are fundamental and important processes in organic chemistry. More recently, these reactions attracted also considerable attention for alternative energy technologies from the viewpoint of hydrogen storage.¹ Some catalysts, both heterogeneous² and homogeneous,^{3,4} can bring about either hydrogenation or dehydrogenation of N-heterocyclic substrates, but there are only very few homogeneous catalysts capable of carrying out both reactions under relatively mild conditions.⁴ A single catalyst for both hydrogenation and dehydrogenation requires activity in reduction as well as oxidation catalysis. Accordingly, iridium complexes containing 1,2,3-triazolederived carbene ligands are attractive candidates as the triazolylidene iridium platform has been shown to be highly active for several stoichiometric⁵ and catalytic bond activation processes, such as transfer hydrogenation,⁶ hydrosilylation,⁷ oxidative transformations⁸ and water oxidation.9 However, to the best of our knowledge, triazolylidene iridium complexes have not been investigated as catalysts for (de)hydrogenation of quinolines as potential liquid organic hydrogen carriers (LOHC) with remarkably low dehydrogenation enthalpy.¹⁰ Of note, iridium(III) centers ligated by a benzimidazole-derived N-heterocyclic carbene have shown activity in the catalytic hydrogenation of quinolines.¹¹ Subsequent work indicated that these complexes also catalyze the dehydrogenation of tetrahydroquinoline, albeit at rather high temperatures (145 °C) and with moderate activity (turnover frequency (TOF) of 0.8 h⁻¹).¹²

Herein we describe the catalytic hydrogenation of quinolines as liquid organic hydrogen carrier in the presence of the known triazolebased iridium complexes **1–4** (Fig. 1)^{9a,13} under 5 atm of H₂ without the use of any additives. Some of these complexes are also efficient for the reverse reaction, *viz.* the dehydrogenation of tetrahydroquinolines in the same solvent, achieving appreciable initial TOFs up to 18 h^{-1} .



Figure 1. NHC-based iridium complexes used in this study.

The activity of triazolylidene iridium as catalyst precursors for the hydrogenation of quinoline **5a** to form 1,2,3,4-tetrahydroquinoline **6a** was investigated initially using

Table 1. Benchmark hydrogenation of quinoline: Variation of the reaction conditions.^a



Entry	H ₂ (bar)	T (°C)	Additive (mol%)	Solvent	Conv. (%) ^b	Yield (%) ^b
1	50	120	-	ⁱ PrOH	100	100
2	50	90	-	ⁱ PrOH	48	46
3°	50	90	-	ⁱ PrOH	53	48
4	50	90	$CF_3COOH(7)$	ⁱ PrOH	51	49
5	50	90	$CF_3COOH(3)$	ⁱ PrOH	51	49
6	50	90	CH ₃ COOH (15)	ⁱ PrOH	50	49
7	50	90	p-TsOH.H ₂ O (8)	ⁱ PrOH	51	49
8	50	90	Pyridinium <i>p</i> -toluensulfonate (2)	ⁱ PrOH	31	30
9	50	90	Pyridinium <i>p</i> -toluensulfonate (7)	ⁱ PrOH	38	38
10	50	90	-	<i>p</i> -xylene	3	2
11	50	90	-	THF	10	8
12	50	90	-	DCE	32	30
13	50	90	-	water	99	95
14	50	70	-	water	98	97
15	35	70	-	water	99	98
16	20	70	-	water	64	54
17	20	90	-	water	100	98
18	10	90	-	water	100	96
19	5	90	-	water	100	85
20	1	90	-	water	15	15
21^{d}	5	90	-	water	100	96
22 ^e	5	90	-	water	18	18

a) General reaction conditions: quinoline (0.5 mmol), Ir complex **1a** (1 mol%), solvent (2 mL), H₂ (50–1 bar), 120-70 °C, 16 h; b) Conversion of quinoline and yield of 1,2,3,4-tetrahydroquinoline calculated from GC samples using hexadecane as internal standard; c) 2 mol% Ir complex; d) 0.5 mol% Ir complex; e) 0.1 mol% Ir complex.

the known iridium complex **1a** (Table 1). This complex was selected for the optimization of reaction conditions, as it has previously been established as an effective catalyst for water oxidation.^{9a} Initial reactions were performed at 120 °C under high hydrogen gas pressure (50 bar) using isopropanol as solvent (entry 1).

With 1 mol% of complex 1a (120 °C, PrOH), complete transformation into the hydrogenated product 1,2,3,4-tetrahydroquinoline was observed after 16 h (entry 1). When decreasing the temperature to 90 °C the conversion decreased to 48% (entry 2), and yields did not improve even when increasing the catalyst loading to 2 mol% (entry 3). Likewise, the introduction of acetic acid, trifluoroacetic acid, p-toluensulfonic acid or pyridinium p-toluensulfonate as additives did not increase the desired yields (entries 4–9). However, the catalyst activity is strongly solvent-dependent, and conversions were excellent in water¹⁴ (entry 13), whilst almost nil conversion was achieved in p-xylene or THF (entries 10, 11) and just 32% was obtained in 1,2-dichloroethane (entry 12). Further modification of conditions involved variation of temperature and H2 pressure using water as a solvent. The reaction temperature is critical and while full conversion was reached even at 70 °C, a H2 pressure of 35 bar is required. At 20 bar H_2 , the reaction was incomplete (entries 14–16). When the reaction is performed at 90 °C, however, the H₂ pressure

can be as low as 5 bar without compromising the conversion. At ambient pressure, however the reaction is slow and reaches only 15% conversion (entries 17–20). When keeping the pressure at 5 bar H_2 , lowering of the catalyst loading to 0.5 mol% is feasible and increases the turnover number to appreciable 200 (entry 21). Further lowering of the catalyst loading provides similar turnover numbers and incomplete conversion (entry 22), possibly indicating the current limit of this catalytic system.

Having established optimized reaction conditions, catalytic quinoline reduction was performed with different triazolylidene iridium complexes, including neutral, mono-, and dicationic complexes containing C,N-bidentate chelate motifs $(1a, 1b)^{9a}$ and C,C-bidentate bonding triazolylidenes resulting from cyclometalation (complexes 2, 3)^{13a,b} or from bis(carbene) bonding (complex 4, see Fig. 1).^{13c} When the reaction is carried out with the di-cationic iridium complex 1b as catalyst precursor, the yield is comparable to that obtained with complex 1a (Table 2, entry 2 vs. 5).¹⁵ The essentially identical performance of the two catalytic systems is in agreement with a rapid solvolysis of the iridium chloride complex 1a when dissolved in aqueous media, hence interconverting this complex to 1b (albeit with a different counter ion).¹⁶ The neutral complex **2** containing an anionic phenyl group as chelating ligand instead of a pyridyl fragment in 1 induces only very low conversions when reactions are performed in water (entry 6; cf entry 15 in Table 1), though switching the solvent to [']PrOH enhanced yields considerably (Table 2, entries 7,8).

Full conversions were reached also when decreasing the catalyst loading to 0.5% (entry 9). An appreciable 56% conversion of quinoline was achieved even when the reaction was performed under just 1 atm of H₂ (entry 10), which is considerably higher than the 15% conversion obtained with the monocationic complex **1a** under the same conditions.¹⁷ Cyclometalated complex **3** is markedly less active than complexes **1** and **2** which is demonstrated in catalytic runs performed at 70 °C (38% *vs.* > 99%; entries 1,7,11). With this complex, the solvent had no critical influence (entries 11,12). As observed for complex **1a**, the cationic biscarbene complex **4** shows higher activity in water than in 'PrOH (74% *vs.* 50% at 70 °C; entries 14,15), though in both solvents, either complex **1** or **2** are more efficient.

The facile dissociation of the ancillary chloride ligand in complex 1a offers some hint on the mechanism of the reaction. Ligand dissociation provides access to a free site in the iridium coordination sphere for coordination of the N-heterocyclic substrate under catalytic conditions. Indeed, when complex 1a was dissolved in D2O in the presence of an excess of quinoline, formation of the N-adduct was easily identified by the appearance of a new set of signals with a downfield shifted doublet at 9.3 ppm as most prominent feature (Fig. S1). When this sample was charged with 1 atm of H₂, no significant changes were noticed by NMR spectroscopy. However, when the H2-saturated mixture was heated to 90 °C, a new iridium species appeared. After continued heating at this temperature for 18 h, the major component was a new iridium species $1a-d_1$ with the ligand selectively deuterated at the pyridyl C(6) position (Scheme 1). Deuteration was indicated in the ¹H NMR spectrum by the disappearance of the doublet at 8.14 ppm, and the concomitant simplification of the coupling pattern for the C(5)-H and C(4)-H protons, both from ddd to a doublet of doublets (Fig. S2). No such deuteration process was observed when complex 1a was exposed to the same conditions in the absence of H₂, even when heated in presence of a base (1.5 mol equiv. DBU). These results therefore suggest the formation of hydride species in which H/D exchange with the D₂O solvent takes place.¹⁸ Deuteration of the pyridyl C(6) position can then occur through a reversible roll-over cyclometalation,¹⁹ which transiently forms a 5-membered iridacycle with a C,C-bidentate coordinating triazolylidene-pyridyl ligand. The reversibility of this rollover process accounts for the isotope scrambling and formation of **1a**-*d*₁, and it rationalizes the selective deuteration of the *ortho* position with respect to the triazolylidene linkage (Scheme S1).







a) General reaction conditions: quinoline (0.5 mmol), Ir complex (1 mol%), solvent (2 mL), H_2 (1–50 bar), 70–120 °C, 16 h; b) Conversion of quinoline and yield of 1,2,3,4-tetrahydroquinoline calculated from GC samples using hexadecane as internal standard; c) 0.5 mol% Ir complex.

Scheme 1. Deuteration of iridium complexes **1a** and **2**, and proposed intermediate in the rollover process leading to $1a-d_1$.

In line with this model, exposure of a solution of complex **2** in *iso*propanol– d_8 :D₂O (5:1 v/v) in presence of quinoline and H₂ (1 bar) afforded after 20 h complex **2**– d_3 , in which all *ortho* positons are deuterated (Scheme 1; Fig. S3). As noted for complex **1a**, deuteration is evidenced by the disappearance of the doublet of doublet resonance at 7.65 ppm, attributed to C(6)-H, as well as by the change of multiplicity of the signals for the coupled protons. Remarkably, isotope exchange also occurred on the pendant phenyl ring, which suggests transient metalation of either of the two aromatic rings during the reaction. In the ground state, however, cyclometalation exclusively involves the N_{trz}-bound phenyl ring. Such reversible ligand cyclometalation may be key for the observed activity of these complexes in quinoline hydrogenation.

With complexes **1a** and **2** as the most active hydrogenation catalysts, the scope of quinoline hydrogenation was investigated under optimized conditions. The results are summarized in Table 3 and demonstrate the efficient conversion of a variety of quinolines, including substitutions at 2-, 3-, 4-, 6- and 8- positions as in **5b–f** to afford the corresponding 1,2,3,4-tetrahydroquinoline products (Table 3, entries 1–6). Excellent yields were obtained, with the exception of the 4-Me derivative.^{4a,20} With that substrate, almost no reaction was observed with complex **1a**, while complex **2** achieved some

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 Table 3. Hydrogenation of quinolines catalyzed by complexes

 1a and 2.ª



Entry	Substrate	Conversion (%) ^b 1a / 2	Isolated Yield (%)
1	5a (R = H)	100 / 100	96 / 100 ^b
2	5b $(R = 2-Me)$	100 / 100	85 ^d
3	5c $(R = 3-Me)$	100 / 100	96 ^d
4	5d (R = 4-Me)	7 / 51	-
5	5e $(R = 6-Me)$	100 / 100	86 ^d
6	5f ($R = 8-Me$)	100 / 100	85 ^d
7	5g (R = 6-Cl)	100 / 100	98°
8	5h ($R = 6 - NO_2$)	2 / 72	-
9	5i (R = 6-COOH)	nd° / 100	87°
10	5 j (R = 2-Me, 6-OMe)	40 / 46	-

a) Reaction conditions: substrate (0.5 mmol), catalyst (0.5 mol%), solvent (2 mL), H_2 (5 bar), 90 °C, 16 h; solvent = water for reactions with complex 1, and 'PrOH for complex 2; b) conversion and yields calculated from GC samples using hexadecane as internal standard, isolated yields only determined for near-quantitative conversion; c) nd = not determined, due to substantial formation of side products; d) isolated yields from runs with complex 1a; e) isolated yields from runs with complex 2.

51% conversion. Tentatively, we suggest that the *C*,*N*-chelating ligand in complex **1** prevents coordination of the C3–C4 double bond, while the Ir–C_{Ph} bond may easily be hydrogenated during catalyst activation to yield a monodentate carbene iridium complex as active species. Functional groups such as –Cl, –NO₂ and –COOH substituents (entries 7–9) are also tolerated, and the resulting hydrogenated heterocycles were obtained in good to excellent yields when catalyst **2** was used. Complex **1** was narrower in substrate scope and did not induce significant conversion with nitro and carboxylate functional groups. Only moderate performance was observed with both complexes **1** and **2** in the hydrogenation of the di-substituted quinoline 6-methoxy quinaldine **5**j (entry 10).

Having established the effectiveness of complexes **1a** and **2** for quinoline hydrogenation, we explored the potential of these complexes as catalyst precursors for the reverse reaction, *i.e.* the dehydrogenation of saturated N-heterocyclic substrates. In a first set of experiments, complex **1a** was used for the oxidation of 1,2,3,4-tetrahydroquinoline under different reaction conditions. The results indicate again a strong solvent dependence as was observed for the hydrogenation reaction. While conversions were low when *p*-xylene or 2,2,2-trifluoroethanol were used as solvents (Table 4, entries 1, 2), a moderate 50% conversion of 1,2,3,4-tetrahydroquinoline was ob tained when the reaction was performed in 1,2-dichlorobenzene at 160 °C (entry 3), yet conversions were almost complete when the catalyst loading was raised from 1 to 2 mol% (entry 4). Interestingly, the best results were achieved when the reaction was performed in water at reflux temperature, leading to 90% conversion after 20 h (entry 6). This result implies that complex **1a** provides a catalytic system that is able to do both, the hydrogenation and the opposite reaction in one and the same solvent, and that the course of the reaction is only dependent on the partial pressure of the reaction medium.

Conversion was nil after 20 h when complex 2 was used for the dehydrogenation reaction using the same conditions as applied for the reverse quinoline hydrogenation, viz. PrOH at 90 °C (entry 7), presumably because this solvent adversely affects the dehydrogenation equilibrium. With 2 mol% of catalyst loading and using 1,2-dichloromethane, 64% conversion was achieved (entry 8), which is lower than the yield obtained with complex **1a** (*cf* entry 4). Most efficient dehydrogenation with complex 2 took place when the reaction was performed in water (entries 9-11), with good yields even in the presence of as little as 0.5 mol% of catalyst. Time-dependent monitoring of the conversion indicates turnover frequencies up to 20 h⁻¹ for the quinoline dehydrogenation (Fig. S4), which is more than one order of magnitude larger than related iridium complexes featuring a less electron-donating and monodentate coordinating benzimidazolylidene ligand or a pyridinol system (TOF ca. $1 h^{-1}$),^{4a,12} or a cobalt system (TOF ca. $0.1 h^{-1}$).^{4c} These values emphasize the high capacity of the triazolylidene iridium platform for mediating bond activation

Table 4. Dehydrogenation of tetrahydroquinoline catalyzed	by
complexes 1a or 2.ª	

6a		[lr] (1 mol%) solvent (2 mL) 20 h	Sa		
Entry	[Ir]	Solvent	Т (°С)	Conv. (%) ^b	Yield (%) ^b
1	1a	2,2,2-TFE	95	17	15
2	1a	<i>p</i> -xylene	150	7	6
3	1a	1,2-DCB	160	48	40
4 ^c	1a	1,2-DCB	160	82	67
5	1a	Water	100	69	68
6°	1a	Water	100	90	83
7	2	ⁱ PrOH	90	0	0
8°	2	1,2-DCB	160	64	53
9°	2	water	100	99	96
10	2	water	100	85	80
11 ^d	2	water	100	66	64

a) Reaction conditions: substrate (0.5 mmol), catalyst (1 mol%), solvent (2 mL), 20 h (TFE = trifluoroethanol, DCB = dichlorobenzene);
b) Conversion and yield calculated by GC using hexadecane as internal standard; c) 2 mol% of catalyst; d) 0.5 mol% of catalyst.

processes.

In conclusion, We have developed a homogeneous system consisting of a triazolylidene-based iridium complex for efficient hydrogenation and dehydrogenation of quinoline derivatives without the use of any additive. The reversible catalytic transformation takes 1

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59 60 place favorably in aqueous media and swapping between hydrogenation and dehydrogenation processes exclusively depends on the presence or absence of dihydrogen gas. Such a simple and reversibly operating catalytic system holds great promise for reversible hydrogen storage in N-heterocyclic compounds. Investigations on further improving the catalyst performance for the reversible dehydrogenation-hydrogenation reaction of quinolines as well as other liquid organic hydrogen carriers containing a larger hydrogen storage capacity as one of the many requirements for efficient LOHCs¹⁰ are currently in progress.

ASSOCIATED CONTENT

Supporting Information. NMR spectra from deuteration and reaction intermediates, time-conversion profile for dehydrogenation, NMR spectra of products, and experimental procedures. This material is available free of charge on the ACS Publication website at DOI: 10.1021/xxxxx.

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Notes

The authors declare no competing financial interest.

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(15) The reaction with catalyst **1b** has not been tried in H_2O , as solvolysis of complex **1a** in water is fast and produces in fact **1b**. For reactions in aqueous phase, it therefore is irrelevant whether **1a** or **1b** is the starting material as both compounds produce the di-cationic aqua compound **1b**.

(16) Solvolysis of this complex has been established, see: Petronilho, A.; Llobet, A.; Albrecht, M. *Inorg. Chem.* **2014**, *53*, 12896–12901.

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(**De**)**Hydrogenation:** Triazolylidene iridium complexes are efficient catalysts for both the hydrogenation of quinolines to tetrahydroquinolines and for the oxidation of the hydrogenated products. These reactions take place in aqueous media under mild conditions.



