

Supported Catalysis

Catalytic Hydrogen Production by Ruthenium Complexes from the Conversion of Primary Amines to Nitriles: Potential Application as a Liquid Organic Hydrogen Carrier

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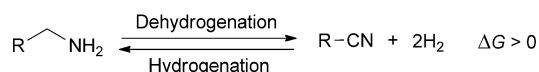
Abstract: The potential application of the primary amine/nitrile pair as a liquid organic hydrogen carrier (LOHC) has been evaluated. Ruthenium complexes of formula $[(p\text{-cym})\text{-Ru}(\text{NHC})\text{Cl}_2]$ (NHC = N-heterocyclic carbene) catalyze the acceptorless dehydrogenation of primary amines to nitriles with the formation of molecular hydrogen. Notably, the reaction proceeds without any external additive, under air, and under mild reaction conditions. The catalytic properties of a ruthenium complex supported on the surface of graphene have been explored for reutilization purposes. The ruthenium-supported catalyst is active for at least 10 runs without any apparent loss of activity. The results obtained in terms

of catalytic activity, stability, and recyclability are encouraging for the potential application of the amine/nitrile pair as a LOHC. The main challenge in the dehydrogenation of benzylamines is the selectivity control, such as avoiding the formation of imine byproducts due to transamination reactions. Herein, selectivity has been achieved by using long-chain primary amines such as dodecylamine. Mechanistic studies have been performed to rationalize the key factors involved in the activity and selectivity of the catalysts in the dehydrogenation of amines. The experimental results suggest that the catalyst resting state contains a coordinated amine.

Introduction

The use of molecular hydrogen as an alternative energy source is a highly desirable process.^[1–3] The key is the production of energy with the formation of water as the only byproduct. From environmental and sustainability points of view, the advantages versus other technologies are notorious.^[4–6] Nevertheless, there are still some limitations to overcome that should be addressed by technological and scientific approaches: 1) hydrogen production and 2) hydrogen storage.^[7–9] The production of hydrogen is well-known, the problem arises from the bulk production. In an ideal situation, industrial hydrogen production would require the use of renewable energy sources to obtain hydrogen from the electrolysis of water. Many efforts have pursued this goal and the achievements in the last few years have been considerable.^[10,11] The success of hydrogen as an alternative energy source relies on the development of efficient hydrogen storage and transport systems.^[12–14] Nowadays, hydrogen storage represents a technological challenge.^[15,16] Among all the possibilities, chemical hydrogen storage in the form of organic liquids represents an attractive route for the development of hydrogen carrier systems.^[17–20] In this sense, the technological problems are minimized as the actual infrastructure is based in liquids for storage and transport.^[21,22] The

future of liquid organic hydrogen carriers (LOHC) depends on a reversible chemical reaction based on the release and uptake of hydrogen.^[23–27] In this work, we have evaluated the potential of the amine/nitrile pair as a liquid organic hydrogen carrier, as suggested by Grellier and Sabo-Etienne in a frontier-type article (Scheme 1).^[28]



Scheme 1. (De)hydrogenation of the amine/nitrile pair.

The acceptorless dehydrogenation of primary amines generates the corresponding nitrile and two moles of hydrogen. The reaction is not favored at room temperature and an effective catalyst is needed for practical purposes. Efficient catalysts for the acceptorless dehydrogenation of amines are scarce and were first developed by the group of Szymczak based on a ruthenium pincer complex.^[29] The viability of the amine/nitrile pair as a potential organic hydrogen carrier also lies in the effectiveness of the reverse process, that is, the hydrogenation of nitriles. Fortunately, the hydrogenation of nitriles is a well-documented catalytic reaction and efficient catalysts have been described in the literature.^[30–35] Nitriles are versatile intermediates in organic synthesis owing to their direct conversion into a variety of functional groups. Conventional organic procedures require nucleophilic displacement of suitable leaving groups producing stoichiometric amounts of waste and with

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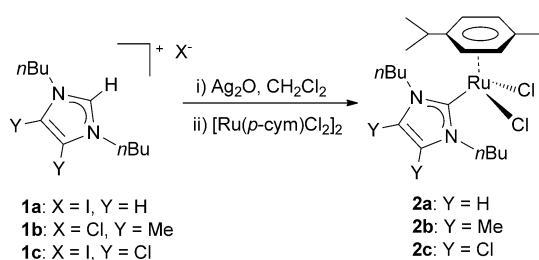
limited selectivity.^[36,37] A novel and green method for the synthesis of nitriles consists in the acceptorless dehydrogenation of primary amines. This method does not require the use of stoichiometric oxidants and the only byproduct is molecular hydrogen.

In this work, we describe the production of hydrogen from primary amines by using ruthenium catalysts, showing the potential application of the primary amine/nitrile pair as a liquid organic hydrogen carrier. Studies on the catalytic activity and selectivity have allowed us to propose a plausible mechanism for the dehydrogenation of amines.

Results and Discussion

Synthesis of ruthenium complexes

A series of ruthenium complexes (**2a–c**) were obtained in good yield from the corresponding imidazolium salts (**1a–c**) by transmetallation using silver oxide (Scheme 2). The complexes were fully characterized by NMR, electrospray mass ionization, and elemental analysis. The ruthenium complexes^[38–40] differ in the substituents at the 4- and 5-positions of the N-heterocyclic carbene ligand (NHC). Fine-tuning of the electronic properties of the NHC ligands is achieved by the introduction of electron-donating ($-\text{CH}_3$) or -withdrawing groups ($-\text{Cl}$).^[41] Modifying the substituents at the backbone of the azol ring does not alter significantly the steric properties of the NHC ligands, which are controlled by the substituents at the nitrogen positions 1 and 3 (*n*-butyl groups).^[42,43] The catalytic properties of ruthenium complexes of general formula $[(p\text{-cym})\text{Ru}(\text{NHC})\text{Cl}_2]$ have been described previously in the dehydrogenation of alcohols and homocoupling of amines.^[44,45]



Scheme 2. Synthesis of ruthenium complexes.

Catalytic properties

In a first set of experiments, the dehydrogenation of benzylamine was chosen as the model reaction for the optimization of the reaction conditions (Table 1). One equivalent of benzylamine and 2 mol% of catalyst were dissolved in 3 mL of solvent and heated at vigorous reflux. A control experiment showed that the dehydrogenation reaction did not proceed in the absence of catalyst (Table 1, entry 1). When the reaction was carried out in the presence of a halide abstractor additive, benzylamine was converted to an equimolar mixture of nitrile

and imine (entry 2). The use of different bases slightly increased the selectivity towards the nitrile compound without altering the conversion, except in the case of *t*BuOK. The use of such a strong base was detrimental for the dehydrogenation of benzylamine and only 34% conversion was reached (entries 3–5). The best results were achieved in the absence of any external additive (entries 6–8). The reaction of benzylamine with catalyst **2a** in toluene without any additive afforded full conversion after 8 h. The reaction selectivity favored the formation of the nitrile product. The ruthenium catalysts **2a–c** with different electronic properties displayed no significant difference in terms of catalytic activity or product selectivity. We observed that the selectivity in the dehydrogenation of amines was largely dependent on the reaction conditions. When the reaction of benzylamine using catalysts **2a–c** was carried out in a closed vessel, the only product formed was the imine (the acceptorless dehydrogenative coupling or transamination product). The homocoupling of primary amines by using catalyst **2a** had previously been described in a closed system showing the sole formation of the imine product.^[44] The dehydrogenation of amines is a nonspontaneous thermodynamic process. The release of hydrogen from the reaction media produces an equilibrium shift towards product formation. We thus conclude that vigorous refluxing conditions favor the reaction by facilitating the release of hydrogen. When the reaction is carried out with intense solvent bubbling, the conversion is increased. Solvent optimization was carried out for catalyst **2c** (entries 9–13). The best results were obtained using *p*-methylbenzylamine as the substrate and toluene as the solvent. The use of acetonitrile or alcohols as the solvent decreased the reaction conversion and selectivity of dehydrogenation. Two different experiments served to evaluate whether oxygen from air is the final oxidant in the dehydrogenation of amines (entries 14–15). The reaction of benzylamine was carried out under intense nitrogen bubbling. The results suggest that oxygen is not needed in the dehydrogenation process. Confirmation was obtained when carrying out the same experiment under an oxygen atmosphere. The presence of oxygen afforded less than 5% conversion. This result implies that oxygen is not the final oxidant in the dehydrogenation of amines; in fact, the results show that the catalyst is inactive under catalytic conditions in the presence of oxygen.

The reaction scope and limitations of the catalytic dehydrogenation of benzylamines were evaluated using complexes **2c** and **3** as catalyst precursors (Table 2). The reaction conditions consisted of toluene as the solvent at 110 °C and a catalyst loading of 2 mol%. Complex **3** was used for comparative reasons. The immobilization of complex **3** on graphene has been previously described and we wanted to assess the catalytic properties of a supported molecular ruthenium catalyst in the dehydrogenation of amines.^[45] The evaluation of the catalytic properties revealed that both ruthenium complexes are active in the dehydrogenation of a variety of amines containing different substituents. In all cases, full conversions were achieved in approximately 8 h. Only in the case of bulky amines, such as 1-naphtylmethylamine, was the dehydrogenation process slower (Table 2, entries 12 and 13). The best results in terms of

Table 1. Optimization parameters for the catalytic dehydrogenation of primary amines.^[a]

Entry	Cat.	R	Additive	Solvent	Conv. [%] ^[b]	Selectivity [%]	
						nitrile	imine
1	–	H	–	toluene	0	–	–
2	2a	H	AgOTf	toluene	92	49	51
3	2a	H	tBuOK	toluene	34	68	32
4	2a	H	Cs ₂ CO ₃	toluene	88	70	30
5	2a	H	NaOAc	toluene	97	60	40
6	2a	H	–	toluene	98	74	26
7	2b	H	–	toluene	95	73	27
8	2c	H	–	toluene	100	75	25
9	2c	CH ₃	–	toluene	100	74	26
10	2c	CH ₃	–	MeCN	24	50	50
11	2c	CH ₃	–	iPrOH	54	68	32
12	2c	CH ₃	–	tBuOH	75	65	35
13	2c	CH ₃	–	nBuOH	39	64	36
14	2c	H	N ₂ (bubbling)	toluene	98	71	29
15	2c	H	O ₂ (1 atm)	toluene	<5	n.d. ^[c]	n.d. ^[c]

[a] Reaction conditions: substrate (0.3 mmol), catalyst (2 mol%), 3 mL of solvent at reflux for 8 h. [b] Conversion determined by GC analysis using anisole as the internal standard. [c] n.d. = not determined.

Table 2. Reaction scope and limitations of the catalytic dehydrogenation of primary amines.^[a]

Entry	Cat.	R	Conv. [%] ^[b]	Selectivity [%]	
				nitrile	imine
1	2c	H	100	75	25
2	3	H	99	82	18
3	NHC–Ru–rGO (4)	H	100 ^[c]	65	35
4	2c	Cl	95	50	50
5	3	Cl	83	57	43
6	2c	Me	100	74	26
7	3	Me	93	70	30
8	2c	OMe	99	69	31
9	3	OMe	97	68	32
10	2c	CF ₃	95	62	38
11	3	CF ₃	78	52	48
12	2c	naphtyl	80	55	45
13	3	naphtyl	82	57	43

[a] Reaction conditions: substrate (0.3 mmol), catalyst (2 mol%), 2 mL of toluene at 110 °C for 8 h. [b] Conversion determined by GC analysis using anisole as the internal standard. [c] After 6 h of reaction.

catalytic activity were obtained in the case of benzylamine using catalyst **3** and in the case of 4-methoxybenzylamine using catalyst **2c**. A comparative reaction profile was carried out using 4-methoxybenzylamine as a model substrate and complexes **2c** and **3** as the catalyst precursors (Figure S1, Supporting Information). In general, the differences observed in catalytic activity of complexes **2c** and **3** are negligible. The formation of molecular hydrogen was confirmed by injection of the gases released in the reactions described in entries 7 and 8 directly into a gas chromatograph. The challenge in the dehydrogenation of benzylamines is to control the selectivity of the reaction. In general, it has been found that controlling the factors that govern the formation of the different products is difficult. The use of ruthenium complexes with different ligands has proved inefficient to control the selectivity and further efforts to design highly selective catalysts are thus required. The best results in terms of selectivity were obtained for benzylamine using complex **3** as the catalyst (entry 2).

The catalytic properties and recycling studies of the hybrid material NHC–Ru–rGO (**4**) were carried out using benzylamine (entry 3 and Figure 1). The results show that immobilization of complex **3** on the graphene surface increases the catalytic activity. Full conversion was achieved in 6 h, in contrast to the 8 h required with molecular complex **3**. These results support our previous catalytic studies using molecular complexes anchored on graphene.^[45,46] The immobilization of molecular complexes on graphene by noncovalent interactions shows a catalytic benefit compared to the molecular complexes most probably due to the increased stability of the catalytically active species.

The reaction scope of the catalytic dehydrogenation of alkyl primary amines was evaluated (Table 3). The results show that

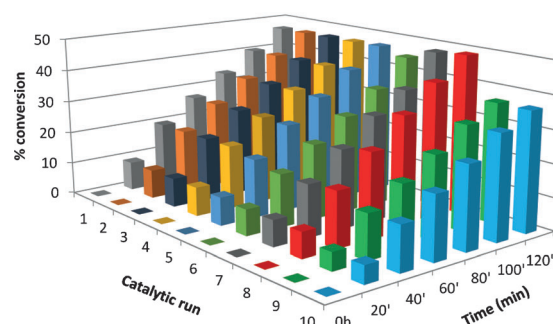
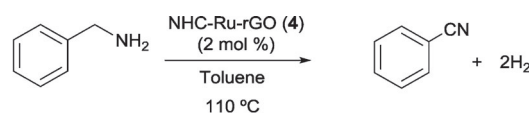


Figure 1. Recycling experiments on the dehydrogenation of benzylamine using the hybrid material NHC–Ru–rGO (**4**). Reaction profile for each run determined by GC analysis at a maximum of approximately 50% conversion.

the ruthenium complexes [(*p*-cym)Ru(NHC)Cl₂] are active in the dehydrogenation of alkylamines under the same reaction conditions as described for the benzylamines. In the case of alkylamines, we observed a better control of the selectivity towards nitrile formation. Increasing the number of carbon atoms of the alkyl chain inhibited the formation of the transamination product. For example, dehydrogenation of heptylamine yielded 78% of nitrile product, octylamine afforded 89% and, in the case of dodecylamine, the nitrile product was obtained in 100% yield (Table 3, entries 1–3).

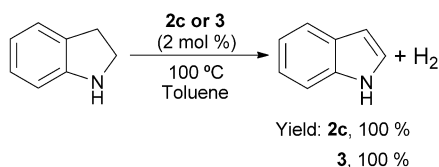
The formation of the transamination product is thus inhibited for long-chain alkylamines. In the case of tetradecylamine, hexadecylamine, and octadecylamine, the only product ob-

Table 3. Dehydrogenation of alkyl primary amines.^[a]

Entry	Amine	<i>n</i>	Conv. [%] ^[b]	Selectivity [%]	
				nitrile	imine
1	heptylamine	5	95	78	22
2	octylamine	6	99	89	11
3	dodecylamine	10	100	100	0
4	tetradecylamine	12	95	100	0
5	hexadecylamine	14	97	100	0
6	octadecylamine	16	95	100	0

[a] Reaction conditions: substrate (0.3 mmol), catalyst (2 mol %), 2 mL of toluene at 110 °C for 24 h. [b] Conversion determined by GC analysis using anisole as the internal standard.

served was the nitrile compound. The use of long-chain alkylamines to control the selectivity in the oxidation of primary amines has recently been described.^[47] Control over the selectivity is an important issue when considering the amine/nitrile pair as a promising candidate for LOHC. It has been described that N-heterocycles are considered good LOHCs and control of the selectivity can be easily achieved. For comparative purposes, we studied the activity of the ruthenium complexes in the dehydrogenation of indoline (Scheme 3). The ruthenium complexes **2c** and **3** catalyzed the dehydrogenation of indoline quantitatively in 6 h at 110 °C.



Scheme 3. Dehydrogenation of indoline.

Recycling studies

We have recently described a methodology for obtaining supported catalyst on the surface of graphene by means of non-covalent interactions.^[45,46] The catalytic properties of the hybrid materials in terms of activity and stability have demonstrated the potential of transition metals immobilized on gra-

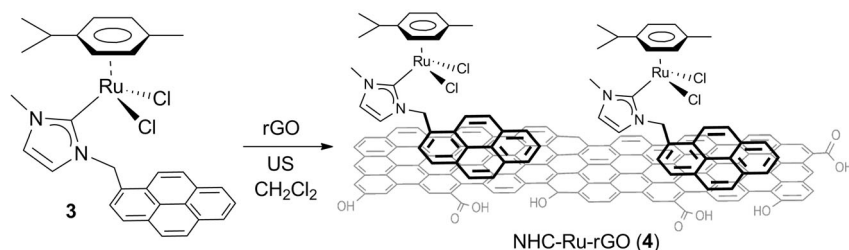
phene.^[48–50] The catalytic results improve when the metal complexes are anchored on graphene and the hybrid materials can be recycled up to 10 times due to their enhanced stability. In view of the good results obtained, we decided to assess the catalytic activity of a similar ruthenium-based hybrid material derived from complex **3** in the hydrogen production from primary amine dehydrogenation (Scheme 4).

The catalytic properties of molecular complex **3** and its derived hybrid material **4** were analyzed under the same reaction conditions (Table 2, entries 2 and 3). The results show that the catalytic activity of the molecular complex is maintained after immobilization. In general, one of the drawbacks of supported molecular catalysis is the decrease in the reaction rate due to diffusion problems. The catalytic activity of **3** was not altered after immobilization on graphene most probably because of the 2D character of graphene that facilitates the accessibility to all catalytic active centers. The same behavior has been previously observed when comparing the catalytic activity of other molecular complexes and their corresponding immobilized hybrid materials.^[45]

Recycling experiments were carried out using benzylamine as the model substrate. The reactions were performed using a catalyst loading of 2 mol % (based on ruthenium), and 3 mL of toluene at 110 °C. The reaction profile for each run was monitored by GC until a maximum of approximately 50% conversion. After each run, the mixture was allowed to cool down to room temperature and the solid catalyst was separated by decantation, washed thoroughly with toluene, and used in the next run (Figure 1).

The hybrid material NHC–Ru–rGO (**4**) was reused up to 10 times without any significant decrease in activity. There is a slight decrease of the catalytic activity in run 9 that is maintained in run 10. The reaction profile for each run allows comparison of the catalytic activity for different reaction times. The results show that the catalytic activity is maintained for the different runs. The morphology of the catalytic hybrid material NHC–Ru–rGO (**4**) was analyzed by HRTEM after the recycling experiments. Comparison of the images before and after the recycling experiments reveal a well-dispersed ruthenium distribution without the presence of metal nanoparticles (Figure 2). The morphology of graphene does not display significant changes apart from an increase in the number of wrinkles.

To establish the mode of action of the hybrid material NHC–Ru–rGO (**4**) during catalysis, a hot filtration experiment was carried out. This experiment rules out the possibility of release-and-return of the molecular complex from the surface of gra-



Scheme 4. Synthesis of the hybrid material NHC–Ru–rGO (**4**).

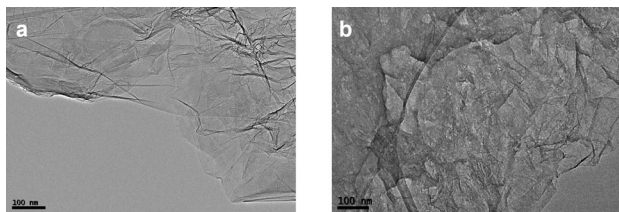


Figure 2. HRTEM images of PhF-Ru-rGO (4): a) before, and b) after ten catalytic runs.

phene. If the molecular complex is retained on the surface of graphene, the catalysis is heterogeneous in nature; however, if the molecular complex is released, the catalysis is homogeneous. The hot filtration experiment was carried out using NHC-Ru-rGO (4) (2 mol%) as the catalyst and benzylamine as the substrate. The catalytic hybrid material NHC-Ru-rGO (4) was removed from the reaction medium by filtration at high temperature (110 °C) when the conversion reached 50% (ca. 2 h). The filtrate was stirred for 2 h more under identical conditions. After this time, GC analysis indicated that no further amine dehydrogenation had occurred (GC conversion remained at 50%). The catalytic hybrid material NHC-Ru-rGO (4), previously removed from the reaction medium, was then treated with more benzylamine. After 2 h at 110 °C, we observed that the reaction had proceeded, indicating that the hybrid material NHC-Ru-rGO (4) was still active. The hot filtration experiment confirmed the absence of catalytic species in solution due to catalyst desorption from the graphene surface and demonstrated the heterogeneous nature of the catalytic process. The recycling properties of the hybrid material NHC-Ru-rGO (4) are excellent and most probably due to the stabilization of molecular ruthenium complex 3 on the surface of graphene.

Mechanistic considerations

Preliminary studies for the mechanism in the acceptorless dehydrogenation of amines were performed by monitoring the reaction profile by ^1H NMR spectroscopy (Figure 3). The catalytic dehydrogenation of *p*-methoxybenzylamine was carried out using complex 2c in deuterated toluene using NMR tubes closed with a perforated septum using a needle. The results show that signals corresponding to the nitrile product start to appear after 2 h, suggesting that dehydrogenation towards nitrile is fast. However, the reaction needed four days to achieve full conversion. In general, the kinetics of catalytic reactions carried out in NMR tubes is slow due to diffusion problems. We have observed that the reaction conditions have an important influence in the kinetics in regard to the facile release of hydrogen. The reaction is slowed down when there is not a vigorous bubbling as occurs in the NMR tube. Importantly, the only products observed during all the catalytic reactions are the nitrile and imine, no other products were detected. In general, it should be possible to detect the presence of dissolved molecular hydrogen by ^1H NMR spectroscopy. In our case, we did not observe the formation of molecular hydrogen. Most probably, hydrogen needs to be released for reaction evolu-

tion. In order to confirm the presence of hydrogen, a similar experiment was carried out using a sacrificial hydrogen acceptor. The reaction was carried out with benzylamine, complex 2c, and two equivalents of *tert*-butyl ethylene (tbe) in deuterated toluene. The ^1H NMR recorded after the experiment showed the formation of products but no ethylene hydrogenation. This result suggests that our ruthenium complex is a poor hydrogenation catalyst. Further evidence is that the imine product was not hydrogenated to the corresponding amine. The formation of H_2 in the dehydrogenation of amines was analyzed in a different experiment by gas chromatography (GC). A solution of complex 2c and benzylamine in toluene was heated under catalytic conditions. A sample of the generated gas was collected and injected directly into the GC using a gas-syringe. The results confirmed the presence of molecular hydrogen generated from the dehydrogenation of amines.

Further mechanistic investigations were carried out by single-stage ESI-MS (Figure 4). An equimolar mixture of complex 2c and *p*-methylbenzylamine was dissolved in toluene, heated at 70 °C for 10 min, and analyzed by direct injection into ESI-MS. The results show the presence of two species in solution. The peak at m/z : 521.1 was assigned to complex 2c with a vacant coordination site, formulated as $[\text{M}-\text{Cl}]^+$. A second and more intense peak at m/z : 642.1 was assigned to complex 2c, which contains a coordinated *p*-methylbenzylamine $[\text{M}-\text{Cl}+\text{H}_2\text{NCH}_2\text{PhMe}]^+$. The proposed molecular composition was further confirmed by the simulated isotopic pattern distribution. When the same experiment was reproduced at 110 °C instead of 70 °C, neither the formation of this reaction intermediate nor any other ruthenium species was detected. The results suggest that 1) at low temperatures, a chloride ligand in complex 2c is replaced by a *p*-methylbenzylamine and 2) at high temperatures, the amine is converted to the nitrile product and no other ruthenium intermediates are detected. These results support that complex 6 is the resting state in the dehydrogenation of amines. Metal-halide bond-breaking and coordination of an L-type ligand yielding cationic species has previously been reported for ruthenium *p*-cymene species.^[51] A further experiment was performed to confirm the coordination of *p*-methylbenzylamine to ruthenium and discard the possibility that this product is only formed under ESI-MS conditions. Ruthenium complex 5 and *p*-methylbenzylamine were dissolved in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (3:2 v/v). Addition of sodium tetrafluoroborate afforded the amine-coordinated product 6 in high yield (Figure 5). Ruthenium complex 6 is stable in solution and in the solid state. The molecular structure of complex 6 was confirmed by single-crystal X-ray diffraction.

A mechanism for the dehydrogenation of primary amines is proposed in Figure 6 based on experimental evidence. Mechanistic reports for the dehydrogenation of primary amines are scarce. Brookhart et al. proposed a reaction mechanism for an iridium complex using a hydrogen acceptor.^[52] The only mechanistic cycle for the acceptorless amine dehydrogenation reaction was proposed by Szymczak et al.^[53] More mechanistic information is available for the reverse reaction, the hydrogenation of nitriles, but still, a complete catalytic cycle for all the steps involved in the process is needed.^[54–56] Starting from

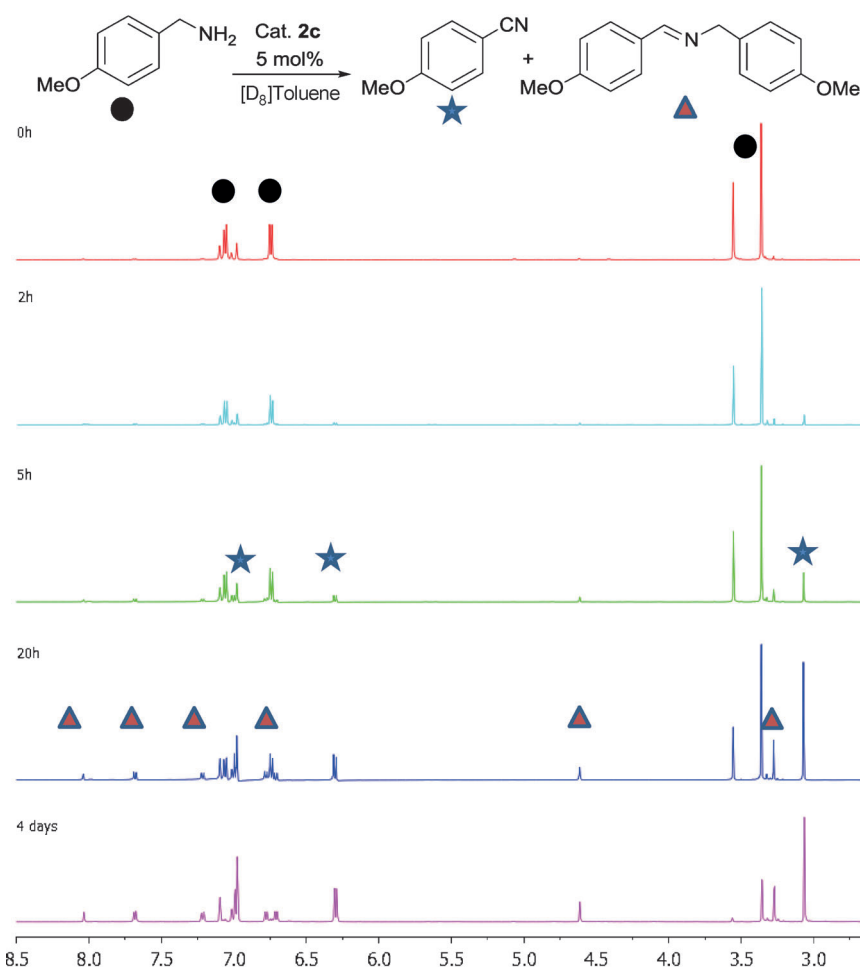


Figure 3. Catalytic dehydrogenation profile of *p*-methoxybenzylamine by using complex **2c** in deuterated toluene showing the full conversion and the formation of nitrile and imine products.

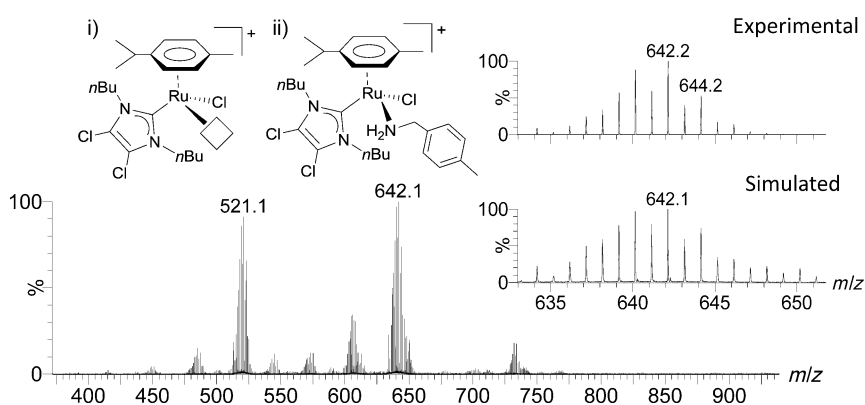


Figure 4. ESI mass spectrum of complex **2c** in the presence of *p*-methylbenzylamine under stoichiometric conditions. Schematic drawings of the species detected: i) with a vacant coordination site $[M-Cl]^+$, and ii) with a coordinated *p*-methylbenzylamine $[M-Cl+H_2NCH_2PhMe]^+$. Inset: experimental and simulated isotopic pattern of $[M-Cl+H_2NCH_2PhMe]^+$.

complex **5**, the first step is the substitution reaction of a chloride by benzylamine. The cationic complex **6** was prepared, isolated, and fully characterized using a sodium tetrafluoroborate salt. Complex **6** is the catalyst resting state and is in acid/base equilibrium with the amido complex (**I**). A second mole-

cule of benzylamine promotes this equilibrium. Compound (**I**) is converted into the ruthenium hydride-imine complex (**II**) by β -hydride elimination. The attack of a second benzylamine to complex **II** generates the imine byproduct. This transformation has been proposed for the acceptorless dehydrogenative cou-

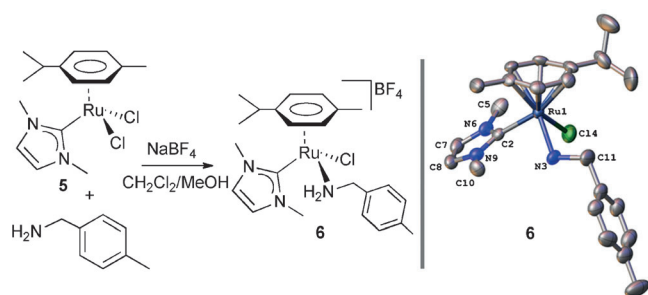


Figure 5. Synthesis and molecular diagram of compound **6**. Ellipsoids are at the 50% probability level. Hydrogen atoms and counter anion (BF_4^-) have been omitted for clarity.

pling of amines (transamination). A similar species has been detected by ESI-MS in the dehydrogenative coupling of alcohols.^[57] Nitrile ruthenium complex (**IV**) is proposed based on the catalytic results on which nitrile was used as the solvent, inhibiting the reaction (Table 1, entry 10). The two hydrogen release steps are the key points of this catalytic cycle. We propose that H₂ is released from ruthenium hydride species with either coordinated imine (**II**) or benzylamine (**IV**) ligands, and most probably through dihydrogen species. The proposed mechanism is one of the possible scenarios for the acceptorless dehydrogenation of primary amines. Additional mechanistic data are required to understand all the elementary catalytic steps of the reaction.

Conclusions

In this manuscript, we have explored the potential application of the amine/nitrile pair as a LOHC. Molecular ruthenium complexes of general formula $[(p\text{-cym})\text{Ru}(\text{NHC})\text{Cl}_2]$ are active in the dehydrogenation of primary amines to nitriles with the simultaneous formation of two moles of molecular hydrogen. The reaction proceeds without any external additive under mild reaction conditions. Both catalyst activation and product formation are temperature dependent. The acceptorless dehydrogenation of primary amines is a nonspontaneous process. Hydrogen removal from the reaction medium is required for effective nitrile formation. Mechanistic investigations have shown that the catalyst is activated by chloride/amine substitution. We have observed that the catalyst resting state contains a coordinated benzylamine. We have assessed the catalytic properties of an analogous ruthenium complex supported on the surface of graphene in the dehydrogenation of benzylamine. The results are promising as the catalytic system can be recycled up to 10 times without significant loss of activity. The main challenge in the dehydrogenation of benzylamines is the control of the selectivity. To be suitable for applications in the field of hydrogen storage, the transamination reaction that leads to imine formation should be suppressed. We have achieved selectivity control using long-chain aliphatic amines. The nitrile species is the sole product. Although the gravimetric percentage of hydrogen content in primary amines is not high compared to other systems, the versatility of amine-type compounds and their easy access makes the amine/nitrile pair a potential candidate for LOHCs. In addition, the reverse process,

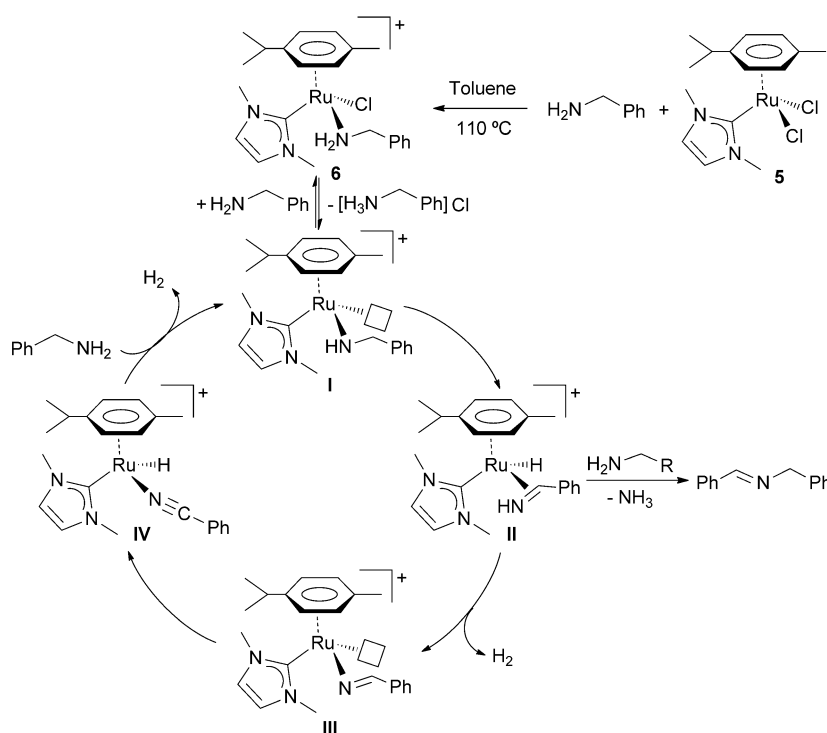


Figure 6. Proposed mechanism for the dehydrogenation of primary amines by using [(*p*-cym)Ru(NHC)Cl₂] complexes.

nitrile hydrogenation, is a well established reaction and very active and effective catalysts have been described in this regard. Future research in the field is needed, in particular, to develop industry compatible catalysts, but the preliminary results shown here are very encouraging.

Experimental Section

General procedures

Anhydrous solvents were obtained using a solvent purification system (SPS M BRAUN) or purchased from commercial suppliers and degassed prior to use by purging with dry nitrogen and keeping over molecular sieves. All other reagents were used as received from commercial suppliers. The imidazolium salts 1,3-bis(*n*-butyl)-imidazolium iodide (**1a**),^[58] 4,5-dimethyl-1,3-bis(*n*-butyl) imidazolium chloride (**1b**),^[59] 4,5-dichloro-1,3-bis(*n*-butyl) imidazolium iodide (**1c**),^[60] [RuCl₂(*p*-cymene)]₂,^[61] and complexes **2a**,^[62] **3**,^[45] and **5**^[63] were obtained according to published methods.

NMR spectra were recorded on Varian Innova spectrometers operating at 300 or 500 MHz (¹H NMR) and 75 or 125 MHz (¹³C NMR). ESI-MS were recorded on a Micromass Quattro LC instrument, and nitrogen was employed as the drying and nebulizing gas. HRMS were obtained in a QTOF I (quadrupole-hexapole-TOF) mass spectrometer with an orthogonal Z-spray-electrospray interface (Micromass, Manchester, UK). The drying and nebulizing gas was nitrogen at a flow of 400 and 80 L h⁻¹, respectively. The temperature of the source block was set to 120 °C and the desolvation temperature to 150 °C. A capillary voltage of 3.5 kV was used in the positive scan mode and the cone voltage was set to 30 V. The mass calibration was performed using a solution of sodium iodide in isopropanol/water (50:50) from *m/z*: 150 to 1000 a.m.u. Sample solutions (ca. 1 × 10⁻⁴ M) were infused via syringe pump directly connected to the interface at a flow of 10 μL min⁻¹. A 1 μg mL⁻¹ solution of 3,5-diiodo-L-tyrosine was used as the lock mass. Hydrogen analysis was carried out by gas chromatography (GS-MOL 15 meters, column ID 0.55 mm, TCD from J&W Scientific).

Crystal structure determination

Single crystals of complex **6** were mounted on a polymer tip in a random orientation. Data collection was performed on a SuperNova dual source equipped with a CCD Atlas detector diffractometer. The structure was solved using Olex2^[64] with the SIR2004^[65] structure solution program using direct methods and refined with the ShelXL^[66] refinement package using least squares minimization. Crystal data: orthorhombic; space group: *Pna*21 (no. 33); *a* = 13.5393(8), *b* = 16.4138(11), *c* = 11.4752(8) Å; *V* = 2550.1(3) Å³; *Z* = 4; *T* = 200.00(14) K; *μ*(Mo_{Kα}) = 0.765 mm⁻¹; *ρ*_{calcd} = 1.497 g cm⁻³; 13725 reflections measured (5.804° ≤ 2θ ≤ 51.98°), 4498 unique (*R*_{int} = 0.0679, *R*_{sigma} = 0.0628), which were used in all calculations. The final *R*₁ was 0.0448 (*I* > 2σ(*I*)) and *wR*₂ was 0.1140 (all data). CCDC 1509771 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Synthesis of 2b

Silver oxide (126 mg, 0.54 mmol) was added to a solution of 4,5-dimethyl-1,3-bis(butyl)imidazolium chloride (**1b**) (178 mg, 0.73 mmol) in CH₂Cl₂. The mixture was stirred at room temperature overnight and filtered through Celite. Then, [Ru(*p*-cymene)Cl₂]₂ (200 mg, 0.36 mmol) was added to the solution and it was stirred at room temperature overnight. After solvent removal, the crude

product was purified by column chromatography. The pure compound **2b** was eluted with dichloromethane/acetone (9:1) and precipitated in a mixture of dichloromethane/hexane to give an orange solid (44 mg, 13.1%). ¹H NMR (500 MHz, CDCl₃): δ = 5.37 (d, ³*J* = 5.9 Hz, 2H, CH_{*p*-cym}), 5.00 (d, ³*J* = 5.9 Hz, 2H, CH_{*p*-cym}), 4.40 (m, 2H, CH_{2,*n*-Bu}), 3.98 (m, 2H, CH_{2,*n*-Bu}), 2.93 (m, 1H, CH_{*iPr*,*p*-cym}), 2.17 (s, 6H, CH_{3,imid}), 1.96 (s, 3H, CH_{3,*p*-cym}), 1.96 (m, 2H, CH_{2,*n*-Bu}), 1.48 (m, 4H, CH_{2,*n*-Bu}), 1.31 (m, 2H, CH_{2,*n*-Bu}), 1.26 (d, ³*J* = 7.0 Hz, 6H, CH_{3,*iPr*,*p*-cym}), 0.93 ppm (t, ³*J* = 7.1 Hz, 6H, CH_{3,*n*-Bu}); ¹³C {¹H} NMR (75 MHz, CDCl₃): δ = 169.9 (C_{NHC-Ru}), 126.9 (C=C_{imid}), 107.9 (C_{*p*-cym}), 98.7 (C_{*p*-cym}), 85.9 (C_{*p*-cym}), 85.9 (C_{*p*-cym}), 82.3 (C_{*p*-cym}), 82.3 (C_{*p*-cym}), 49.8 (CH_{2,*n*-Bu}), 33.9 (CH_{2,*n*-Bu}), 30.7 (CH_{*iPr*,*p*-cym}), 22.7 (CH_{3,*iPr*,*p*-cym}), 20.3 (CH_{2,*n*-Bu}), 18.6 (CH_{3,*p*-cym}), 14.0 (CH_{3,*n*-Bu}), 9.8 ppm (CH_{3,imid}); electrospray MS (cone 20 V; *m/z*, fragment): 479.3 [M-Cl]⁺; HRMS ESI-TOF-MS (positive mode): [M-Cl]⁺ monoisotopic peak: 479.1770; calcd: 479.1770, *εr*: 0 ppm.

Synthesis of 2c

The reaction was carried out by following the same procedure as the one described for **2b**, with 4,5-dichloro-1,3-bis(butyl)imidazolium iodide (**1c**) (138 mg, 0.37 mmol) and Ag₂O in CH₂Cl₂. Subsequent reaction with [Ru(*p*-cymene)Cl₂]₂ (200 mg, 0.36 mmol) afforded **2c** as an orange solid (67 mg, 37.7%). ¹H NMR (300 MHz, CDCl₃): δ = 5.45 (d, ³*J* = 6.0 Hz, 2H, CH_{*p*-cym}), 5.08 (d, ³*J* = 6.0 Hz, 2H, CH_{*p*-cym}), 4.53 (m, 2H, CH_{2,*n*-Bu}), 4.19 (m, 2H, CH_{2,*n*-Bu}), 2.95 (m, 1H, CH_{*iPr*,*p*-cym}), 2.02 (s, 3H, CH_{3,*p*-cym}), 2.02 (m, 2H, CH_{2,*n*-Bu}), 1.74 (m, 2H, CH_{2,*n*-Bu}), 1.41 (m, 4H, CH_{2,*n*-Bu}), 1.29 (d, ³*J* = 6.9 Hz, 6H, CH_{3,*iPr*,*p*-cym}), 0.96 ppm (t, ³*J* = 7.3 Hz, 6H, CH_{3,*n*-Bu}); ¹³C {¹H} NMR (75 MHz, CDCl₃): δ = 175.2 (C_{NHC-Ru}), 117.8 (CH_{imid}), 108.4 (C_{*p*-cym}), 98.9 (C_{*p*-cym}), 86.4 (C_{*p*-cym}), 82.8 (C_{*p*-cym}), 51.4 (CH_{2,*n*-Bu}), 33.2 (CH_{2,*n*-Bu}), 30.6 (CH_{*iPr*,*p*-cym}), 22.5 (CH_{3,*iPr*,*p*-cym}), 20.0 (CH_{2,*n*-Bu}), 18.7 (CH_{3,*p*-cym}), 13.7 ppm (CH_{3,*n*-Bu}); electrospray MS (cone 20 V; *m/z*, fragment): 519.1 [M-Cl]⁺; HRMS ESI-TOF-MS (positive mode): [M-Cl]⁺ monoisotopic peak: 519.0671; calcd: 519.0672, *εr*: 0.2 ppm.

Synthesis of 6

Complex **5** (10 mg, 0.0248 mmol) and sodium tetrafluoroborate (26 mg, 0.23 mmol) were suspended in 3 mL of dichloromethane and 2 mL of methanol. The mixture was stirred for 5 min. Then, 0.024 mmol of 4-methylbenzylamine was added and the solution was stirred for 1 h. After solvent removal, complex **6** was obtained as a pale-yellow solid. ¹H NMR (500 MHz, CDCl₃): δ = 7.35 (d, *J* = 7.9 Hz, 2H, CH_{amine}), 7.17–6.99 (m, 4H, CH_{amine}; CH_{imid}), 5.81 (d, *J* = 6.0 Hz, 1H, CH_{*p*-cym}), 5.76 (d, *J* = 6.0 Hz, 1H, CH_{*p*-cym}), 5.68 (d, *J* = 6.0 Hz, 1H, CH_{*p*-cym}), 5.45 (d, *J* = 6.0 Hz, 1H, CH_{*p*-cym}), 4.09 (m, 2H, CH₂), 3.99 (s, 3H, N-CH₃), 3.75 (s, 3H, N-CH₃), 2.84 (m, 1H, CH_{*iPr*,*p*-cym}), 2.27 (s, 3H, CH_{3,amine}), 2.06 (s, 3H, CH_{3,*p*-cym}), 1.29 (d, *J* = 7.0 Hz, 3H, CH_{3,*iPr*,*p*-cym}), 1.09 ppm (d, *J* = 6.8 Hz, 3H, CH_{3,*iPr*,*p*-cym}); ¹³C NMR (126 MHz, CDCl₃): δ = 172.56 (C_{NHC-Ru}), 138.03, 136.62, 129.78, 129.11 (C_{amine}), 125.07, 124.29 (CH_{imid}), 112.18, 99.96 (C_{*p*-cym}), 85.42, 84.18, 83.39, 82.81 (CH_{*p*-cym}), 53.62 (Ph-CH₂-NH₂), 39.66, 38.39 (N-CH₃), 31.07 (CH_{*iPr*,*p*-cym}), 23.98, 21.29 (CH₃), 20.89, 18.43 ppm (CH_{3,*iPr*,*p*-cym}).

Catalytic dehydrogenation reactions

Catalytic runs were performed in a round-bottomed flask by using one equivalent of amine, 2 mol% of catalyst, and 3 mL of toluene, and heating for a suitable period of time at 110 °C. The yields and conversions were determined by GC analysis using anisole as the internal standard.

Procedure for hydrogen identification

All glassware was carefully cleaned with Milli-Q water and rinsed with acetone prior to use. A 25 mL round-bottomed flask was charged with 0.30 mmol of amine, 2 mol% of ruthenium catalyst, and 2 mL of toluene and heated at 110 °C. At selected times (ca. 50% conversion), a 1.5 mL sample of the generated gas was collected and the hydrogen content was qualitatively analyzed by gas chromatography (GS-MOL 15 meters, column ID 0.55 mm, TCD from J&W Scientific).

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Keywords: dehydrogenation • hydrogen production • nitrile synthesis • ruthenium • supported catalysis

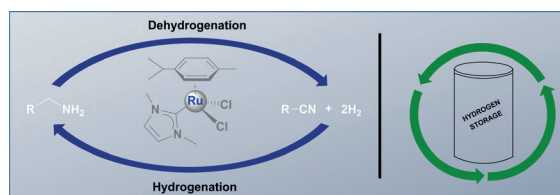
- [1] M. Ball, M. Weeda, *Compendium of Hydrogen Energy*, Elsevier, **2016**.
- [2] V. Blagojević, D. Minić, J. G. Novaković, D. Minić, *Hydrogen Energy: Challenges and Perspectives* (Ed.: D. Minić), InTech, **2012**, pp. 3–28.
- [3] A. Midilli, M. Ay, I. Dincer, M. A. Rosen, *Renewable Sustainable Energy Rev.* **2005**, *9*, 255–271.
- [4] N. Armaroli, V. Balzani, in *Energy for a Sustainable World: From the Oil Age to a Sun-Powered Future*, Wiley-VCH, Weinheim, **2010**.
- [5] A. Zuttel, A. Remhof, A. Borgschulte, O. Friedrichs, *Philos. Trans. R. Soc. London Ser. A* **2010**, *368*, 3329–3342.
- [6] L. Jörissen, *Green Energy Technol.* **2012**, *45*, 189–203.
- [7] A. F. Dalebrook, W. Gan, M. Gräsemann, S. Moret, G. Laurenczy, *Chem. Commun.* **2013**, *49*, 8735–8751.
- [8] P. Jena, *J. Phys. Chem. Lett.* **2011**, *2*, 206–211.
- [9] S. Sahler, M. H. G. Precht, *ChemCatChem* **2011**, *3*, 1257–1259.
- [10] A. J. Esswein, D. G. Nocera, *Chem. Rev.* **2007**, *107*, 4022–4047.
- [11] J. D. Holladay, J. Hu, D. L. King, Y. Wang, *Catal. Today* **2009**, *139*, 244–260.
- [12] M. H. G. Precht, S. Sahler, *Curr. Org. Chem.* **2013**, *17*, 220–228.
- [13] S. Satyapal, J. Petrovic, C. Read, G. Thomas, G. Ordaz, *Catal. Today* **2007**, *120*, 246–256.
- [14] R. K. Ahluwalia, X. Wang, *J. Power Sources* **2008**, *177*, 167–176.
- [15] K. Müller, W. Arlt, in *Renewable Energy: Economics, Emerging Technologies and Global Practices* (Ed.: A. Poullikkas), Nova Science, **2013**, pp. 45–60.
- [16] U. Eberle, M. Felderhoff, F. Schüth, *Angew. Chem. Int. Ed.* **2009**, *48*, 6608–6630; *Angew. Chem.* **2009**, *121*, 6732–6757.
- [17] R. H. Crabtree, *Energy Environ. Sci.* **2008**, *1*, 134–138.
- [18] O. R. Luca, T. Wang, S. J. Konezny, V. S. Batista, R. H. Crabtree, *New J. Chem.* **2011**, *35*, 998–999.
- [19] E. Clot, O. Eisenstein, R. H. Crabtree, *Chem. Commun.* **2007**, 2231–2233.
- [20] M. Markiewicz, Y. Q. Zhang, A. Bosmann, N. Brückner, J. Thöming, P. Wasserscheid, S. Stolte, *Energy Environ. Sci.* **2015**, *8*, 1035–1045.
- [21] T. He, Q. Pei, P. Chen, *J. Energy Chem.* **2015**, *24*, 587–594.
- [22] M. Yadav, Q. Xu, *Energy Environ. Sci.* **2012**, *5*, 9698–9725.
- [23] P. Hu, Y. Ben-David, D. Milstein, *Angew. Chem. Int. Ed.* **2016**, *55*, 1061–1064; *Angew. Chem.* **2016**, *128*, 1073–1076.
- [24] P. Hu, E. Fogler, Y. Diskin-Posner, M. A. Iron, D. Milstein, *Nat. Commun.* **2015**, *6*, 6859–6866.
- [25] D. Teichmann, K. Stark, K. Mueller, G. Zoettl, P. Wasserscheid, W. Arlt, K. Müller, G. Zöttl, P. Wasserscheid, W. Arlt, *Energy Environ. Sci.* **2012**, *5*, 9044–9054.
- [26] D. Teichmann, W. Arlt, P. Wasserscheid, R. Freymann, *Energy Environ. Sci.* **2011**, *4*, 2767–2773.
- [27] P. J. Bonitatibus, S. Chakraborty, M. D. Doherty, O. Siclován, W. D. Jones, G. L. Soloveichik, *Proc. Natl. Acad. Sci. USA* **2015**, *112*, 1687–1692.
- [28] M. Grellier, S. Sabo-Etienne, *Dalton Trans.* **2014**, *43*, 6283–6286.
- [29] K.-N. T. Tseng, A. M. Rizzi, N. K. Szymczak, *J. Am. Chem. Soc.* **2013**, *135*, 16352–16355.
- [30] F. Gould, G. Johnson, A. Ferris, *J. Org. Chem.* **1960**, *25*, 1658–1660.
- [31] S. Gomez, J. A. Peters, T. Maschmeyer, *Adv. Synth. Catal.* **2002**, *344*, 1037–1057.
- [32] C. de Bellefon, P. Fouilloux, *Catal. Rev.* **1994**, *36*, 459–506.
- [33] S. Werkmeister, K. Junge, M. Beller, *Org. Process Res. Dev.* **2014**, *18*, 289–302.
- [34] D. B. Bagal, B. M. Bhanage, *Adv. Synth. Catal.* **2015**, *357*, 883–900.
- [35] A. Mukherjee, D. Srimani, S. Chakraborty, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **2015**, *137*, 8888–8891.
- [36] H. T. Clarke, R. R. Read, *J. Am. Chem. Soc.* **1924**, *46*, 1001–1003.
- [37] C. F. Koelsch, A. G. Whitney, *J. Org. Chem.* **1941**, *6*, 795–803.
- [38] G. C. Vougioukalakis, R. H. Grubbs, *Chem. Rev.* **2010**, *110*, 1746–1787.
- [39] E. Colacino, J. Martinez, F. Lamaty, *Coord. Chem. Rev.* **2007**, *251*, 726–764.
- [40] C. Samojłowicz, M. Bieniek, K. Grela, *Chem. Rev.* **2009**, *109*, 3708–3742.
- [41] K. M. Kuhn, J.-B. Bourg, C. K. Chung, S. C. Virgil, R. H. Grubbs, *J. Am. Chem. Soc.* **2009**, *131*, 5313–5320.
- [42] T. Dröge, F. Glorius, *Angew. Chem. Int. Ed.* **2010**, *49*, 6940–6952; *Angew. Chem.* **2010**, *122*, 7094–7107.
- [43] S. Díez-González, S. P. Nolan, *Coord. Chem. Rev.* **2007**, *251*, 874–883.
- [44] A. Prades, E. Peris, M. Albrecht, *Organometallics* **2011**, *30*, 1162–1167.
- [45] S. Sabater, J. A. Mata, E. Peris, *ACS Catal.* **2014**, *4*, 2038–2047.
- [46] S. Sabater, J. A. Mata, E. Peris, *Organometallics* **2015**, *34*, 1186–1190.
- [47] A. Primo, M. Puche, O. D. Pavel, B. Cojocaru, A. Tirsoaga, V. Parvulescu, H. García, *Chem. Commun.* **2016**, *52*, 1839–1842.
- [48] J. Albero, H. Garcia, *J. Mol. Catal. A* **2015**, *408*, 296–309.
- [49] B. F. Machado, P. Serp, *Catal. Sci. Technol.* **2012**, *2*, 54–75.
- [50] M. R. Axet, O. Dechy-Cabaret, J. Durand, M. Gouygou, P. Serp, *Coord. Chem. Rev.* **2016**, *308*, 236–345.
- [51] P. Csabai, F. Joó, *Organometallics* **2004**, *23*, 5640–5643.
- [52] W. H. Bernskoetter, M. Brookhart, *Organometallics* **2008**, *27*, 2036–2045.
- [53] K.-N. Tseng, N. Szymczak, *Synlett* **2014**, 2385–2389.
- [54] R. Reguillo, M. Grellier, N. Vautravers, L. Vendier, S. Sabo-Etienne, *J. Am. Chem. Soc.* **2010**, *132*, 7854–7855.
- [55] R. V. Jagadeesh, H. Junge, M. Beller, *Nat. Commun.* **2014**, *5*, 1–8.
- [56] S. E. Clapham, A. Hadzovic, R. H. Morris, *Coord. Chem. Rev.* **2004**, *248*, 2201–2237.
- [57] C. Vicent, D. G. Gusev, *ACS Catal.* **2016**, *6*, 3301–3309.
- [58] I. Dinareš, C. Garcia de Miguel, A. Ibáñez, N. Mesquida, E. Alcalde, *Green Chem.* **2009**, *11*, 1507–1510.
- [59] G. Mlostko, J. Romański, M. Jasiński, H. Heimgartner, *Tetrahedron: Asymmetry* **2009**, *20*, 1073–1080.
- [60] R. Corberán, M. Sanaú, E. Peris, *J. Am. Chem. Soc.* **2006**, *128*, 3974–3979.
- [61] M. A. Bennett, A. K. Smith, *J. Chem. Soc. Dalton Trans.* **1974**, 233–241.
- [62] L. Mercs, A. Neels, M. Albrecht, *Dalton Trans.* **2008**, *3*, 5570–5576.
- [63] W. A. Herrmann, M. Elison, J. Fischer, C. Köcher, G. R. J. Artus, *Chem. Eur. J.* **1996**, *2*, 772–780.
- [64] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
- [65] M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Casciarano, L. De Caro, C. Giacovazzo, G. Polidori, D. Siliqi, R. Spagna, *J. Appl. Crystallogr.* **2007**, *40*, 609–613.
- [66] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *71*, 3–8.

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FULL PAPER

Supported Catalysis

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 **Catalytic Hydrogen Production by Ruthenium Complexes from the Conversion of Primary Amines to Nitriles: Potential Application as a Liquid Organic Hydrogen Carrier**

A system of support: The potential application of the primary amine/nitrile pair as a liquid organic hydrogen carrier (LOHC) has been evaluated. Molecular ruthenium complexes, [(*p*-cym)-Ru(NHC)Cl₂] (NHC = N-heterocyclic car-

bene; see scheme), are active in the dehydrogenation of primary amines to nitriles with the simultaneous formation of two moles of molecular hydrogen. The reaction proceeds without any external additive under mild conditions.