Iridium Catalyzed Reversible Dehydrogenation – Hydrogenation of Quinoline Derivatives Under Mild Conditions

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Abstract

The potential of a hydrogen-based energy economy is limited by the fact that hydrogen gas is difficult to store and transport. Storing hydrogen in the form of liquid organic hydrogen-carriers (LOHCs) is a highly attractive alternative to current options but it requires the development of catalytic means of reversibly hydrogenating and dehydrogenating these carriers under mild conditions and ideally using a single catalyst for both processes. We report the optimization of two families of previously reported hydrogenation catalysts for the reverse reaction, dehydrogenation of N-heterocyclic substrates. These complexes are capable of catalyzing both dehydrogenation and hydrogenation reactions in alternation, giving high yields in both directions. Importantly,

our complexes do not require high temperatures, high pressures of H₂ or strong base for the hydrogenation step.

Introduction

The development of highly efficient catalysts for the reversible hydrogenation and dehydrogenation of suitable organic molecules is of great interest to the field of alternative energy research.¹ Hydrogenated organic liquids can in principle be used to transport hydrogen in the covalently bound form, with subsequent catalyzed release of free H₂.^{2,3} Ongoing research at GE Global Research and elsewhere is directed toward using such compounds in fuel cells or flow batteries.⁴ The use of such liquid organic hydrogen carrier molecules (LOHCs) holds promise as an attractive alternative to the transportation and storage of gaseous hydrogen, which may otherwise require high pressure cylinders that give rise to a large weight penalty.^{2,5} The dehydrogenated carrier molecule can then be recycled and regenerated by catalytic hydrogenation. The current global energy transport and storage infrastructure utilizes liquid hydrocarbon fossil fuels and could arguably be adapted for LOHCs with less disruption than for some other strategies.²⁻⁶ Prior work indicates that the presence of a heteroatom in the LOHC minimizes the unfavorable thermodynamics of the dehydrogenation reaction, allowing for both hydrogenation and dehydrogenation to occur under mild conditions.⁶ In order to make use of heterocycles as hydrogen storage molecules, both the catalytic hydrogenation and dehydrogenation processes must be feasible under mild conditions.⁶ A number of catalysts, both heterogeneous^{7,8,9,10} and homogeneous,^{11,12,13,14} can bring about *either* hydrogenation or dehydrogenation of N-heterocyclic substrates, but there are

very few homogeneous catalysts capable of carrying out *both* reactions on model quinoline derivatives under mild conditions.¹²⁻¹⁴ Such a catalyst would be potentially applicable to reversible hydrogen storage, by allowing for easy hydrogenation and later dehydrogenation of an LOHC all in one reactor and without the need to add or remove any additional compounds aside from H₂ gas.

The iridium complexes reported by Fujita *et al.* are unusual in being very efficient catalysts for both the hydrogenation and dehydrogenation of quinolines.^{12,14} Although the conditions reported for the hydrogenation of quinaldine were not ideal, requiring either elevated temperature or H₂ pressures of 3-10 atm, they were able to dehydrogenate tetrahydroquinaldine in *p*-xylene at reflux (145°C) in less than 24 hours. Xiao and co-workers recently found an iridium pincer complex to be highly active for dehydrogenation of a range of tetrahydroquinolines under even milder conditions (74 °C) in 2,2,2-trifluoroethanol;^{11d} however, the corresponding hydrogenation was achieved only after modification of the pincer ligand.^{11e} Recently, the Jones group discovered a “two-way” system for the sequential hydrogenation-dehydrogenation of quinoline derivatives with an iron(II)-(PNP) pincer complex.¹² While this system is not as active as the Fujita system, it utilizes a much cheaper catalyst which makes it very attractive. Unfortunately, this system also requires 10 mol % of strong base, in addition to 5-10 atm H₂, in order to carry out the hydrogenation reaction. Interestingly, in contrast to the Fujita system, these iron(II) complexes are not hindered by sterically unencumbered substrates which might have been thought likely to bind to the active site via the N lone pair and inhibit the reaction.

Prior work in our lab has focused on two families of iridium catalysts capable of efficiently catalyzing the conversion of quinaldine to 1,2,3,4-tetrahydroquinaldine under 1 atm of H₂ at room temperature (Figure 1).^{15,16} To our knowledge, these catalysts still rank amongst the most efficient homogeneous hydrogenation catalysts for such reactions, only being surpassed recently by a family of Cp*Ir(III)(N-C)Cl complexes,^{10e} and are superior to the Fujita catalysts discussed above with regards to hydrogenation activity under mild conditions. The first generation precatalyst, **1**, and its activated form, **2** (Figure 2), were found to be the more active of our two classes of complexes. Compounds **1** and **2** are capable of catalyzing the reduction of a wider range of N-heterocyclic substrates than complex, **3**, but at the cost of solvent scope. Both classes of catalysts are believed to operate via an outer-sphere mechanism entailing the sequential delivery of a proton followed by a hydride to the unbound substrate from a coordinated H₂ molecule. As a natural extension of this work, we sought to explore the potential for dehydrogenation of saturated N-heterocyclic substrates under mild conditions using these same families of complexes. Based on the principles of microscopic reversibility, it is plausible to think that these catalysts would be competent for the reverse reaction and that the process could be optimized by variation of the conditions.

Figure 1. Compounds **1** and **3** are highly active precatalysts for quinaldine hydrogenation under mild conditions.

Results and Discussion

Precatalyst **1-PF₆** was first screened for the dehydrogenation of 1,2,3,4-tetrahydroquinaldine in toluene in the presence of 1 equivalent of triphenylphosphine. It was found that in reactions run below reflux temperature, no appreciable reactivity was observed; however, small quantities of dehydrogenated product were observed when the reaction was refluxed (Table 1, Entries 1-2). This is believed to arise in large part from the reflux action itself sweeping the product H₂ out of the solution, driving the equilibrium in the dehydrogenative direction by mass action, as previously seen in catalytic alkane dehydrogenation.¹⁷ In order to increase the catalytic activity, **2**, the proposed active catalyst, was preformed according to a previously published procedure by stirring **1-PF₆** under 1 atm of H₂ and in the presence of 1 equivalent of triphenylphosphine (Figure 2). Indeed, **2** gave a marked increase in yield under identical

conditions (Table 1, Entries 3-4). By changing the solvent to chlorobenzene (Table 1, Entry 5) or *p*-xylene and thus increasing the reflux temperature, activity increased further, with complete conversion observed after 72 hours (Table 1, Entry 7). In contrast, under these optimized conditions, less conversion was observed for 1,2,3,4-tetrahydroquinoline (Table 1, Entry 8) than for the more sterically hindered 1,2,3,4-tetrahydroquinoline, having an additional methyl group at the 2-position. This result follows the trend observed in our hydrogenation work where substrates lacking a bulky substituent at the 2-position give lower yields, presumably due to coordination of the nitrogen lone-pair to the metal, leading to catalyst deactivation.

Figure 2. Formation of active species **2** by hydrogenation in the presence of PPh₃. The conversion from can be tracked visually by a distinct color change.

Table 1. Dehydrogenation of Tetrahydroquinoline Derivatives by 1

Entry	Solvent	R	Temp. (°C)	Time (h)	Yield
1	Toluene	Me	80	24	<2%
2	Toluene	Me	115	24	7%
3	Toluene ^a	Me	80	24	<2%
4	Toluene ^a	Me	115	24 / 72	10 / 20%
5	Chlorobenzene ^a	Me	135	24/ 72	45/ 85%
6	<i>p</i> -Xylene	Me	145	24	12%
7	<i>p</i> -Xylene ^a	Me	145	24 / 72	48 / ~95%
8	<i>p</i> -Xylene ^a	H	145	24 / 72	19 / 61%

Experiments run under 1 atm N₂, 1,2,3,4-tetrahydroquinaldine or 1,2,3,4-tetrahydroquinoline (0.112 mmol), **1** and PPh₃ (both 5 mol% with respect to substrate), solvent (3 ml). ^aExperiments run with pre-activation of catalyst by heating to 100 °C and bubbling H₂ gas for 20 minutes prior to catalysis. Yields determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. Control experiments for these reactions can be found in Table S1.

Following our prior work,¹⁶ derivatives of **3** were also screened for the dehydrogenation of tetrahydroquinoline compounds (Table 2). Variants of complex **3** are generally less active as hydrogenation catalysts than **1** but do not require the addition of phosphine additives or pre-activation with H₂. In analogy to our prior hydrogenation studies, **1** was more active than **3b** (Table 2); over 24 hours in *p*-xylene at 145°C, **1** gave almost twice the yield that **3b** did. Change of the counterion from PF₆ to tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (B(Ar^F)₄) had little effect (Table 2, Entries 1-2, 6-7). Significantly, changing the solvent to chlorobenzene gives a marked increase in yield (Table 2, Entry 5), likely due to the increased solubility of the complex or possibly also to its mild coordinating power. As was observed with **1**, increasing the temperature and reaction time increased the overall yield and reactivity proved to be greater with 1,2,3,4-tetrahydroquinoline than with 1,2,3,4-tetrahydroquinoline (Table 2, Entries 2-5). Additionally, both variants of **3** were tested for dehydrogenation in the presence of a H₂ accepting substrate (N-benzylideneaniline) in an attempt to further drive the dehydrogenation (Table 2, Entries 6-8). A slight increase in activity was observed but yields remained relatively low.

Table 2. Dehydrogenation of Tetrahydroquinoline Derivatives by 3a and 3b

Entry	Complex	Solvent	R	Temp. (°C)	Time (hour)	Yield
1	3a	Toluene	H	115	24 / 48	8 / 17%
2	3b	Toluene	H	115	24 / 48	9 / 18%
3	3b	Toluene	Me	115	24	16%
4	3b	<i>p</i> -Xylene	Me	145	24	21%
5	3b	Chlorobenzene	Me	135	24 / 72	46 / 66%
6	3b	<i>p</i> -Xylene ^a	Me	145	24	25%
7	3a	Toluene ^a	H	115	24	13%
8	3b	Toluene ^a	H	115	24 / 48	18 / 29%

Experiments run under 1 atm N₂, 1,2,3,4-tetrahydroquinoline or 1,2,3,4-tetrahydroquinoline (0.112 mmol), **3a** or **3b** (both 5 mol% with respect to substrate), solvent (3 ml). ^aExperiments run with N-benzylideneaniline as a H₂ acceptor. Yield determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. Control experiments for these reactions can be found in Table S1.

In order to investigate the robustness of complexes **1** (preactivated to form **2**) and **3b** under the reaction conditions, which relates to their potential to perform 2-way dehydrogenation-hydrogenation reactions, we monitored their activity over time using a gas-burette at low catalyst loading (0.5 mol %) (Figure 3 and SI, page S2). Over 72 hours, **1** and **3b** give TONs of 43 and 32, respectively, similar to TONs achieved by other heterocycle dehydrogenation systems.^{11d,12,13} The complexes show similar, approximately linear activity for the first ~30 h, with a TOF of approximately 0.8 h⁻¹; however at longer times, complex **3b** decreases in activity. This is in agreement with the 24 and 72 hour experiments in chlorobenzene (Table 1 entry 5; Table 2, Entry 5), where yield is similar for the two complexes after 24 h, but is much higher for **1** after 72 h. The latter complex may therefore better resist deactivation. Indeed, ¹H NMR spectra of a catalytic reaction mixture containing **3b** show a hydride peak corresponding to **3b** after 24 h (~ 70 % of added amount), while at 72 h, this peak is no longer present, consistent with decomposition into inactive species. Because of the durability of **1**, as well as its ability to perform the dehydrogenation reaction in high yield, we attempted dehydrogenation followed by hydrogenation using this complex. Notably, no activity for hydrogenation was observed after exposure to H₂ at room temperature following a 72 h dehydrogenation reaction in p-xylene or chlorobenzene.

Figure 3. Reaction Profiles for Dehydrogenation with Pre-catalysts 1 and 3b Generated by Gas-burette.

Experiments run with iridium complex (0.02 mmol, 0.5 mol %), tetrahydroquinaldine (4 mmol) and chlorobenzene (10 mL). Precatalyst **1** was pre-activated by adding 1 eq. PPh_3 , heating to 100 °C and bubbling H_2 gas for 20 minutes prior to catalysis. Reaction progress was monitored by gas burette, with 1 TON defined as 2 molecules of H_2 produced per molecule of catalyst (See SI for details).

In the hope of accomplishing dehydrogenation faster and potentially retaining enough active catalyst for the subsequent hydrogenation, we ran reactions at higher

substrate and precatalyst concentrations (Table 3). Chlorobenzene was selected as solvent because it dissolves the iridium complexes at high concentration and has a relatively high boiling point. Indeed, for both **1** and **3b**, increasing the tetrahydroquinaldine concentration from 0.04 to 1.1 M gives increased conversion for dehydrogenation over 24 h at 5 % catalyst loading (Table 3, Entries 3 and 6). Following this improved dehydrogenation step, subsequent hydrogenation is possible under 1 atm H₂ at ambient temperature, giving >95 % yield for **1** and 75 % yield for **3b**, thus demonstrating the ability of our catalysts to carry out both reactions in alternation as appropriate for a hydrogen storage application. Importantly, our complexes do not require high temperatures, high pressures of H₂ or strong base for the hydrogenation step as in previous “2-way” systems, while giving slightly lower but comparable yields in both directions.^{12,13} Thus, we have developed a system for reversible quinaldine hydrogenation that functions under unprecedentedly mild conditions for the hydrogenation step.

Table 3: Reversible dehydrogenation of tetrahydroquinaldine in chlorobenzene with 5 mol % iridium complex under mild conditions

Entry	Complex	Substrate Concentration (M)	Dehydrogenation yield (%) ^b	Hydrogenation yield (%) ^b
1	1^c	0.04	45	- ^a
2	1^c	0.24	63	- ^a
3	1^c	1.1	73	>95
4	3b	0.04	46	- ^a
5	3b	0.24	60	- ^a
6	3b	1.1	85	76

Experiments run with chlorobenzene, iridium complex (5 mol %), tetrahydroquinaldine, and 1,3,5-trimethoxybenzene as internal standard. Dehydrogenation reaction performed at reflux (135 °C) for 24 h. Subsequently, for entries 3 and 6, reaction mixture cooled to room temperature and hydrogenation carried out by stirring for 24 h at ambient temperature under 1 atmosphere of H₂. ^aHydrogenation not attempted for these entries. ^bYields determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard; Hydrogenation yield calculated as amount of quinaldine hydrogenated divided by initial amount of quinaldine after dehydrogenation step. ^cComplex pre-activated by adding 1 eq. PPh₃, heating to 100 °C and bubbling H₂ gas for 20 minutes prior to catalysis.

Conclusion

Two iridium catalysts previously developed by our group for the hydrogenation of N-heterocycles have been applied to the reverse reaction, dehydrogenation of the saturated N-heterocycles. In addition, these complexes are able to perform reversible dehydrogenation-hydrogenation reactions in sequence with high yields for both directions. Neither system surpassed the best prior “two-way” literature catalyst for the hydrogenation/dehydrogenation of quinaldine in terms of dehydrogenation efficiency^{12,14} but both **1** and **3** are much more efficient than the prior “two-way” systems for the hydrogenation of quinaldine.

Experimental

General Methods. The syntheses of the metal complexes were conducted under nitrogen using dry degassed solvents unless otherwise indicated. Solvents were dried and degassed prior to use. Iridium species used in these experiments were synthesized according to literature procedures (see SI).^{14,15} All other reagents were commercially available from Airgas, Sigma-Aldrich, Alfa-Aesar and Strem Chemicals and used as received unless otherwise indicated. NMR spectra were recorded at room temperature on a 400 or 500 MHz Bruker or Varian spectrometer.

Procedure for dehydrogenation of 1,2,3,4-tetrahydroquinaldine and 1,2,3,4-tetrahydroquinoline using 1. To a flame-dried 15 ml Schlenk tube under nitrogen was added a stir bar, 1,2,3,4-tetrahydroquinaldine or 1,2,3,4-tetrahydroquinoline (16.2 μ l and 14.1 μ l respectively, 0.112 mmol), trimethoxybenzene (10.0 mg, internal ¹H NMR

standard), triphenylphosphine (5.5 mol% with respect to 1,2,3,4-tetrahydroquinaldine, 1.6 mg) and **1** (5 mol% with respect to 1,2,3,4-tetrahydroquinaldine, 4.7 mg). Dry solvent (3 ml of toluene or *p*-xylene, sparged with N₂) was then added to the flask. The flask was purged with H₂ by bubbling through the solution for ~20 minutes, activating the catalyst; a distinct color change from red-orange to yellow was observed. The H₂ atmosphere was removed with three cycles of evacuation and N₂ replacement, leaving the system under 1 atm of nitrogen with an oil bubbler outlet. The reaction mixture was then stirred and heated to just above the reflux temperature of the solution (115°C for toluene, 145°C for *p*-xylene) and aliquots were collected at 24, 48 and 72 hours. The solvent was removed in vacuo and the resulting mixture was redissolved in CD₂Cl₂. Conversion was assessed by comparative integration of the product and starting material peaks to the internal standard in the ¹H NMR spectrum. Spectra of pure quinaldine and 1,2,3,4-tetrahydroquinaldine from commercially obtained samples were used as peak references in identifying the products.

Procedure for dehydrogenation of 1,2,3,4-tetrahydroquinaldine and 1,2,3,4-tetrahydroquinoline using 3a and 3b. To a flame dried 15 ml Schlenk tube under nitrogen was added a stir bar, 1,2,3,4-tetrahydroquinaldine or 1,2,3,4-tetrahydroquinoline (16.2 µl and 14.1 µl respectively, 0.112 mmol), trimethoxybenzene (10.0 mg, internal ¹H NMR standard) and **3a** or **3b** (5 mol% with respect to 1,2,3,4-tetrahydroquinaldine, 0.1 ml of 9.95 mg **3a** or 5.9 mg **3b** in 1 ml stock solution of appropriate solvent). For reactions run with a hydrogen acceptor, N-benzylideneaniline (20.3 mg, 0.112 mmol) was added. Dry solvent (3 ml of toluene or *p*-xylene, sparged with N₂) was then added to the flask. The mixture was then stirred and heated to just above its reflux temperature the

reac (115°C for toluene, 145°C for *p*-xylene) and aliquots were collected at 24 and 48 hours. The solvent was removed in vacuo and the resulting mixture was treated as above.

Procedure for 2-way dehydrogenation-hydrogenation of 1,2,3,4-tetrahydroquinaldine For the optimized reaction run at 1.1 M substrate loading, the dehydrogenation was carried out as described above, using 0.022 mmol of either **1** or **3b**, 66 μ L (0.44 mmol) tetrahydroquinoline, 0.5 mL chlorobenzene and 5 mg 1,3,5 trimethoxybenzene as internal standard. After heating at reflux under N₂ for 24 h, the reaction mixture was cooled to room temperature and a 50 μ L aliquot was taken for ¹H NMR analysis. 0.5 mL additional chlorobenzene, was added to the reaction mixture, and the reaction was stirred under an atmosphere of H₂ for 24 h.

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References

- ¹ (a) Sartbaeva, A.; Kuznetsov, V. L.; Wells, S. A.; Edwards, P. P. *Energy Environ. Sci.*, **2008**, *1*, 79-85. (b) Armaroli, N.; Balzani, V. *ChemSusChem*, **2011**, *4*, 21-36 (c) Eberle, U.; Felderhoff, M.; Schüth, F. *Angew. Chem. Int. Ed.* **2009**, *48*, 6608-6630. (d)

Makowski, P.; Thomas, A.; Kuhn, P.; Goettmann, P. *Energy & Environ. Sci.*, **2009**, *2*, 480-490. (e) Teichmann, D.; Arlt, W.; Wasserscheid, P.; Freymann, R. *Energy & Environ. Sci.*, **2011**, *4*, 2767-2773. (f) Fukuzumi, S.; Suenobu, T. *Dalton Trans.*, **2013**, *42*, 18-28.

² Klebanoff L. Hydrogen storage technology: materials and applications. 1st ed. Taylor and Francis; 2012, p. 287-328.

³ Mueller, K.; Voelkl, J.; Arlt, W. *Energy Technol.*, **2013**, *1*, 20-24.

⁴ (a) General Electric Global Research: <http://ge.geglobalresearch.com/> (accessed December 28, 2014). (b) Luca, O.R.; Wang, T.; Konezny, S.J.; Batista, V.S.; Crabtree, R.H.; *New J. Chem.* 2011, *35*, 998.

⁵ Züttel, A.; Borgschulte, A.; Schlapbach, L. *Hydrogen as a Future Energy Carrier*; Wiley-VCH: Weinheim, Germany, 2008.

⁶ (a) Moores, A.; Poyatos, M.; Luo, Y.; Crabtree, R. H. *New J. Chem.* **2006**, *30*, 1675.

(b) Clot, E.; Eisenstein, O.; Crabtree, R. H. *Chem. Commun.* **2007**, *22*, 2231-2233. (c) Crabtree, R. H. *Energy & Environ. Sci.*, **2008**, *1*, 134-138. (d) Cui, Y.; Kwok, S.; Bucholtz, A.; Davis, B.; Whitney, R. A.; Jessop, P. G. *New J. Chem.* **2008**, *32*, 1027-1037. (e) Jessop, P. G. *Nature Chem.* **2009**, *1*, 350-351. (f) Lu, R.-F.; Boëthius, G.; Wen, S.-H.; Su, Y.; Deng, W.-Q. *Chem. Commun.* 2009, 1751.

⁷ (a) Mikami, K.; Ebata, K.; Mistudome, T.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. *Heterocycles* **2011**, *82*, 1371.

⁸ Ren, D.; He, L.; Yu, L.; Ding, R.-S.; Liu, Y.-M.; Cao, Y.; He, H.-Y.; Fan, K.-N. *J. Am. Chem. Soc.* **2012**, *134* 17592-17598.

⁹ Dell'Anna, M. M.; Capodiferro, V. F.; Mali, M.; Manno, D.; Cotugno, P.; Monopoli, A.; Mastrorilli, P., *Appl. Catal., A*, **2014**, *481* 89-95. and references contained therein.

¹⁰ Zhu, D.; Jiang, H.; Zhang, L.; Zheng, X.; Fu, H.; Yuan, M.; Chen, H.; Li, R. *ChemCatChem*, **2014**, *6* 2954-2960.

¹¹(a) Wang, W. B.; Lu, S. M.; Yang, P. Y.; Han, X. W.; Zhou, Y. G. *J. Am. Chem. Soc.*, **2003**, *125*, 10536-10537. (b) Zhou, H.; Li, Z.; Wang, Z.; Wang, T.; Xu, L.; He, Y.; Fan, Q.-H.; Pan, J.; Gu, L.; Chan, A. S. C. *Angew. Chem. Int. Ed.* **2008**, *47*, 8464 -8467 (c) Manaeka, Y.; Suenobu, T.; Fukuzumi, S. *J. Am. Chem. Soc.* **2011**, *134*, 367-374. (d) Wu, J.; Talwar, D.; Johnston, S.; Yan, M.; Xiao, J. *Angew. Chem., Int. Ed.* **2013**, *52*, 6983-6987. (e) Wu, J.; Barnard, J. H.; Zhang, Y.; Talwar, D.; Robertson, C. M.; Xiao J. *Chem. Commun.*, 2013, **49**, 7052--7054 (f) Cai, X.-F.; Huang, W.-X.; Chen, Z.-P. and Zhou, Y.-G. *Chem. Commun.*, **2014**, *50*, 9588. (g) Wendlandt, A. E.; Stahl, S. S. *J. Am. Chem. Soc.*, **2014**, *136*, 11910-11913.

¹² Yamaguchi, R.; Ikeda, C.; Takahashi, T.; Fujita, K. *J. Am. Chem. Soc.* **2009**, *131*, 8410-8412.

¹³ Chakraborty, S.; Brennessel, W. W.; Jones, W. D. *J. Am. Chem. Soc.*, **2014**, *136*, 8564-8567.

-
- ¹⁴ Fujita, K.; Tanaka, Y.; Kobayashi, M.; Yamaguchi, R.; *J. Am. Chem. Soc.* **2014**, *136*, 4829-4832.
- ¹⁵ Dobereiner, G. E.; Nova, A.; Schley, N. D.; Hazari, N.; Miller, S. J.; Eisenstein, O.; Crabtree, R. H., *J. Am. Chem. Soc.* **2011**, *133*, 7547-7562.
- ¹⁶ Manas, M. G.; Graeupner, J.; Allen, L. J.; Dobereiner, G. E.; Rippy, K. C.; Hazari, N.; Crabtree, R. H., *Organometallics* **2013**, *32*, 4501-4506.
- ¹⁷ Fujii, T.; Saito, Y. *Chem. Comm.* **1990** 757-758.