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Efficient Hydrogen Production from Alcohols under Mild Reaction Conditions**

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Today more than 80% of the energy consumed worldwide is based on fossil fuels.[1] It is undisputable that the resulting CO_2 release has unwanted environmental consequences, such as global warming. In addition, fossil fuels are inherently limited. Therefore, developing a benign, unlimited energy system based on renewable resources represents one of the major challenges for the future. Among the different concepts for alternative energy carriers, the development of a "hydrogen-economy" has been proposed.[2] In this respect in recent years, the use of biomass for hydrogen production has attracted much attention. Here, the dehydrogenation of bioalcohols and carbohydrates shows high potential. In the past, significant progress for this process has been achieved by using heterogeneous catalysts.[2,3] Unfortunately, relatively drastic reaction conditions (> 200 °C) have to be used. Hence, the development of more-active molecularly defined complexes represents an important challenge. However, the complexity of most carbohydrates renders this field rather cumbersome. Consequently, until now, most of the attention has been given to the dehydrogenation of model substrates,[4] such as isopropyl alcohol.

Since the explorative work by Robinson an co-workers,[4l,m] and Cole-Hamilton and co-workers[4f–h] in the 1970s and 1980s, the concept of acceptorless dehydrogenation of alcohols has attracted significant interest.[4,5] Currently, the state-of-the-art catalyst for dehydrogenation of the model substrate isopropyl alcohol has a turnover frequency (TOF), after 2 hours [TOF(2 h)], of 519 h^{-1}. This TOF is achieved by using a 1:20 mixture of $[\{RuCl_2(p\text{-cymene})\}_2]$ and tetramethylethylene diamine (TMEDA) at a 4.0 ppm loading of ruthenium.[4a] The same system provided the highest turnover number (TON) measured to date (17215); however, this required an 11 day reaction time. In addition, strongly basic (0.8 M NaO*i*Pr) conditions were necessary for the reaction to proceed and attempts to broaden the scope to biorelevant ethanol proved unfeasible.

For the development of hydrogen production from aliphatic primary alcohols there has been very little progress since Cole-Hamilton and co-workers showed that ethanol can be dehydrogenated using $[RuH_2(N_2)(PPh_3)_3]$ (TOF(2 h): 210 h^{-1}).[4f–h] An excess of base (NaOH), high temperatures (150 °C), and an intense light source were needed to achieve this value.

New catalytic systems capable of more efficient hydrogen production from, for example, ethanol at neutral conditions are a prerequisite for additional advancements in this area. Herein, we present the combination of $[RuH_2(PPh_3)_3CO]$/*H*PNP^{iPr} (**2b**/**3b**; see Table 2 for structures.) which shows unprecedented high efficiency in hydrogen production from isopropyl alcohol under mild reaction conditions without an activation additive. In addition, this system can be extended to ethanol, which represents to the best of our knowledge, the first example of a catalytic system capable of efficient hydrogen production from a renewable alcohol source below 100 °C.

Recently, important progress has been achieved in acceptorless dehydrogenation of alcohols.[6] In these reactions, metal complexes coordinated by non-innocent pincer ligands such as **1a**,[7] have been shown to be particularly selective and active (Table 1).[8] Based on this work we were attracted to the use of these novel catalysts and derivatives thereof for hydrogen production from alcohols.

At the start of our investigation, we tested the activity of Milstein's catalyst **1a**[8i] with isopropyl alcohol using neat conditions (Table 1, entry 1). To our delight, high initial efficiency was observed but, unfortunately, the catalyst was deactivated at unpredictable reaction times. Hence, we performed a series of experiments in the presence of various amounts of base (NaO*i*Pr). Employing 100 equivalents of NaO*i*Pr relative to **1a** led to an unprecedented and efficient initial hydrogen production with a TOF(2 h) of 855 h^{-1}. Notably, the system becomes stable for a prolonged reaction time with a reproducible TOF(6 h) of 379 h^{-1} (Table 1, entry 2). Using even more base such as 2000 equivalents, corresponding roughly to a 0.8 M NaO*i*Pr solution, did not show any improvements (Table 1, entry 3).

In realizing the potential of this type of catalyst, we decided to test a range of complexes containing pincer-type ligands. The rutheniun complex **1b** containing an *H*PNP^{Ph} ligand with an aliphatic NH moiety was tested in neutral isopropyl alcohol and in both the presence of 1.3 and 100 equivalents of NaO*i*Pr (Table 1, entries 4–6). In contrast to Milstein's catalyst, a base additive is required to achieve any hydrogen production with **1b**. However, with merely 1.3 equivalents of NaO*i*Pr, a TOF(2 h) of 1165 h^{-1} is

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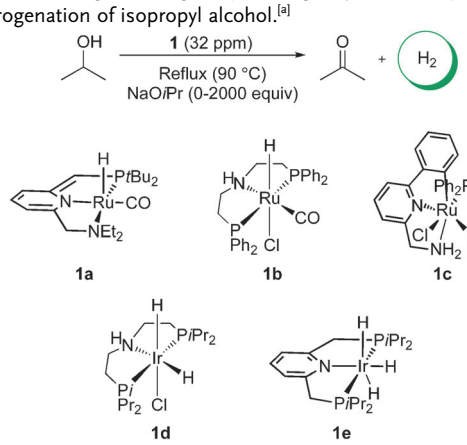
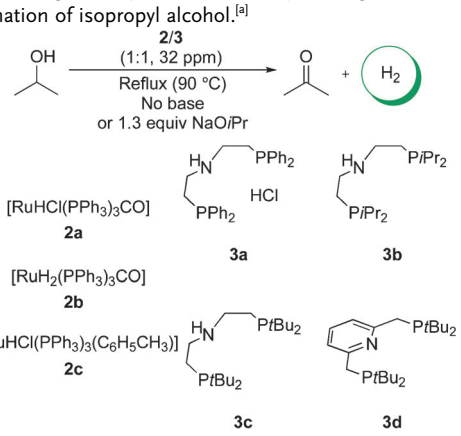
Table 1: Screening of a range of pincer-ligand/metal complexes for the dehydrogenation of isopropyl alcohol.[a]



Entry	1	NaO*i*Pr [equiv]	TOF(2 h) [h^{-1}][b]	TOF(6 h) [h^{-1}][b]
1	**1a**	–	–[c]	–
2	**1a**	100	855	379
3	**1a**	2000	826	407
4	**1b**	–	< 100[d]	–
5	**1b**	1.3	1231	644
6	**1b**	100	929	346
7	**1c**	2000	313	217
8	**1d**	2000	< 100	–
9	**1e**	2000	< 100	–

[a] Performed under argon atmosphere with isopropyl alcohol (10 mL), **1** (4.2 μmol, 32 ppm), and NaO*i*Pr (indicated in table) at reflux. Hexadecane (1 mL) was used as an internal standard. All reproducible reactions were reproduced with an error margin of 10%. [b] Determined by burette measurements. [c] No value was assigned because the reaction was irreproducible. Two attempts were made at this reaction and a reproducible TOF(1 h) value of 1012 h^{-1} is observed; however, already after 2 h, each of the reactions had TOF(2 h) values of 686 and 459 h^{-1}, respectively. After 4 h, TOF(4 h) values of 417 and 100 h^{-1}, respectively, were observed. [d] A minimum value of 100 h^{-1} for TOF(2 h) is set as a reasonable lower limit. This corresponds approximately to a minimum 20 mL of evolved hydrogen.

Table 2: Screening of the precursors **2** and pincer ligands **3** for dehydrogenation of isopropyl alcohol.[a]



Entry	2	3	NaO*i*Pr [equiv]	TOF(2 h) [h^{-1}][b]	TOF(6 h) [h^{-1}][b]
1	**2a**	–	1.3	< 100[c]	–
2	**2b**	–	–	< 100	–
3	**2c**	–	1.3	< 100	–
4	**2a**	**3a**	1.3[d]	460	384
5	**2a**	**3b**	1.3	1187	851
6	**2b**	**3b**	1.3	1843	1009
7	**2c**	**3b**	1.3	< 100	–
8	**2a**	**3b**	–	–[e]	–
9	**2b**	**3b**	–	2048	1109
10	**2b**	**3c**	–	< 100	–
11	**2a**	**3d**	1.3	< 100	–
12	**2b**	**3d**	–	111	–

[a] Performed under an argon atmosphere with isopropyl alcohol (10 mL), **2** (4.2 μmol, 32 ppm), **3** (4.2 μmol, 32 ppm), and NaO*i*Pr (indicated in the table) at reflux; neat conditions. Hexadecane (1 mL) was used as an internal standard. All reproducible reactions were reproduced with an error margin of 10%. [b] Determined by burette measurements. [c] A minimum value of 100 h^{-1} for TOF(2 h) was set as a reasonable lower limit. This corresponds approximately to a minimum of 20 mL for evolved hydrogen. [d] One additional equivalent of NaO*i*Pr used to quench the hydrogen chloride on the ligand. [e] In the two reactions performed, two very different TOF(2 h), 455 h^{-1} and < 100 h^{-1}, respectively, are observed.

observed. Employing 100 equivalents of NaO*i*Pr led to an inferior result with a TOF(2 h) of 961 h^{-1}, which is probably due to faster degradation of the catalyst under the more harsh basic conditions. Furthermore, the Baratta-type ruthenium catalyst **1c**[9] was tested in the presence of 2000 equivalents of NaO*i*Pr, but unfortunately lower activity was observed (Table 1, entry 7). The two PNP/Ir complexes **1d** and **1e**[10,11] were also analyzed for activity. However, neither of them resulted in any significant hydrogen production (Table 1, entry 8 and 9). Typically, no or merely trace amounts of mesityl oxide—arising from the aldol condensation of acetone—are found in any of the reactions. The same is true for Guerbet products. For example, the simplest Guerbet, product 4-methyl-2-pentanone, which consists of the reductive condensation of two molecules of acetone and one molecule of hydrogen, is not observed. This strongly indicates that all hydrogen produced is released as molecular hydrogen and not transferred to other sources. In previously known systems, these types of side products have been observed.[4a,b]

We next turned our attention to investigate the catalytic potential of a range of ruthenium precursors (**2**) and pincer ligands (**3**; Table 2). First, the precursors **2a–c** were found to be devoid of catalytic activity under the given reaction conditions (Table 2, entries 1–3). With the analogue of **1b** (Table 1, entry 5) prepared in situ from **2a** and ligand **3a**, the TOF(2 h) and TOF(6 h) values of 460 and 384 h^{-1}, respectively, are observed (Table 2, entry 4). Compared to the preformed complex the in situ analogue is approximately half as active. We were pleased to find that replacing the bis(diphenylphosphine)-based *H*PNP^{Ph} ligand **3a** with the bis(di(isopropyl)phosphine-based *H*PNP^{iPr} **3b** led to a significant increase in activity with a TOF(2 h) of 1187 h^{-1} (Table 2, entry 5). An even more active system was observed when employing precursor **2b** instead of **2a** and a TOF(2 h) of 1843 h^{-1} was observed (Table 2, entry 6). In contrast, the activity almost entirely disappeared when using **2c** (Table 2, entry 7), thus implying a fundamental role of the carbon monoxide. Then, we tested some of the catalytic systems in isopropyl alcohol without a base. Unfortunately, this led to inconsistent results when using **2a**/**3b** (Table 2, entry 8). However, employing **2b**/**3b**, which does not need any base activation, led to an improved TOF(2 h) of 2048 h^{-1} in neutral

isopropyl alcohol, which is even higher than using 1.3 equivalents of base (Table 2, entry 9 versus 6). In the latter case we speculate that isopropanoate might negatively interfere with the catalytic intermediates, for example, by coordination to the metal center. Interestingly, replacing the four *i*Pr substituents in **3b** with the *t*Bu groups (*H*PNP^{tBu}) results in **3c**, a completely inactive system (Table 2, entry 10). The same is true for the pyridine derivative **3d**, though very little activity is observed when employing the precursor **2b** (Table 2, entries 11–12). This deactivation might be due to a spatial block of ruthenium by the more sterically demanding *t*Bu substituents.[12] Again, the reactions are very clean with acetone and hydrogen as the only products (> 99 %). Of all the tested catalytic systems the combination of **2b**/**3b** in neutral media showed the highest activity and was hereafter used.

To compare our results with the known state-of-the-art data, catalyst concentrations similar to those in previous publications[4] were used (Table 3). Lowering the catalyst concentration in isopropyl alcohol from 32 ppm (Table 3, entry 1) to 4.0 ppm gave a TOF(2 h) of 8382 h^{-1}, which is approximately 16 times higher than the best one obtained before (Table 3, entry 2). The maximum turnover frequency was observed after 20 minutes with a TOF(max) of 14145 h^{-1}. In addition, a TON of more than 40000 is observed after 12 hours, which should be compared with 17215 after 11 days in the previously unsurpassed work. Notably, our system is still highly active after 12 hours.

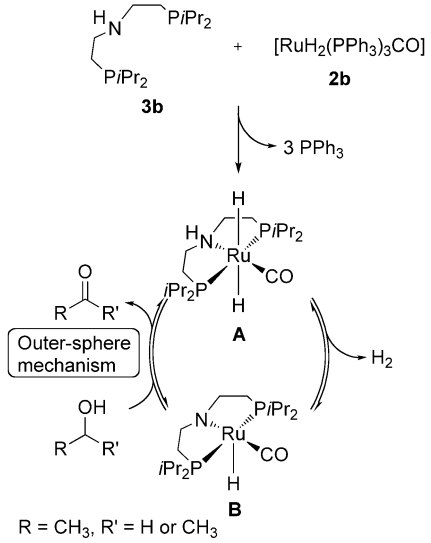
Table 3: Hydrogen production of different alcohols under the optimal reaction conditions with the **2b**/**3b** catalytic system.[a]

Entry	Alcohol	**2b**/**3b** [ppm]	TOF(2 h) [h^{-1}][b]	TOF(6 h) [h^{-1}][b]
1		32	2048	1109
2		4.0	8382	4835
3[c]		3.1	1483	690

[a] Performed under an argon atmosphere and at reflux in the given alcohol (10 mL for entry 1, and 40 mL for entries 2 and 3), and an equivalent amount of **2b** and **3b** (indicated in the table). Hexadecane (1 mL for entry 1, and 4 mL for entries 2 and 3) was used as an internal standard. All reactions are reproduced with an error margin of 10%. [b] Determined by burette measurements. [c] An oil trap between the condenser and measuring burette was employed.

Having found a highly active catalytic system that efficiently produces hydrogen from isopropyl alcohol under mild reaction conditions, we turned our attention to ethanol, which is more relevant as a renewable hydrogen source. Employing ethanol instead of isopropyl alcohol leads to a TOF(2 h) of 1483 h^{-1} (Table 3, entry 3), which is more than a sevenfold improvement compared to the previous state-of-the-art. Furthermore, no base is needed and much milder reaction conditions are employed. For the first time it is possible to dehydrogenate the thermodynamically less-favorable primary aliphatic alcohols below 100 °C efficiently. Hydrogen production was accompanied by the formation of acetaldehyde and ethyl acetate, both in substantial amounts.

The mechanistic proposal for the catalytic cycle of our alcohol dehydrogenation is presented in Scheme 1 (shown for **2b**/**3b**). First, complex **A** is formed by an exchange of the



Scheme 1. Proposed catalytic cycle for the **2b**/**3b**-catalyzed dehydrogenation of isopropyl alcohol.

three triphenylphosphine ligands in **2b** with ligand **3b**.[13,14] Upon heating, **A** loses a molecule of hydrogen to form the highly active complex **B**. This type of hydrogen loss from analogues of **A** has been suggested by Schneider et al.[14b–d] The fact that NaO*i*Pr has a negative influence on the **2b**/**3b** system suggests that this step proceeds through an intramolecular and concerted mechanism. This step was shown to occur at a reduced rate with the **2a**/**3b** system (Table 2, entry 5 versus 6), which contained a chloride coordinated trans to the hydride atom. Therefore, adding a base additive to this catalyst system is beneficial because of the exchange of the chloride with a hydride, thus leading to an *H*PNP^{Ph} analogue of complex **A**. Employing **2c**/**3b** should lead to a metal complex similar to **A**, but with a toluene ligand instead of the carbon monoxide. As shown in Table 2 this complex is not active at all. We believe the carbon monoxide ligand is necessary to lower the overall energy of **B** because of its higher π-accepting properties, which stabilize the amide. Next, dehydrogenation of the alcohol with simultaneous regeneration of **A** takes place. The tridentate ligand **3b** strongly binds to the ruthenium center, which suggests that β-hydride elimination of a coordinated alcoholate is not feasible as a result of the lack of free sites. This fact combined with the presence of an amide ligand suggest that the dehydrogenative step occurs through an outer-sphere mechanism.[15] The detrimental effect of adding isopropanoate to the reaction additionally supports this proposal.[15e]

In conclusion, we have developed the first example of an effective alcohol acceptorless dehydrogenation that employs mild, neutral reaction conditions. Importantly, the protocol is

extended beyond the typical model substrate isopropyl alcohol to the biorelevant ethanol. Unprecedented high turnover frequencies for both isopropyl alcohol and ethanol are observed at low temperatures (< 100 °C).

Experimental Section

All compounds **1**, **2**, and **3**, except **1c**, were bought from fine-chemical suppliers and used as received. **1c** was synthesized according to a literature procedure.[9g] Isopropyl alcohol and ethanol were bought with the highest purities and contained molecular sieves; and were distilled over sodium prior to use. All substances were stored under an argon atmosphere.

All experiments were carried out under an argon atmosphere with the exclusion of air. The amount of hydrogen generated over time was measured by manual gas burette (100 mL, 500 mL, and 1000 mL burettes were used). Subsequently, the gas purity was established by GC analysis. Typically, only hydrogen and argon are observed, though trace amounts of impurities may occasionally be found. The total hydrogen volume determined by burette measurement was verified indirectly by GC quantification of the substances in the reaction liquid phase. All reproducible reactions were reproduced with an error margin of 10 %.

For the standard procedure with prepared complexes **1** (Table 1), 10 mL isopropyl alcohol with the given amount of base (ranging from no base to 2000 equiv to the complex) and an internal standard (1 mL hexadecane) were heated to reflux (90 °C). Then the complex **1** (4.2 μmol, 32 ppm) was added, which marked the starting point for measuring the gas volume.

For the standard procedure with the in situ complex **2**/**3** using 32 ppm of the metal precursor **2** (Table 2 and Table 3, entry 1), the ligand **3** (4.2 μmol) was dissolved in 10 mL isopropyl alcohol containing the given amount of base (ranging from no base to 1.3 equiv to the metal precursor) and the internal standard (1 mL hexadecane). After heating to reflux (90 °C), the metal precursor **2** (4.2 μmol) was added, which marked the starting point for measuring the gas volume.

For the standard reactions in entries 2 and 3 of Table 3, **3b** (2.1 μmol) was dissolved in 40 mL of the alcohol containing the internal standard hexadecane (4 mL), and the mixture was then heated to reflux (90 °C). **2b** (2.1 μmol) was then added, which marked the starting point for measuring the gas volume. For entry 3, an oil-trap between the condenser and measuring burette was employed to avoid excessive ethanol flux into the gas phase after the condenser.

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[1] For a review on "The Legacy of Fossil Fuels", see: N. Armaroli, V. Balzani, *Chem. Asian J.* **2011**, *6*, 768.

[2] For reviews, see: a) N. Armaroli, V. Balzani, *ChemSusChem* **2011**, *4*, 21; b) D. Chen, L. He, *ChemCatChem* **2011**, *3*, 490; c) R. M. Navarro, M. A. Peña, J. L. G. Fierro, *Chem. Rev.* **2007**, *107*, 3952; d) K. Nath, D. Das, *Curr. Sci.* **2003**, *85*, 265; e) P. R. de La Piscina, N. Homs, *Chem. Soc. Rev.* **2008**, *37*, 2459; f) H. Balat, E. Kirtay, *Int. J. Hydrogen Energy* **2010**, *35*, 7416; g) F. Schüth, *Nature* **2005**, *434*, 712; h) F. Schüth, *ChemSusChem* **2008**, *1*, 155; i) U. Eberle, M. Felderhoff, F. Schüth, *Angew. Chem.* **2009**, *121*, 6732; *Angew. Chem. Int. Ed.* **2009**, *48*, 6608; j) M. Ni, D. Y. C. Leung, M. K. H. Leung, K. Sumathy, *Fuel Process. Technol.* **2006**, *87*, 461; k) R. R. Davda, J. W. Shabaker, G. W. Huber, R. D. Cortright, J. A. Dumesic, *Appl. Catal. B* **2005**, *56*, 171; l) E. Chornet, S. Czernik, *Nature* **2002**, *418*, 928; m) B. E. Logan, *Environ. Sci. Technol.* **2004**, *38*, 160A; n) J. R. Rostrup-Nielsen, *Science* **2005**, *308*, 1421; o) H. Jacobsen, *Angew. Chem.* **2004**, *116*, 1948; *Angew. Chem. Int. Ed.* **2004**, *43*, 1912.

[3] a) A. Tanksale, Y. Wong, J. N. Beltramini, G. Q. Lu, *Int. J. Hydrogen Energy* **2010**, *32*, 717; b) R. R. Davda, J. W. Shabaker, G. W. Huber, R. D. Cortright, J. A. Dumesic, *Appl. Catal. B* **2003**, *43*, 13; c) J. W. Shabaker, R. R. Davda, G. W. Huber, R. D. Cortright, J. A. Dumesic, *J. Catal.* **2003**, *215*, 344; d) G. W. Huber, J. W. Shabaker, J. A. Dumesic, *Science* **2003**, *300*, 2075; e) G. W. Huber, J. W. Shakaber, S. T. Evans, J. A. Dumesic, *Appl. Catal. B* **2006**, *62*, 226; f) N. Wang, N. Perret, A. Foster, *Int. J. Hydrogen Energy* **2011**, *36*, 5932; g) R. D. Cortright, R. R. Davda, J. A. Dumesic, *Nature* **2002**, *418*, 964; h) A. Lulianelli, P. K. Seelam, S. Liguori, T. Longo, R. Keiski, V. Calabro, A. Basile, *Int. J. Hydrogen Energy* **2011**, *36*, 3827; i) D. Ö. Özgür, B. Z. Uysal, *Biomass Bioenergy* **2011**, *35*, 822; j) Y.-W. Chen, S.-Y. Wu, J.-J. Ho, *Chem. Phys. Lett.* **2011**, *501*, 315; k) R. L. Manfro, A. F. da Costa, N. F. P. Ribeiro, M. M. V. M. Souza, *Fuel Process. Technol.* **2011**, *92*, 330; l) J. Liu, B. Sun, J. Hu, Y. Pei, H. Li, M. Qiao, *J. Catal.* **2010**, *274*, 287; m) G. A. Deluga, J. R. Salge, L. D. Schmidt, X. E. Verykios, *Science* **2004**, *303*, 993; n) S. P. Annen, V. Bambagioni, M. Bevilacqua, J. Filippi, A. Marchionni, W. Oberhauser, H. Schönberg, F. Vizza, C. Bianchini, H. Grützmacher, *Angew. Chem.* **2010**, *122*, 7387; *Angew. Chem. Int. Ed.* **2010**, *49*, 7229.

[4] a) H. Junge, B. Loges, M. Beller, *Chem. Commun.* **2007**, 522; b) H. Junge, M. Beller, *Tetrahedron Lett.* **2005**, *46*, 1031; c) L.-C. Yang, T. Ishida, T. Yamakawa, S. Shinoda, *J. Mol. Catal. A* **1996**, *108*, 87; d) T. Matsubara, Y. Saito, *J. Mol. Catal.* **1994**, *92*, 1; e) T. Fujii, Y. Saito, *J. Mol. Catal.* **1991**, *67*, 185; f) D. Morton, D. J. Cole-Hamilton, I. D. Utuk, M. Paneque-Sosa, M. Lopez-Poveda, *J. Chem. Soc. Dalton Trans.* **1989**, 489; g) D. Morton, D. Cole-Hamilton, *J. Chem. Soc. Chem. Commun.* **1988**, 1154; h) D. Morton, D. J. Cole-Hamilton, *J. Chem. Soc. Chem. Commun.* **1987**, 248; i) H. Itagaki, S. Shinoda, Y. Saito, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2291; j) S. Shinoda, H. Itagaki, Y. Saito, *J. Chem. Soc. Chem. Commun.* **1985**, 860; k) S. Shinoda, T. Kojima, Y. Saito, *J. Mol. Catal.* **1983**, *18*, 99; l) A. Dobson, S. D. Robinson, *Inorg. Chem.* **1977**, *16*, 137; m) A. Dobson, S. D. Robinson, *J. Organomet. Chem.* **1975**, *87*, c52; For a review see: n) T. C. Johnson, D. J. Morris, R. Wills, *Chem. Soc. Rev.* **2010**, *39*, 81.

[5] For acceptorless dehydrogenation reactions with synthetic applications, see: a) G. R. A. Adair, J. M. J. Williams, *Tetrahedron Lett.* **2005**, *46*, 8233; b) K.-I. Fujita, N. Tanino, R. Yamaguchi, *Org. Lett.* **2007**, *9*, 109; c) K.-I. Fujita, T. Yoshida, Y. Imori, R. Yamaguchi, *Org. Lett.* **2011**, *13*, 2278; d) G. B. W. L. Ligthart, R. H. Meijer, M. P. J. Donners, J. Meuldijk, J. A. J. M. Vekemans, L. A. Hulshof, *Tetrahedron Lett.* **2003**, *44*, 1507; see also Ref. [6] and [8].

[6] For recent reviews, see: a) G. E. Dobereiner, R. H. Crabtree, *Chem. Rev.* **2010**, *110*, 681; b) T. D. Nixon, M. K. Whittlesey, J. M. J. Williams, *Dalton Trans.* **2009**, 753; c) M. H. S. A. Hamid, P. A. Slatford, J. M. J. Williams, *Adv. Synth. Catal.* **2007**, *349*, 1555; d) G. Guillena, D. J. Ramón, M. Yus, *Chem. Rev.* **2010**, *110*, 1611; e) G. Guillena, D. J. Ramon, M. Yus, *Angew. Chem.* **2007**, *119*, 2410; *Angew. Chem. Int. Ed.* **2007**, *46*, 2358.

[7] For reviews on pincer and non-innocent ligands, see: a) J. I. van der Vlugt, J. N. H. Reek, *Angew. Chem.* **2009**, *121*, 8990; *Angew. Chem. Int. Ed.* **2009**, *48*, 8832; b) H. Grützmacher, *Angew. Chem.* **2008**, *120*, 1838; *Angew. Chem. Int. Ed.* **2008**, *47*, 1814; c) M. E. van der Boom, D. Milstein, *Chem. Rev.* **2003**, *103*, 1759; d) M. Albrecht, G. van Koten, *Angew. Chem.* **2001**, *113*, 3866; *Angew. Chem. Int. Ed.* **2001**, *40*, 3750.

[8] a) C. Gunanathan, L. J. W. Shimon, D. Milstein, *J. Am. Chem. Soc.* **2009**, *131*, 3146; b) S. Musa, I. Shaposhnikov, S. Cohen, D. Gelman, *Angew. Chem. Int. Ed.* **2011**, *50*, 3533; c) J. Zhang, M. Gandelman, L. J. W. Shimon, D. Milstein, *Dalton Trans.* **2007**,

107; d) J. van Buijtenen, J. Meuldijk, J. A. J. M. Vekemans, L. A. Hulshof, H. Kooijman, A. L. Spek, *Organometallics* **2006**, *25*, 873; e) J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **2005**, *127*, 10840; f) B. Gnanaprakasam, J. Zhang, D. Milstein, *Angew. Chem.* **2010**, *122*, 1510; *Angew. Chem. Int. Ed.* **2010**, *49*, 1468; g) C. Gunanathan, D. Milstein, *Science* **2007**, *317*, 790; h) J. Zhang, M. Gandelman, L. J. W. Shimon, H. Rozenberg, D. Milstein, *Organometallics* **2004**, *23*, 4026; for a review see: i) D. Milstein, *Top. Catal.* **2010**, *53*, 915.

[9] a) W. Baratta, G. Chelucci, S. Gladiali, K. Siega, M. Toniutti, M. Zanette, E. Zangrando, P. Rigo, *Angew. Chem.* **2005**, *117*, 6370; *Angew. Chem. Int. Ed.* **2005**, *44*, 6214; W. Baratta, K. Siega, P. Rigo, *Adv. Synth. Catal.* **2007**, *349*, 1633; c) W. Baratta, G. Chelucci, S. Magnolia, K. Siega, P. Rigo, *Chem. Eur. J.* **2009**, *15*, 726; d) W. Baratta, G. Bossi, E. Putignano, P. Rigo, *Chem. Eur. J.* **2011**, *17*, 3474; e) W. Baratta, K. Siega, P. Rigo, *Chem. Eur. J.* **2007**, *13*, 7479; f) W. Baratta, M. Ballico, G. Esposito, P. Rigo, *Chem. Eur. J.* **2008**, *14*, 5588; g) W. Baratta, E. Herdtweck, K. Siega, M. Toniutti, P. Rigo, *Organometallics* **2005**, *24*, 1660.

[10] For the synthesis and application of the catalyst **1d**, see: a) Z. E. Clarke, P. T. Maragh, T. P. Dasgupta, D. G. Gusev, A. J. Lough, K. Abdur-Rashid, *Organometallics* **2006**, *25*, 4113; b) X. Chen, W. Jia, R. Guo, T. W. Graham, M. A. Gullons, K. Abdur-Rashid, *Dalton Trans.* **2009**, 1407; c) N. Andrushko, V. Andrushko, P. Roose, K. Moonen, A. Börner, *ChemCatChem* **2010**, *2*, 640.

[11] For the synthesis and application of the catalyst **1e**, see: a) R. Tanaka, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2009**, *131*, 14168; b) M. S. G. Åhlquist, *J. Mol. Catal. A* **2010**, *324*, 3.

[12] This trend of seeing a negative influence on catalytic activity when shifting from *i*Pr to *t*Bu substituents within the PNP ligands on ruthenium has also been observed elsewhere: B. Gnanaprakasam, Y. Ben-David, D. Milstein, *Adv. Synth. Catal.* **2010**, *352*, 3169.

[13] During the very latest stage of this project, Gusev and coworkers published a report showing that the isolated complex is identical to what we propose for **2b**/**3b** forming in situ: M. Bertoli, A. Choualeb, A. J. Lough, B. Moore, D. Spasyuk, D. G. Gusev, *Organometallics* **2011**, *30*, 3479.

[14] This assumption is based on the following reports: a) A. N. Marziale, E. Herdtweck, J. Eppinger, S. Schneider, *Inorg. Chem.* **2009**, *48*, 3699; b) M. Käß, A. Friedrich, M. Drees, S. Schneider, *Angew. Chem.* **2009**, *121*, 922; *Angew. Chem. Int. Ed.* **2009**, *48*, 905; c) A. Friedrich, M. Drees, M. Käss, E. Herdtweck, S. Schneider, *Inorg. Chem.* **2010**, *49*, 5482; d) A. Friedrich, M. Drees, J. Schmedt auf der Günne, S. Schneider, *J. Am. Chem. Soc.* **2009**, *131*, 17552; e) B. Askevold, M. M. Khusniyarov, E. Herdtweck, K. Meyer, S. Scheider, *Angew. Chem.* **2010**, *122*, 7728; *Angew. Chem. Int. Ed.* **2010**, *49*, 7566; f) A. Friedrich, M. Drees, S. Schneider, *Chem. Eur. J.* **2009**, *15*, 10339; see also ref. [11].

[15] a) O. Blum, D. Milstein, *J. Organomet. Chem.* **2000**, *593–594*, 479; b) J. C. M. Ritter, R. G. Bergman, *J. Am. Chem. Soc.* **1998**, *120*, 6826; c) Ref. [9e]; d) Ref. [9f]; e) M. Yamakawa, H. Ito, R. Noyori, *J. Am. Chem. Soc.* **2000**, *122*, 1466; f) J.-W. Handgraaf, E. J. Meijer, *J. Am. Chem. Soc.* **2007**, *129*, 3099.

