Renewable Energy

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Selective Hydrogen Production from Methanol with a Defined Iron Pincer Catalyst under Mild Conditions

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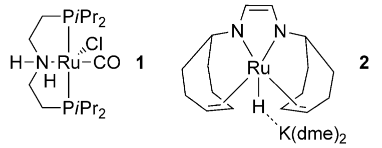
Abstract: *Molecularly well-defined iron pincer complexes promote the aqueous-phase reforming of methanol to carbon dioxide and hydrogen, which is of interest in the context of a methanol and hydrogen economy. For the first time, the use of earth-abundant iron complexes under mild conditions for efficient hydrogen generation from alcohols is demonstrated.*

Hydrogen is discussed as a possible benign energy carrier within the frame of an H_2-based economy.[1] In combination with low-temperature proton-exchange membrane fuel cells (PEM-FCs) it allows for the efficient conversion of chemical energy into electricity. Due to its physical properties, hydrogen poses safety issues as to handling and transportation. Most conveniently, it can be "chemically" stored in the form of methanol, which is liquid at room temperature and has a relatively high gravimetric hydrogen content (12.6 %).[2] In order to use methanol as hydrogen source, reformed-methanol fuel cells (RMFCs) have been developed where reforming takes place according to Equation (1) in Scheme 1. This latter reaction, known as methanol steam-reforming, is usually promoted by heterogeneous catalysts and requires high temperatures.[3]

$$CH_3OH + H_2O \longrightarrow 3H_2 + CO_2 \qquad (1)$$

$$CH_3OH + 2\,OH^- \longrightarrow 3H_2 + 2\,CO_3^{2-} \qquad (2)$$

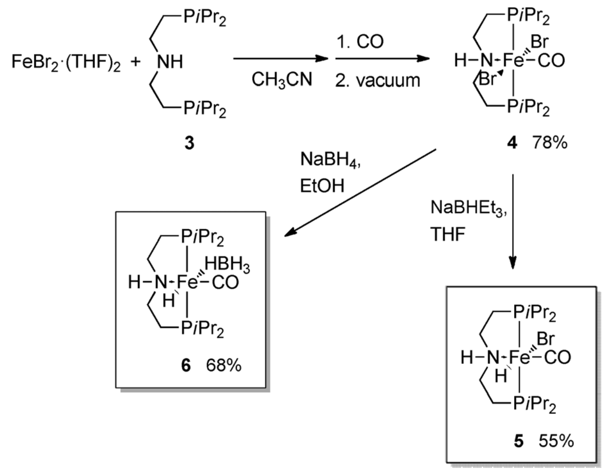


Scheme 1. Catalysts for homogeneously catalyzed aqueous-phase methanol dehydrogenation under mild conditions.

Recently, molecularly defined ruthenium catalysts have been developed by our group[4] (Scheme 1, complex 1, Equation (2)) and Grützmacher et al.[2c] (Scheme 1, complex 2, Equation (1)) that make aqueous-phase dehydrogenation of methanol feasible at low temperatures (< 100 °C) and ambient pressure. Both catalysts make use of "non-innocent" pincer-type ligands,[5] which allow for improved activities and selectivities in alcohol dehydrogenations.[6,7]

Because of the limited availability and high cost of precious metals, the development of catalytic systems for alcohol dehydrogenation that are based on non-noble metals is highly desirable. For instance, the cationic cobalt(II) alkyl complex $[(HN(CH_2CH_2PCy_2)Co(CH_2SiMe_3)]BAr^F_4$ is effective in the acceptorless dehydrogenation of secondary alcohols as well as in the hydrogenation of olefins and ketones.[8] In addition, complexes of several transition metals, including first-row ones,[9] have been prepared with aliphatic pincer ligands of the type $HN(CH_2CH_2PR_2)_2$. However, to the best of our knowledge, no report is known describing the corresponding Fe complexes. Based on our experience in iron catalysis and inspired by the work of Milstein et al. using different Fe complexes with pyridine-based PNP pincer ligands,[10] we set out to develop an iron-catalyzed dehydrogenation of methanol.

Before attempting the synthesis of discrete iron pincer complexes, we explored the reactivity of in situ generated catalysts. Hence, we tested various iron precursors ($[Fe(H_2O)_6](BF_4)_2$, FeF_2, $FeCl_2$, $FeBr_2$, FeI_2, and $[Fe_3(CO)_{12}]$) in combination with 1 equivalent of ligand **3** (see Scheme 2).[11] Unfortunately, no hydrogen evolution was observed. On the other hand, the preformed iron complexes **5** and **6** (Scheme 2)



Scheme 2. Synthesis of Fe^{II} complexes **5** and **6**.

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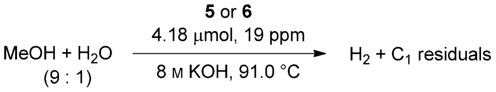
were indeed able to promote the dehydrogenation of aqueous methanol at low temperature with a turnover frequency (TOF) of 414 h^{-1} and 702 h^{-1}, respectively, in the first hour (Scheme 3).[12]



$$\underset{(9:1)}{MeOH + H_2O} \xrightarrow[8\ \text{M KOH, 91.0 °C}]{\substack{\mathbf{5}\text{ or }\mathbf{6}\\ 4.18\ \mu\text{mol, 19 ppm}}} H_2 + C_1\ \text{residuals}$$

	5	**6**
TOF_{1h}	414 h^{-1}	702 h^{-1}
TOF_{2h}	385 h^{-1}	594 h^{-1}
TOF_{3h}	353 h^{-1}	510 h^{-1}

Scheme 3. Dehydrogenation of aqueous methanol catalyzed by Fe^{II} complexes **5** and **6**.

The common precursor to both complexes **5** and **6** is the blue complex **4** which was prepared in good yield from the reaction of $FeBr_2{\cdot}(THF)_2$ with amine **3** under an atmosphere of CO (see Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at $\delta = 67.8$ ppm, indicating that the two phosphorus atoms of the ligand are equivalent, although the methyl protons of the *i*Pr groups give rise to four doublets and the methinic protons to two almost superimposed multiplets in the $^1H\{^{31}P\}$ NMR spectrum. The IR spectrum of **4** shows a strong band at 1929 cm^{-1} indicative of a coordinated CO molecule.

The hydride complex **5** was prepared by treating **4** with 1 equivalent of $NaHBEt_3$ in THF and was isolated in 55% yield as an orange-brownish solid (Scheme 2). The complex was characterized by multinuclear NMR spectroscopy, high-resolution mass spectrometry, and IR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum in benzene shows the presence of two species: two singlets at $\delta = 93.9$ ppm and $\delta = 95.5$ ppm in a ratio of 84:16 are observed. These signals correlate with the two triplets having the same relative intensity at $\delta = -22.7$ ppm ($^2J_{HP} = 52.8$ Hz) and $\delta = -22.6$ ppm ($^2J_{HP} = 54.8$ Hz), respectively, in the ^1H NMR spectrum which account for the hydride ligand in the two species. The chemical shifts of the hydride ligands suggest a *trans* position with respect to the bromide ligand in both complexes which are most likely isomers that differ in the relative orientation, either *syn* or *anti*, of the hydrogen atoms at N and Fe. Two bands at 1897 cm^{-1} and 1853 cm^{-1} in the IR spectrum indicate that CO is retained in the coordination sphere of the metal, a fact further supported by the detection of a triplet at $\delta = 224.1$ ppm ($^2J_{CP} = 26.0$ Hz) in the ^{13}C NMR spectrum for the major isomer.

To perform catalytic experiments in the absence of base, the bright yellow hydrido hydroborato complex **6** was prepared in 68% yield by treating **4** with excess $NaBH_4$ in ethanol (Scheme 2). As shown in the case of Ru[13] and Fe[10b] hydrido tetrahydroborato complexes, the BH_4^- anion is labile and can easily dissociate from the metal affording an active hydride species ready to enter the catalytic cycle. The $^{31}P\{^1H\}$ NMR spectrum of **6** shows a mixture of two isomers at $\delta = 99.5$ ppm (major isomer) and $\delta = 100.9$ ppm (minor isomer). In the ^1H NMR spectrum, the hydride ligand resonates at $\delta = -19.5$ ppm ($^2J_{HP} = 50.0$ Hz) as a sharp triplet, while the η^1-BH_4 ligand gives rise to a broad signal centered at $\delta = -2.8$ ppm. In the IR spectrum broad bands at 2349 cm^{-1} and 2051 cm^{-1} are ascribed to the terminal and bridging B–H stretching modes, respectively, of the BH_4^- anion. Bands at 1892 cm^{-1} and 1833 cm^{-1} belong to the coordinated CO in the two isomers. As shown in Figure 1, the X-ray crystal structure analysis of **6** reveals a distorted octahedral coordination geometry around the Fe^{II} center, with the CO ligand located *trans* to the nitrogen atom and the hydride ligand located *trans* to the η^1-coordinated hydroborate ligand. Besides, the hydrogen atoms at Fe and N are arranged *anti* to each other.

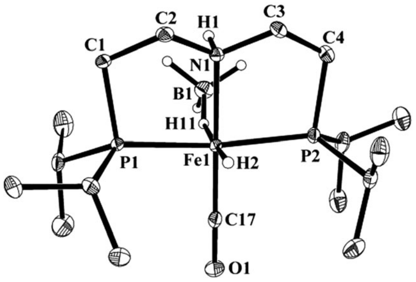


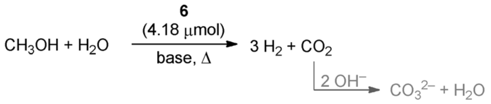
Figure 1. Molecular structure of complex **6** with thermal ellipsoids set at 30% probability (hydrogen atoms, except those on N, B, and Fe, which could be refined from electron density, are omitted for clarity). Selected bond lengths [Å] and angles [°]: Fe1–N1 2.0669(12), Fe1–C17 1.7214(16), Fe1–P1 2.2188(4), Fe1–P2 2.2067(4), Fe1–H2 1.42(2), Fe1–H11 1.691 (18), C17–O1 1.161 (2); N1-Fe1-C17 175.51(7), P1-Fe1-P2 165.74(2), H2-Fe1-H11 176.9(10), N1-Fe1-H2 86.4 (8).

After demonstrating the reactivity of the molecularly defined complexes **5** and **6** for methanol dehydrogenation, the latter complex was chosen to assess the influence of the reaction conditions (base, its concentration, temperature, water content) on the performance of the catalyst (Table 1).

Notably, hydrogen evolution (TOF_{1h} 1.5) was observed even in the absence of base (Table 1, entry 1) from a 9:1 $MeOH/H_2O$ solution. In this case, the evolved gas contained H_2 and CO_2 in a ratio of about 2.3 to 1.[14] This confirms that the hydroborate complex **6** is able to directly generate the active species. However, in the presence of KOH (0.5 M; Table 1, entry 2) the volume of hydrogen evolved increased (TOF_{1h} 10.3), showing that a base effectively promotes catalysis. Under basic conditions, the evolved gas was almost exclusively hydrogen as any produced CO_2 was trapped as carbonate. A boost in activity was observed at higher base concentration (Table 1, entries 3 and 4), allowing to achieve a good TOF_{1h} of 702 h^{-1} with 8.0 M KOH. Lower activities were observed with 8.0 M NaOH (Table 1, entry 5, TOF_{1h} 485 h^{-1}) and 8.0 M *t*BuOK (Table 1, entry 6, TOF_{1h} 646 h^{-1}), and a more rapid catalyst deactivation was observed with the latter.

The addition of 10 equivalents of either potassium formate (a plausible intermediate in the dehydrogenation of methanol) or potassium carbonate only slightly decreased the activity of the catalyst (Table 1, entries 7 and 8, TOF_{1h} 626 h^{-1} and 558 h^{-1}, respectively). Next, the effect of the water

Table 1: Aqueous-phase dehydrogenation of methanol promoted by catalyst precursor **6**: variation of reaction conditions.[a]



$$CH_3OH + H_2O \xrightarrow[\text{base, }\Delta]{\mathbf{6}\ (4.18\ \mu mol)} 3\,H_2 + CO_2 \xrightarrow{2\,OH^-} CO_3^{2-} + H_2O$$

Entry	Additive	c(base)[b] [mol L^{-1}]	T [°C][c]	TOF$_{1h}$ [h^{-1}][d]	TOF$_{2h}$ [h^{-1}]	TOF$_{3h}$ [h^{-1}]	TON$_{3h}$	TON$_{max}$/ duration
1	–	–	65	1.5	4.0	5.3	15.9	69/20 h
2	–	0.5	72	10.3	9.5	8.3	24.9	–
3	–	4.0	79	59	64	59	177	–
4	–	8.0	91	702	594	510	1530	6270/ 43 h
5	–	8.0[e]	91	485	426	380	1140	–
6	–	8.0[f]	91	646	428	333	999	–
7	HCOOK 10 equiv	8.0	91	626	528	465	1395	–
8	K_2CO_3 10 equiv	8.0	91	558	486	433	1299	–
9[g]	–	8.0	89	411	382	362	1086	5303/ 60 h
10[h]	–	8.0	91[i]	734	620	528	1584	–
11[j]	–	8.0	91	635	644	617	1851	9834/ 46 h
12	**3** 1 equiv	8.0	91	613	555	506	1518	–
13	**3** 5 equiv	8.0	91	644	570	520	1560	9184/ 111 h

[a] Reactions were performed under argon and at reflux using MeOH/H_2O (10 mL, ratio 9:1, unless otherwise given) and **6** (4.18 μmol), except for entry 11. H_2/CO_2 ratio >200 and CO <10 ppm were ascertained in all experiments except the one in entry 1 by gas-phase GC. For entry 1 the relative amounts of gases were the following: H_2 69 %, CO_2 29.5 %, CO 1.5 %. Hydrogen evolution by decomposition of BH_4^- would lead to a TON of 2. [b] KOH as base unless otherwise given. [c] Inner temperature of the solution at reflux. [d] Volume of evolved hydrogen determined by burette measurements. [e] NaOH as base. [f] KO*t*Bu as base. [g] MeOH/H_2O = 4:1. [h] Neat MeOH. [i] Set temperature. [j] The experiment was performed using 1 μmol of catalyst.

content was investigated: the activity nearly doubled going from a MeOH/H_2O volume ratio of 4:1 (Table 1, entry 9, TOF$_{1h}$ 411 h^{-1}) to neat MeOH (Table 1, entry 10, TOF$_{1h}$ 734 h^{-1}). When the catalyst loading was lowered from 4.16 μmol to 1 μmol under standard conditions, an increase in activity was observed (Table 1, entry 11, TOF$_{1h}$ 635 h^{-1}) with a good total turnover number (TON) of nearly 10000 after 46 h.

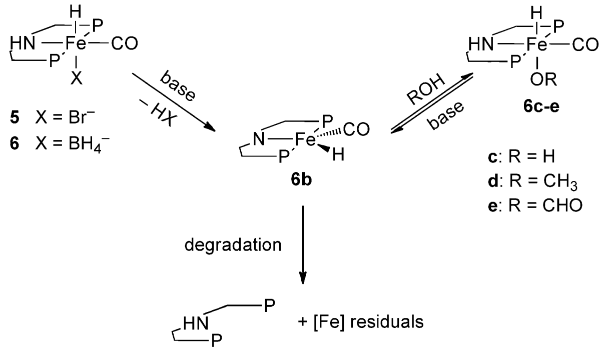
The evolved CO_2, trapped as carbonate, could be released as gas by treating the reaction mixture with HCl, proving the complete decomposition of methanol to H_2 and CO_2 as products (see Section SI4 in the Supporting Information).

Although the complexes were active for 43–66 h, we tried to improve the stability further. Thus, experiments were performed in the presence of an excess of ligand **3** (up to 5 equiv) under standard conditions (MeOH/H_2O 9:1, 8.0 M KOH). While the activity was slightly reduced in the short term (Table 1, entries 12 and 13, TOF$_{1h}$ 613 h^{-1} and 644 h^{-1}, respectively), the positive effect on catalyst stability became apparent in the long term, and evolution of hydrogen proceeded up to 5 days!

To gain more insight into catalyst deactivation, additional experiments were carried out under catalytic-like conditions (see the Supporting Information). Both formate and carbonate/bicarbonate ions[15] were observed by NMR spectroscopy, indicating that dehydrogenation of methanol proceeds beyond the stage of formaldehyde to formate and further to CO_2 which is trapped as carbonate under the basic conditions employed. Besides, free ligand was detected in solution during the reaction, its relative amount increasing over time. The positive effect of added ligand on catalyst lifetime is therefore ascribed to impeding catalyst decomposition.

To assess the homogeneous nature of our catalytic system, poisoning experiments[16a,b] were conducted in the presence of PMe_3 (Figures SI24,25 in the Supporting Information). While a large excess of PMe_3 (20 equiv with respect to iron) almost stopped the catalytic activity, 0.12 equivalents of PMe_3 did not hamper hydrogen evolution. The latter fact argues against the presence of a previously reported kind of nanoparticles.[16c] In addition, none of our gas-evolution curves is sigmoidally shaped (Figures SI21–23 in the Supporting Information), which clearly indicates that there is no induction period, which would be required to form nanoparticles from the iron(II) complex.

Due to the "non-innocent" nature of the ligand,[5] it is reasonable to postulate that this ligand is directly involved in catalysis by means of an outer-sphere mechanism. As the catalytically active species we suggest the amide complex **6b** which is generated from **5** or **6** by the action of base (Scheme 4). Such a complex should be able to abstract hydrogen from the substrate—either methanol, formaldehyde (or its hydrated form methandiol), or formate—to afford a dihydride species from which hydrogen is then released. MeOH, H_2O, and HCOOH may also add to the reactive complex **6b** giving rise to species **6c**–**e**. The analogous Ru complexes have been detected in solution by NMR spectroscopy during methanol dehydrogenation promoted by [Ru(H)(Cl)(CO){HN(CH_2CH_2P*i*Pr_2)$_2$}].[4] The positive effect



Scheme 4. Suggested structures of the catalytically active species and resting states arising from Fe^{II} complexes **5** and **6** during aqueous methanol reforming.

of base on hydrogen evolution can be explained by the base labilizing **6c**–**e** through amine deprotonation and RO^- elimination.[17] Alternatively, an iron dihydride species may originate directly from the corresponding iron alkoxide **6d** or iron formate **6e** through β-hydride elimination. This possibility has been recently suggested by Milstein et al. for the liberation of a molecule of CO_2 from an iron formate complex,[10d] and has before been shown to be a viable reaction pathway by DFT calculations.[18]

In conclusion, we have shown for the first time that molecularly defined iron pincer complexes are able to promote dehydrogenation of methanol at low temperatures. This opens the possibility to perform aqueous methanol reforming with the waste heat from PEM-FCs. Clearly, the observed catalyst turnover numbers (up to 10000) still have to be improved for practical applications. Nevertheless, this work represents a further step[19] towards the implementation of a "methanol/hydrogen economy" based on non-noble metal catalysts.[2a,b]

Experimental Section

All reactions were performed under argon with exclusion of air. A solution (10 mL) of MeOH and H_2O in a given ratio, containing a defined amount of base (and a defined amount of ligand, for experiments with in situ generated catalyst or added ligand), was heated to the desired temperature and let equilibrate for 30 min. Then, the iron precursor (for in situ experiments) or either **5** or **6** (4.18 μmol) was added, which set the starting point for measuring the evolved gas volume. Gas evolution was measured by manual or automatic gas burettes.[20] The identity of the gas components and their ratio were determined by gas-phase chromatography. Synthetic procedures for the preparation of the new complexes **4**, **5**, and **6**, and their characterization, and plots of volume amount of gas evolved as a function of time for all experiments reported in Table 1 can be found in the Supporting Information.

CCDC 949531 (**6**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) N. Armaroli, V. Balzani, *Chem. Asian J.* **2011**, *6*, 768–784; b) *Energy for a Sustainable World. From the Oil Age to a Sun-Powered Future* (Eds.: N. Armaroli, V. Balzani), Wiley-VCH, Weinheim, **2011**; c) *Hydrogen as a future energy carrier* (Eds.: A. Züttel, A. Borgschulte, L. Schlapbach), Wiley-VCH, Weinheim, **2008**.

[2] a) G. A. Olah, *Angew. Chem.* **2013**, *125*, 112–116; *Angew. Chem. Int. Ed.* **2013**, *52*, 104–107; b) G. A. Olah, *Angew. Chem.* **2005**, *117*, 2692–2696; *Angew. Chem. Int. Ed.* **2005**, *44*, 2636–2639; c) R. E. Rodríguez-Lugo, M. Trincado, M. Vogt, F. Tewes, G. Santiso-Quinones, H. Grützmacher, *Nat. Chem.* **2013**, *5*, 342–347; d) J. Choudhury, *ChemCatChem* **2012**, *4*, 609–611; e) A. J. M. Miller, D. M. Heinekey, J. M. Mayer, K. I. Goldberg, *Angew. Chem.* **2013**, *125*, 4073–4076; *Angew. Chem. Int. Ed.* **2013**, *52*, 3981–3984; f) C. A. Huff, M. S. Sanford, *J. Am. Chem. Soc.* **2011**, *133*, 18122–18125; g) Y. Na, P. Lincoln, J. R. Johansson, B. Nordén, *ChemCatChem* **2012**, *4*, 1746–1750; h) F. Liao, Z. Zeng, C. Eley, Q. Lu, X. Hong, S. C. E. Tsang, *Angew. Chem.* **2012**, *124*, 5934–5938; *Angew. Chem. Int. Ed.* **2012**, *51*, 5832–5836.

[3] a) R. M. Navarro, M. A. Peña, J. L. G. Fierro, *Chem. Rev.* **2007**, *107*, 3952–3991; b) D. R. Palo, R. A. Dagle, J. D. Holladay, *Chem. Rev.* **2007**, *107*, 3992–4021.

[4] M. Nielsen, E. Alberico, W. Baumann, H.-J. Drexler, H. Junge, S. Gladiali, M. Beller, *Nature* **2013**, *495*, 85–89.

[5] a) S. Schneider, J. Meiners, B. Askevold, *Eur. J. Inorg. Chem.* **2012**, 412–429; b) D. Gelman, S. Musa, *ACS Catal.* **2012**, *2*, 2456–2466; c) J. I. van der Vlugt, *Eur. J. Inorg. Chem.* **2012**, 363–375; d) B. Askevold, H. W. Roesky, S. Schneider, *ChemCatChem* **2012**, *4*, 307–320; e) B. Zhao, Z. Han, K. Ding, *Angew. Chem.* **2013**, *125*, 4844–4889; *Angew. Chem. Int. Ed.* **2013**, *52*, 4744–4788; f) C. Gunanathan, D. Milstein, *Acc. Chem. Res.* **2011**, *44*, 588–602; g) M. Albrecht, G. van Koten, *Angew. Chem.* **2001**, *113*, 3866–3898; *Angew. Chem. Int. Ed.* **2001**, *40*, 3750–3781.

[6] a) M. Nielsen, H. Junge, A. Kammer, M. Beller, *Angew. Chem.* **2012**, *124*, 5809–5811; *Angew. Chem. Int. Ed.* **2012**, *51*, 5711–5713; b) D. Spasyuk, S. Smith, D. G. Gusev, *Angew. Chem.* **2012**, *124*, 2826–2829; *Angew. Chem. Int. Ed.* **2012**, *51*, 2772–2775; c) R. Kawahara, K. Fujita, R. Yamaguchi, *J. Am. Chem. Soc.* **2012**, *134*, 3643–3646; d) Y. Maenaka, T. Suenobu, S. Fukuzumi, *J. Am. Chem. Soc.* **2012**, *134*, 9417–9427; e) M. Nielsen, A. Kammer, D. Cozzula, H. Junge, S. Gladiali, M. Beller, *Angew. Chem.* **2011**, *123*, 9767–9771; *Angew. Chem. Int. Ed.* **2011**, *50*, 9593–9597; f) M. Bertoli, A. Choualeb, A. J. Lough, B. Moore, D. Spasyuk, D. G. Gusev, *Organometallics* **2011**, *30*, 3479–3482; g) K. Fujita, T. Yoshida, Y. Imori, R. Yamaguchi, *Org. Lett.* **2011**, *13*, 2278–2281; h) W. Baratta, G. Bossi, E. Putignano, P. Rigo, *Chem. Eur. J.* **2011**, *17*, 3474–3481; i) C. Gunanathan, Y. Ben-David, D. Milstein, *Science* **2007**, *317*, 790–792; j) J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **2005**, *127*, 10840–10841.

[7] a) H. Junge, B. Loges, M. Beller, *Chem. Commun.* **2007**, 522–524; b) H. Junge, M. Beller, *Tetrahedron Lett.* **2005**, *46*, 1031–1034; c) L.-C. Yang, T. Ishida, T. Yamakawa, S. Shinoda, *J. Mol. Catal. A* **1996**, *108*, 87–93; d) T. Matsubara, Y. Saito, *J. Mol. Catal.* **1994**, *92*, 1; e) T. Fujii, Y. Saito, *J. Mol. Catal.* **1991**, *67*, 185–190; f) D. Morton, D. J. Cole-Hamilton, I. D. Utuk, M. Paneque-Sosa, M. Lopez-Poveda, *J. Chem. Soc. Dalton Trans.* **1989**, 489–495; g) D. Morton, D. Cole-Hamilton, *J. Chem. Soc. Chem. Commun.* **1988**, 1154–1156; h) D. Morton, D. J. Cole-Hamilton, *J. Chem. Soc. Chem. Commun.* **1987**, 248–249; i) H. Itagaki, S. Shinoda, Y. Saito, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2291–2294; j) S. Shinoda, H. Itagaki, Y. Saito, *J. Chem. Soc. Chem. Commun.* **1985**, 860–861; k) S. Shinoda, T. Kojima, Y. Saito, *J. Mol. Catal.* **1983**, *18*, 99–104; l) A. Dobson, S. D. Robinson, *Inorg. Chem.* **1977**, *16*, 137–142; m) A. Dobson, S. D. Robinson, *J. Organomet. Chem.* **1975**, *87*, c52–c53; n) for a recent review on alcohol and formic acid dehydrogenation, see: T. C. Johnson, D. J. Morris, M. Wills, *Chem. Soc. Rev.* **2010**, *39*, 81–88.

[8] a) G. Zhang, S. K. Hanson, *Org. Lett.* **2013**, *15*, 650–653; b) G. Zhang, K. V. Vasudevan, L. B. Scott, S. K. Hanson, *J. Am. Chem. Soc.* **2013**, *135*, 8668–8681.

[9] a) S. R. Rozenel, J. B. Kerr, J. Arnold, *Dalton Trans.* **2011**, *40*, 10397–10405; b) Q. Dong, M. J. Rose, W.-Y. Wong, H. B. Gray, *Inorg. Chem.* **2011**, *50*, 10213–10224; c) G. Zhang, B. L. Scott, S. K. Hanson, *Angew. Chem.* **2012**, *124*, 12268–12272; *Angew. Chem. Int. Ed.* **2012**, *51*, 12102–12106; d) K. V. Vasudevan, L. B. Scott, S. K. Hanson, *Eur. J. Inorg. Chem.* **2012**, 4898–4906; e) L. Chen, P. Ai, J. Gu, S. Jie, B. G. Li, *J. Organomet. Chem.* **2012**,

697-697, 55–61; f) D. S. McGuinness, P. Wasserscheid, D. H. Morgan, J. T. Dixon, *Organometallics* **2005**, *24*, 552–556; g) D. S. McGuinness, P. Wasserscheid, W. Keim, C. Hu, U. Englert, T. Dixon, C. Grove, *Chem. Commun.* **2003**, 334–335.

[10] a) R. Langer, G. Leitus, Y. Ben-David, D. Milstein, *Angew. Chem.* **2011**, *123*, 2168–2172; *Angew. Chem. Int. Ed.* **2011**, *50*, 2120–2124; b) R. Langer, M. A. Iron, L. Konstantinovski, Y. Diskin-Posner, G. Leitus, Y. Ben-David, D. Milstein, *Chem. Eur. J.* **2012**, *18*, 7196–7209; c) R. Langer, Y. Diskin-Posner, G. Leitus, L. J. W. Shinon, Y. Ben-David, D. Milstein, *Angew. Chem.* **2011**, *123*, 10122–10126; *Angew. Chem. Int. Ed.* **2011**, *50*, 9948–9952; d) T. Zell, B. Butschke, Y. Ben-David, D. Milstein, *Chem. Eur. J.* **2013**, *19*, 8068–8072.

[11] K. Abdur-Rashid, T. Graham, C.-W. Tsang, X. Chen, R. Guo, J. Wenli, D. Amoroso, C. Sui-Seng, WO 2008/141439A1: in the patent the authors report that treatment of $[Fe(H_2O)_6](BF_4)_2$ with **3** in CH_3CN affords a mixture of complexes but they provide no characterization. The mixture is claimed to be applied in ammonia–borane hydrolysis.

[12] TOF: moles of H_2 produced per mole of catalyst per hour. Because complete dehydrogenation of methanol proceeds through three consecutive steps, each catalyzed by the same catalyst, three turnovers of the latter are necessary to afford three molecules of hydrogen and this corresponds to a TON/productivity of 3.

[13] C. A. Sandoval, T. Ohkuma, K. Muniz, R. Noyori, *J. Am. Chem. Soc.* **2003**, *125*, 13490–13503.

[14] The system under investigation is very complex and made up of three discrete reactions which run parallel and possibly at different rates that vary over time depending on the actual concentrations of the species involved. In order to observe the exact ratio of H_2 to CO_2 expected for aqueous MeOH reforming (H_2/CO_2 3:1), the relative concentrations of the reagents and possible intermediates competing for the catalyst must reach suitable steady-state values. This has been shown for the analogous Ru system, see Ref. [4].

[15] It has been shown that, due to fast equilibration, the HCO_3^-/CO_3^{2-} anions give rise to a single ^{13}C NMR peak the chemical shift of which depends on their relative concentration and therefore on the pH value: F. Mani, M. Peruzzini, P. Stoppioni, *Green Chem.* **2006**, *8*, 995–1000.

[16] a) R. H. Crabtree, *Chem. Rev.* **2012**, *112*, 1536–1554; b) J. A. Widegren, R. G. Finke, *J. Mol. Catal. A* **2003**, *198*, 317–341; c) J. F. Sonnenberg, N. Coombs, P. A. Dube, R. H. Morris, *J. Am. Chem. Soc.* **2012**, *134*, 5893–5899.

[17] R. J. Hamilton, S. H. Bergens, *J. Am. Chem. Soc.* **2006**, *128*, 13700–13701.

[18] a) X. Yang, *ACS Catal.* **2011**, *1*, 849–854; b) X. Yang, *Inorg. Chem.* **2011**, *50*, 12836–12843; c) during the revision of this manuscript, X. Yang reported the DFT study of ethanol dehydrogenation as promoted by Fe-amido complex **6b** or its ruthenium analogue (*ACS Catal.* **2013**, DOI: 10.1021/cs400862x). According to that study, the catalytic reaction proceeds with both metals following an outer-sphere mechanism with involvement of the nitrogen on the ligand.

[19] D. W. Stephan, *Nature* **2013**, *495*, 54–55.

[20] The automatic burette equipment has been developed at the Leibniz-Institut für Katalyse e.V. Rostock together with MesSen Nord (Stäbelow). It can also be used for measuring the gas uptake in hydrogenation reactions. A detailed description of the equipment is provided in H.-J. Drexler, A. Preetz, T. Schmidt, D. Heller in *The Handbook of Homogeneous Hydrogenation*, *Vol. 1* (Eds.: J. G. De Vries, C. J. Elsevier), Wiley-VCH, Weinheim, **2007**, pp. 257–293.