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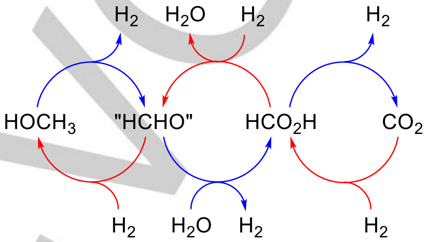
Iridium-PNP Pincer Complexes for Methanol Dehydrogenation At Low Base Concentration

Christoph Prichatz,[a] Elisabetta Alberico,[a] [b] Wolfgang Baumann,[a] Henrik Junge[a] and Matthias Beller*[a]

Abstract: A catalytic system based on an iridium-PNP complex was developed for the aqueous phase reforming of methanol. Investigations revealed higher activity at low base concentration and higher stability at higher base concentration as an opposing trend compared to known Ru and Fe PNP pincer containing systems for methanol dehydrogenation. During mechanistic investigations it was possible to identify a carbonyl species of our catalyst as deactivation species.

The world energy demand constantly increases and still around 80 % of the consumed energy is based on fossil fuels. Hence, the need for more sustainable alternatives is one of the central challenges for the coming decades.[1] Among the various forms of renewable energy, wind and sun light are essential sources. However, due to their intermittent character, applications are limited.[2] Hence, the development of energy storage systems is indispensable. While batteries are well established on small scale with comparable short operation times, chemical energy storage with hydrogen as carrier avoids these limitations.[3] Hence, a surplus of renewable electricity can be used for the straightforward generation of hydrogen by water electrolysis.[4] Later on, the stored energy can be released on demand by combustion of hydrogen both directly or in a fuel cell, which is a clean process with just water as side product. Hydrogen can be physically stored only in high pressure tanks (350-700 bar) or as liquefied gas (-253 °C). Unfortunately, it is a flammable gas, able to diffuse through most commonly used materials. Chemical storage overcomes these disadvantages by reversible conversion of H_2 into (liquid) hydrogen enriched molecules. In this respect, methanol,[5] formic acid, methane as well as aromatic hydrocarbons (LOHC) are investigated as promising storage compounds.[6] Among these materials, especially methanol has a high gravimetric hydrogen content of 12.6 %[7] and can be generated by hydrogenation of CO_2[8] or from natural sources.

As shown in Scheme 1, the dehydrogenation of methanol/water mixtures in the presence of a suitable homogeneous or heterogeneous catalyst evolves three molecules of hydrogen and one molecule of carbon dioxide (aqueous phase methanol reforming).[9] Noteworthy, in this process the dehydrogenation of formic acid is also involved as one of the reaction steps.



Scheme 1. General pathway for aqueous MeOH dehydrogenation (blue) and CO_2 hydrogenation to methanol (red).

In addition to high activity and stability, the selective generation of hydrogen without forming carbon monoxide is crucial for fuel cell applications.[10] In this respect, the low temperature methanol dehydrogenation processes which can be achieved with homogeneous catalysts are interesting. Already in 1985, Saito's group published the first example of a homogenously catalyzed dehydrogenation of aqueous methanol, albeit with a low turnover number (TON = 34).[11] More recently, significantly more efficient molecularly-defined complexes were disclosed for selective dehydrogenation of aqueous methanol at low temperatures and ambient pressure (Figure 1).

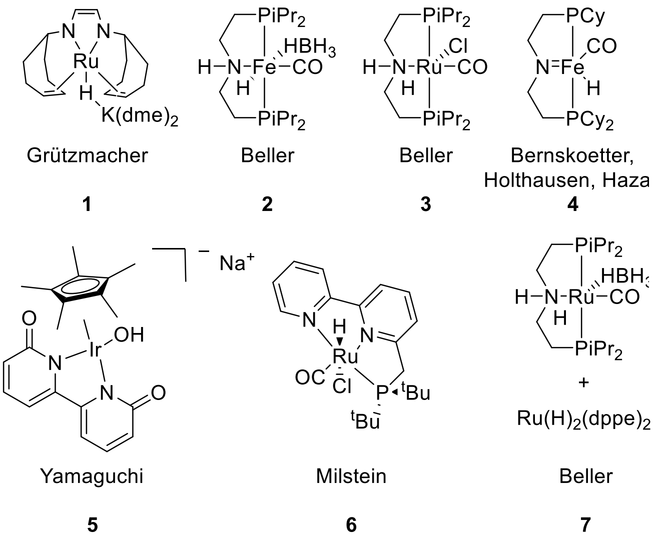


Figure 1. Recently reported homogeneous catalysts for MeOH dehydrogenation.

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In 2013, our group reported the ruthenium based complex $[Ru(H)(Cl)(CO)(HN(CH_2CH_2P(\textit{i}Pr)_2)_2)]$ (**3**) as a highly productive catalyst reaching TON >350,000.[12] At the same time Grützmacher and co-workers showed the dehydrogenation of methanol by utilizing $[K(dme)_2][RuH(trop_2dad)]$ (**1**) without any additives in THF (TON = 540).[13] Later on, the first homogeneous bi-metallic system based on $[Ru(H)(BH_4)(CO)(HN(CH_2CH_2P(\textit{i}Pr)_2)_2)]$ and $[Ru(H)_2(dppe)_2]$ (**7**) was reported under base-free conditions (TON = 4,286).[14] Furthermore, Milstein and co-workers applied $[Ru(H)(Cl)(CO)(NNP^{tBu})]$ (**6**) as catalyst for this reaction and obtained a high TON (28,661) under optimized conditions.[15] Although several iridium catalysts are known for alcohol[16] and formic acid [17] dehydrogenation, interestingly only complex **5** has been described by Yamaguchi and co-workers to catalyze the dehydrogenation of aqueous methanol (TON >10,000).[18]

Apart from all these precious metal-based catalysts, only few iron pincer complexes were successfully applied for aqueous phase reforming (APR) of methanol. For example, complex **2** ($[Fe(H)(BH_4)(CO)(HN(CH_2CH_2P(\textit{i}Pr)_2)_2)]$) gave a TON of around 10,000 under strong basic conditions,[19] while Bernskoetter, Hazari and Holthausen showed that the related complex **4** reached up to 50,000 turnovers in combination with a Lewis acid as co-catalyst.[20] Most of these examples show the general viability of different pincer complexes for the dehydrogenation of methanol. However, so far all catalysts with PNP pincer ligands[21] need large amounts of additives like strong bases[12b] or Lewis acids[20a] to achieve high activity and productivity. Hence, there is a continuing interest to perform methanol dehydrogenation reactions under milder conditions.

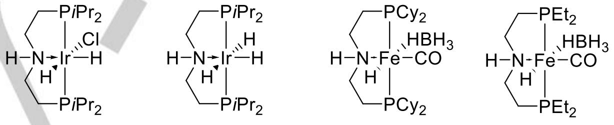
In this respect, hereby we describe for the first time the successful application of Ir PNP pincer complexes in the APR of methanol at low base concentration and the elucidation of catalyst deactivation pathways.

At the start of this project different ruthenium, iron and iridium PNP pincer complexes were compared under previously optimized reaction conditions (4.2 µmol catalyst, 10 mL methanol/water (9:1), 8.0 M KOH at reflux, 91°C). The highest activity was observed when using ruthenium complex **3** (TOF_{1h} = 2276; Table 1, entry 3), followed by the iron complexes **2** (TOF_{1h} = 702; Table 1, entry 2) and **10** (TOF_{1h} = 429; Table 1, entry 6). Surprisingly, the related iron complex **11**, which gave improved performance in hydrogenation reactions [22] exhibited no activity at all. As shown in Table 1, under these conditions (high base concentration) both iridium complexes **8** and **9** ($[Ir(H)_2(Cl)(HN(CH_2CH_2P(\textit{i}Pr)_2)_2)]$ and $[Ir(H)_3(HN(CH_2CH_2P(\textit{i}Pr)_2)_2)]$) were considerably less active compared to the related ruthenium and iron pincer complexes (Table 1, entries 1-7), although **8** had been succesfully already applied in various (de)hydrogenation reactions.[23]

Next, three of these complexes were tested using a 0.5M KOH aqueous methanol solution. Unfortunately, previously identified state-of-the-art catalysts proved to be much less active in this case (Table 1, entries 8-9). To our surprise, the $[Ir(H)_2(Cl)(HN(CH_2CH_2P(\textit{i}Pr)_2)_2)]$ complex **8** was the most active system (TOF_{1h} = 326; Table 1, entry 10). While the activity of the Ru complex **3** dropped by a factor of 50 (Table 1; entries 3, 9) and that of the iron complex **2** by a factor of 70 (Table 1; entries 2, 8), the iridium complex **8** showed a more than threefold increase of activity (Table 1; entries 4, 10). Clearly, this indicates that the related catalysts, Ru and Fe on one side and the Ir one on the other, operate according to different mechanisms, or the rate-determining step under identical reaction conditions is different.

To understand the effect of base in more detail, we performed reactions at different base concentrations in the presence of complex **8**. All reactions were carried out at the reflux temperature allowed by the reaction solution composition. Interestingly, decreasing the amount of base from 2M to 0.1M gradually increased the catalyst activity from TOF_{1h} = 134 to 525, respectively (Table 2, entries 3-6). At lower base loading (8.4 µmol KOH; 2 eq. with respect to Ir) a major loss of activity (TOF_{1h} of 47) was observed. No gas evolution occurred in the absence of base regardless of the catalyst either the Cl-containing complex **8** (Table 2, entry 1) or its trihydride analogue **9** [23a]. Also no hydrogen was detected using complex **8** with 8M KOH at a temperature of 70 °C (Table 2, entry 8).

When different metal hydroxides were tested, 0.5 M KOH led to better results (TOF_{1h} = 326; Table 2, entry 4) than NaOH (TOF_{1h} = 189; Table 2, entry 9) and LiOH (TOF_{1h} = 127; Table 2, entry 10). Aqueous methanol reforming has been shown to be favoured also by a Lewis acid co-catalysts.[20a] However in the presence of $LiBF_4$ (Table 2, entry 11) we did not observe any activity.



8 **9** **10** **11**

Table 1. Different catalysts tested for methanol dehydrogenation.

Entry	Catalyst	Base [molL^{-1}]	T [°C][a]	TOF_{1h} [h^{-1}]	TOF_{3h} [h^{-1}]
1	**1**	KOH 8.0	91	205	107
2	**2**	KOH 8.0	91	702	510
3	**3**	KOH 8.0	91	2276	2205
4	**8**	KOH 8.0	91	97	57
5	**9**	KOH 8.0	91	95	54
6	**10**	KOH 8.0	91	429	302
7	**11**	KOH 8.0	91	-	-
8	**2**	KOH 0.5	70	10	8.3
9	**3**	KOH 0.5	70	45	48
10	**8**	KOH 0.5	70	326	268

Reaction conditions: 10 mL of a 9:1 v:v mixture of MeOH and water, 4.18 µmol of catalyst, T_{set} at 94°C (reflux), evolved gas analysed by gas-phase GC, each molecule of H_2 counted as one turnover, [a] inner temperature, reproduction differed less than 15%.

Next, the influence of water amount relative to methanol on the activity of **8** was investigated. using neat methanol and mixtures of methanol and water of 9:1, 8:2 and 5:5 (v:v) (Table 2, entries 4, 12 and 13). Contrary to the behaviour observed for previously reported ruthenium- and iron-based systems,[12,19] we observed an increase of activity from using neat methanol (Table 2, entry 14, TOF = 223) to methanol/water (9:1) (Table 2, entry 4, TOF = 326). However, increasing the water amount

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Table 2. Ir-catalyzed APR of methanol: Influence of additives.

Entry	Catalyst	Base [molL^{-1}]	T [°C][a]	TOF$_{1h}$ [h^{-1}]	TOF$_{3h}$ [h^{-1}]
1	**8**	-	65	-	-
2	**8**	8.36 x10^{-6}	65	47	deactivated
3	**8**	KOH 0.1	69	525	220
4	**8**	KOH 0.5	70	326	268
5	**8**	KOH 1.0	71	183	160
6	**8**	KOH 2.0	73	134	96
7	**8**	KOH 8.0	91	97	57
8	**8**	KOH 8.0	70	-	-
9	**8**	NaOH 0.5	70	189	114
10	**8**	LiOH 0.5	70	127	197
11	**8**	$LiBF_4$ 0.5	70	-	-
12[b]	**8**	KOH 0.5	70	261	197
13[c]	**8**	KOH 0.5	70	135	87
14[d]	**8**	KOH 0.5	70	223	187
15[e]	**8**	KOH 0.5	70	282	232
16[f]	**8**	KOH 0.5	70	243	148

Reaction conditions: 10 mL of a 9:1 v:v mixture of MeOH and water, 4.18 µmol of catalyst, T$_{set}$ at 94°C (reflux), evolved gas analysed by gas-phase GC, each molecule of H_2 counted as one turnover, [a] internal temperature, [b] v:v (MeOH:H_2O) 4:1, [c] v:v(MeOH:H_2O) 5:5, [d] neat MeOH, [e] 44.4 mmol K_2CO_3 added, [f] 44.4 mmol HCOOK added, reproduction differed less than 15%.

further on, v:v MeOH:H_2O 4:1 (Table 2, entry 12) and MeOH:H_2O 5:5 (Table 2, entry 13), the TOF$_{1h}$ dropped from 326 to 261 and 135, respectively.

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

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

Scheme 2. Reaction equations in presence and absence of hydroxide.

We explain this behaviour by the need of a minimal amount of water or hydroxide necessary to achieve APR of methanol (Scheme 2, equations 1 and 2). As shown in Scheme 1, the presence of water or hydroxides is essential for the conversion of formaldehyde and thus for the formation of formic acid/formate.

Investigations for long term stability of the catalyst system demonstrated that the base concentration has a dramatic influence not only on activity but also on stability. For example, in the reaction with 0.5 M KOH gas evolution ceased after 16 hours to give a TON of 1,400 and the final expected product gas ratio of 3:1 (H_2:CO_2) (Figure 2). In contrast, in the presence of 8.0 M KOH the system was more stable (60 h) and a TON of 1,900 was achieved (SI2, Figure SI2b). Within this time only little drop in activity was observed. Due to the higher base amount the CO_2 was mainly trapped as carbonate and only traces of CO_2 were detected in the gas phase. The addition of 44.4 mmol potassium carbonate (20 % with respect to methanol, 10,000 equivalents with respect to Ir) as a potential catalyst poison showed no significant decrease of activity (TOF$_{1h}$ = 282; Table 2, entry 15). Interestingly, by addition of 44.4 mmol potassium formate as simulation of accumulation during reaction, a lower activity was achieved (TOF$_{1h}$ = 243, TOF$_{3h}$ = 148; Table 2, entry 16) showing that in this case, a high amount of formate could negatively influence activity. In order to investigate the peculiar role of the formate in more detail, complex [Ir(H)$_2$(OOCH)(HN(CH$_2$CH$_2$P(*i*Pr)$_2$)$_2$)], which constitutes a possible catalytic intermediate, was synthesized and tested for its activity.[24] With this complex an almost similar activity (4.2 µmol cat, 10 ml MeOH/H_2O, 0.5 M KOH, T$_{set}$: 94 °C, TOF$_{1h}$ = 278, TOF$_{3h}$ = 229) compared to complex **8** (Table 2, Entry 4) under these conditions was obtained, demonstrating clearly that the dehydrogenation of formate took place in the reaction.

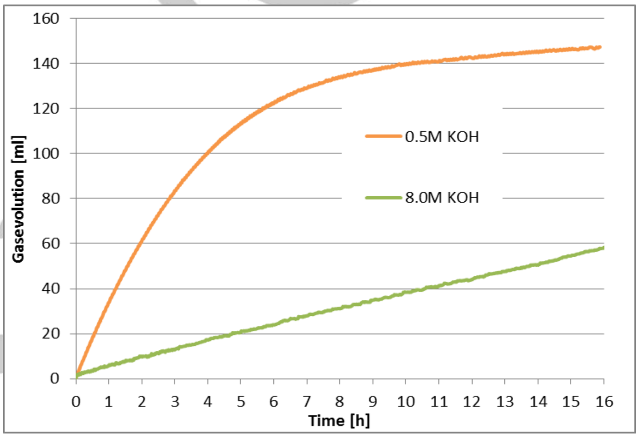


Figure 2. Influence of base on stability: reaction conditions: 10 mL of a 9:1 v:v mixture of MeOH and water, 4.18 µmol of catalyst **8**, T$_{set}$ at 94°C (reflux).

To investigate the reactions with high and low base content in more detail, we performed NMR experiments in order to follow the formation of key species during the reaction. More specifically, we executed two reactions each using 100 mg of **8** (186.9 µmol) in 10 mL of 9:1 methanol/water mixture at reflux, one containing 0.5 M KOH, the other 8.0 M KOH. During the course of the reactions, samples were taken at defined times and NMR spectra recorded at room temperature (SI 3). As shown in Figure 3, in the presence of KOH 0.5 M the applied precursor [Ir(H)$_2$(Cl)(HN(CH$_2$CH$_2$P(*i*Pr)$_2$)$_2$)] (**8**) is immediately converted to the trihydride complex **9** even in low basic environment at room temperature. This transformation can be observed in the hydride region of the ^{1}H and ^{31}P NMR spectra as the signal(s) of the original complex **8** (^{31}P: δ = 51.90 ppm, ^{1}H: δ = -26.42 ppm, δ = -20.50 ppm) disappear and a new set of signals in both the ^{1}H and ^{31}P spectrum emerge that fits the reference spectra of complex **9** (^{31}P: δ = 56.28 ppm, ^{1}H: δ = -12.27 ppm, δ = -12.66 ppm, δ = -22.83 ppm) (Figure 3 and SI, Figures SI3_1, SI3_2, SI3_4).

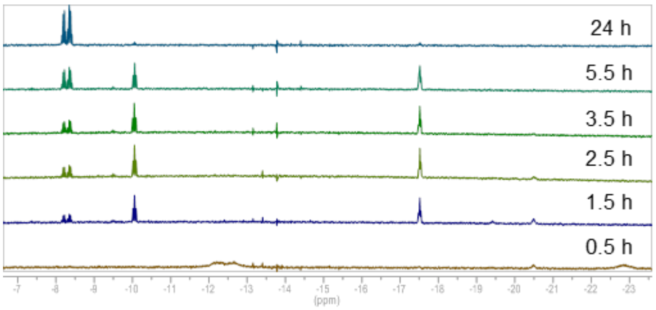
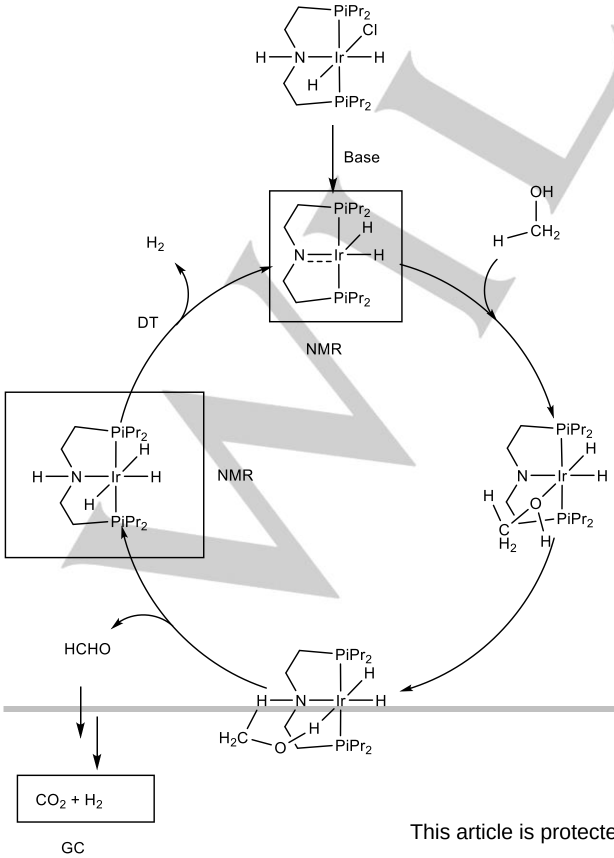


Figure 3. Stacked ^1H NMR spectra (hydride region) of reaction mixture, recorded during after defined times; reaction conditions: 9 mL MeOH, 1 mL water, 0.5 M KOH, 100 mg cat. **8**, T_{set} 94 °C.

Notably, this trihydride species is the main species in the strong basic medium (8.0 M KOH, SI3, Figure SI_4) and the gas evolution rate stayed constant for 24 h (SI3, Figure SI3_6). After that time, new sets of signals appeared corresponding to three species, based on ^{31}P NMR. One set showed two *trans*-hydride signals, both quartets at δ = -8.21 ppm and δ = -8.36 ppm in ^1H NMR (J_{HH}=13.17) and a related singlet at δ = 70.44 ppm in the ^{31}P NMR. The other set of signals represents two hydrides standing *cis* to each other as triplets at δ = -10.06 ppm and δ = -17.55 ppm in the ^1H NMR (J_{HH}=3.13) and an associated singlet at δ = 52.04 ppm in the ^{31}P NMR spectrum are observed. The stability of **9** at high base loadings (Table 1, entry 4) supports the assumption that **9** is indeed an active dehydrogenation catalyst which was also proposed by Abdur-Rashid and co-workers for transferhydrogenation reactions.[23a]

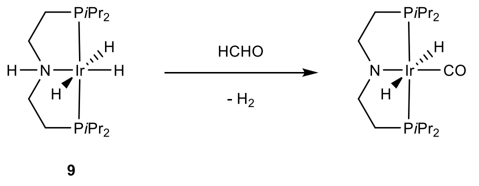
The two dihydride complexes described above were also observed during the reaction in lower basic medium (0.5 M, SI, Figures SI3_1, SI3_2). Here, they became the main species already after 1.5 hours of reaction time. Furthermore, the signals belonging to **9** disappeared even before this. However with respect to the higher activity (Table 1, entry 10), this observation indicates the formation of a more powerful catalyst for the dehydrogenation of methanol in this case. The appearance of new Ir species during the NMR experiments correlated with the observed change in activity (SI, Figure SI3_3). As the *cis*-hydride species disappeared again, the *trans*-hydride species accumulated with ongoing reaction time and stayed present after gas evolution stopped. Hence, this latter complex seems to be a deactivated species. To identify the suggested intermediates of the catalytic cycle, several stoichiometric experiments were performed. By stepwise addition of 1, 2, 5, 10 and 50 equivalents of methanol to the trihydride complex **9** we expected the formation of an iridium methoxy species, which is known to be formed in case of related ruthenium pincer complexes.[12b]



Scheme 3. Proposed reaction mechanism for Ir-catalyzed dehydrogenation of methanol.

However, in contrast to previous works with ruthenium complexes,[12b] no new species arises in the ^1H NMR spectra (SI4). Even treating the amido complex $[Ir(H)_2(N(CH_2CH_2P(iPr)_2)_2)]$ with methanol, no iridium methoxy species, but instead the trihydride complex **9** is formed (SI5).[25] These observations indicate the amido complex to be an important intermediate in the methanol dehydrogenation step to formaldehyde. Based on the combined results of stoichiometric and catalytic NMR experiments, we propose the reaction mechanism shown in Scheme 3.

As mentioned above, catalyst deactivation in our system took place accompanied by the formation of three new species observed in the ^{31}P NMR. On the one hand, one species, not correlating to any hydride signal in the ^1H-^{31}P HMQC NMR (SI 5, Figure SI5_3; ^{31}P NMR: δ= 80.94 ppm, SI6), was identified as $[Ir(CO)(N(CH_2CH_2P(iPr)_2)_2)]$. It could be independently synthetized by reaction of the amido complex $[Ir(H)_2(N(CH_2CH_2P(iPr)_2)_2)]$ with CO (SI 6) and its NMR data compared with the published ones.[26] When this species was used as catalyst precursor in methanol aqueous dehydrogenation no activity was observed. On the other hand, a new iridium dihydride complex was also formed. Although it was not possible to identify this iridium complex clearly by NMR spectroscopy (*trans* dihydride signals in ^1H NMR: δ = -8.21 ppm, δ = -8.36 ppm, SI3) because of overlapping and superimposed signals, based on MS ($(M+H)^+$ = 528.21314, SI, Figure SI5_2) and IR spectroscopy (carbonyl group, SI, Figure SI5_1) we propose the formation of an iridium dihydride carbonyl complex as deactivated species (Scheme 4).



Scheme 4. Proposed deactivation side reaction.

This suggestion of a *trans*-dihydride carbonyl pincer complex formed with formaldehyde as CO source is also supported by reports of Goldberg and co-workers [27] as well as Fryzuk and co-workers.[28, 29] Apparently, this deactivation occurs preferentially in low basic media as it does not impact the reaction under strongly basic conditions. This also explains the impact of the base amount on catalyst activity and stability in the methanol dehydrogenation process.

Conclusions

We developed an iridium-catalyzed dehydrogenation of aqueous methanol under mild conditions. Contrary to most known organometallic catalysts for this transformation no strong basic conditions are necessary for sufficient catalytic activity.

General procedure

All reactions were performed under argon with exclusion of air. A solution of 10 ml MeOH and H_2O in a given ratio, containing a defined amount of base, was heated to the desired temperature and let equilibrate for 30 minutes. The catalyst (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. The identity of the gas components and their ratio was determined by gas-phase chromatography. Plots of volume amount of gas evolved as a function of time for experiments reported in Tables can be found in the supporting information.

Acknowledgements

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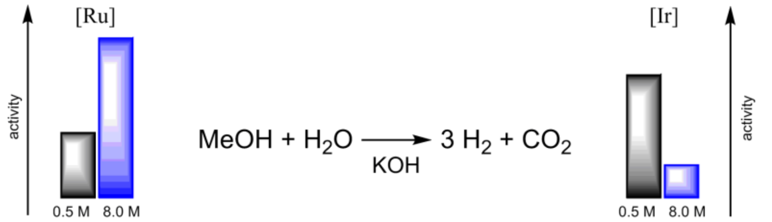
[29] Attempts to prepare *trans*-[Ir(H)$_2$(CO)(N(CH$_2$CH$_2$P(iPr)$_2$)$_2$)] by reaction of the amido complex with paraformaldehyde afforded instead a mixture of the desired product, [Ir(CO)(N(CH$_2$CH$_2$P(iPr)$_2$)$_2$)] and a third species whose signals are consistent with the same *cis*-hydride species observed under the reaction conditions of aqueous methanol dehydrogenation. This prevented its isolation.

COMMUNICATION



A catalytic system based on an iridium-PNP complex was developed for the aqueous phase reforming of methanol. Investigations revealed higher activity at low base concentration and higher stability at higher base concentration as an opposing trend compared to known Ru and Fe PNP pincer containing systems for methanol dehydrogenation.

*Christoph Prichatz, Elisabetta Alberico, Wolfgang Baumann, Henrik Junge and Matthias Beller**

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Iridium-PNP Pincer Complexes for Methanol Dehydrogenation At Low Base Concentration