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Hydrogen Generation

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ortho-Metalation of Iron(0) Tribenzylphosphine Complexes: Homogeneous Catalysts for the Generation of Hydrogen from Formic Acid**

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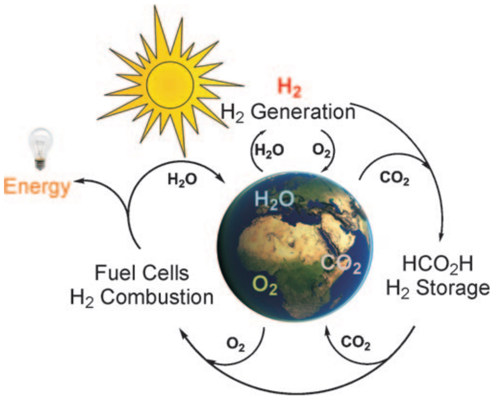
As a result of the ever-increasing global demand for energy, the establishment of alternative resources and more sustainable technologies constitutes a major challenge for science and engineering in the coming decades. Given the limited fossil fuels there is a move towards renewable resources like biomass, wind, hydroelectric and geothermal energy, as well as sunlight as an almost unlimited energy source. In addition, new efficient routes for energy storage have to be established. Among the currently discussed chemical energy carriers, hydrogen in combination with fuel cell technology is generally accepted as a clean technology and has gained remarkable attention in the last decades.[1] Despite research in the field of hydrogen storage, no general process exists that meets all the industrial requirements. Hydrogen storage at ambient temperature and pressure in systems having high power to weight and volume ratios needs to be improved.[2]

In addition to methanol, formic acid is a potential liquid hydrogen-storage media, and in recent years several research groups have developed more and better catalysts for the release of hydrogen from formic acid. The hydrogen content of HCO_2H (4.4 wt % of hydrogen; 5.22 $MJ\,kg^{-1}$) is lower than that of MeOH; however, it has an energy content that is at least five times higher than that of commercially available lithium ion batteries. Advantageously, formic acid is a liquid, it is nontoxic, and most importantly, the reversible hydrogen storage can be achieved under ambient conditions in the presence of suitable catalysts.[3] If hydrogen is produced, for example, by photocatalytic water splitting, and using carbon dioxide (CO_2) as a feedstock, then formic acid can be regarded as a sustainable hydrogen-storage material. Overall, the ideal sustainable hydrogen generation, storage, and utilization cycle is depicted in Scheme 1.

Although several efficient homogeneous[4,5] and heterogeneous[4a,6] catalyst systems for the selective generation of hydrogen from formic acid or formate have been developed, very few efforts have been made in the field of non-noble-metal-catalyzed formic acid decomposition. This is in contrast to the increasing interest in bioinspired homogeneous metal catalysis, e.g. with iron.[7] In 2010, we reported the first homogeneous iron catalyst system capable of generating hydrogen from formic acid under near ambient conditions.[8] By applying an in situ catalyst system formed from $[Fe_3(CO)_{12}]$, 2,2′:6′2″-terpyridine (tpy), and triphenylphosphine (PPh_3), hydrogen generation is possible under irradiation using visible light and ambient temperature. In addition monomeric iron(0)/phosphine complexes were detected as the key intermediates. Under optimized conditions turnover numbers (TONs) of up to 126 were observed, which constitutes the highest activity known to date for nonprecious-metal-catalyzed hydrogen generation from formic acid.

Herein, we present a novel, improved iron phosphine catalyst system, which showed a one order of magnitude improvement in catalyst activity over the iron/triphenylphosphine system. The key to the success of the new system is the use of benzylphosphine as a ligand, which undergoes a remarkable *ortho*-metalation reaction upon irradiation with visible light. Light has an impact on the generation of the



Scheme 1. Cycle for sustainable hydrogen generation, storage, and utilization.

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active complex and hydrogen. This unusual activation process involving *ortho*-metalation was studied in detail by using NMR spectroscopy and DFT calculations.

In our ongoing search for active iron catalysts for the generation of hydrogen from formic acid, we investigated several phosphine ligands in the presence of iron carbonyl complexes. Among the ligands studied, only those bearing benzyl groups showed improved activity compared to our previous triphenylphosphine-based catalyst. Selected results from this screening of ligands for hydrogen generation are shown in Table 1. In standard experiments the catalyst was formed in situ from 10 µmol $[Fe_3(CO)_{12}]$, 1.0 equivalent 2,2′:6′2′′-terpyridine (tpy), and 1.0 equivalent phosphine in *N,N′*-dimethylformamide (DMF) under xenon-light irradiation at 60 °C. Both light and base are necessary for the reaction to occur. The evolved gases were collected by automatic gas burettes and then analyzed by gas chromatography methods. In addition to traces of solvents and a 1:1 mixture of H_2 to CO_2, CO was detected (0.2–2 vol %). To calculate the TONs (TON = H_2/Fe or CO_2/Fe) the total amount of evolved gas was corrected by taking the CO content into account.

Table 1: Investigation of different benzyl phosphine ligands in the iron-catalyzed generation of hydrogen from HCO_2H.

Entry[a]	Iron source	Ligand	*V* [mL][b]	TON[b]
1	$[Fe_3(CO)_{12}]$	PBn_3	203 (1033)	138 (702)
2	$[Fe_3(CO)_{12}]$	PPh_2Bn	132 (344)	90 (234)
3	$[Fe_3(CO)_{12}]$	PPh_3	96 (153)	65 (104)
4	$[Fe_3(CO)_{12}]$	$P(CH_2CH_2Ph)_3$	31 (272)	21 (185)
5[c,d]	**1a**	–	57	77
6[c,d]	**1**	–	125	170
7[c]	**1**	-	182 (573)	247 (778)
8[c]	$[Fe_3(CO)_{12}]$	PBn_3[e]	162 (486)	220 (660)

[a] Reaction conditions: 10 µmol $[Fe_3(CO)_{12}]$ (30 µmol Fe), 1.0 equiv phosphine, 1.0 equiv tpy, 5 mL preformed NEt_3/HCO_2H (2:5) mixture, 1.0 mL DMF, 60 °C, 3 or 15 h, 300 W Xe-light irradiation, no filter; H_2/CO_2 gas mixture is 1:1; gas volumes detected using an automatic gas burette; qualitative gas analysis using GC methods. [b] Values recorded after 3 h; values in parentheses are those recorded after 15 h. [c] Used 15 µmol [Fe]. [d] Without tpy. [e] Used 2.0 equiv phosphine.

Compared to triphenylphosphine, tribenzylphosphine and benzyldiphenylphosphine showed significantly improved activity as well as stability (Table 1, entries 1–3). The system using PPh_3 is deactivated after 3 hours, and the turnover number is 65 (Table 1, entry 3). However, the use tribenzylphosphine gave a TON of 138 after 3 hours, and more importantly remained stable for up to 15 hours (TON of 702; Table 1, entry 1). Notably, this effect is limited to benzyl-substituted phosphines; that is, the more benzyl moieties present in the ligand, the higher the activity and stability of the system (Table 1, entries 1 and 2).

The introduction of an ethyl bridge into the ligand resulted in neither a stable system nor increased activity relative to that of PPh_3 (Table 1, entry 4); thus, it is unlikely that steric effects of the ligands account for the increase in activity. Notably, both light as well as base are essential for catalysis. Next, the model compunds $[Fe(CO)_3(PBn_3)_2]$ (**1**) and $[Fe(CO)_3(PPh_2Bn)_2]$ (**1a**) were synthesized and fully characterized (see Figure 1 and the Supporting Information). Both structures contain a pentacoordinated trigonal-bipyramidal iron(0) center surrounded by two axial phosphine ligands and three equatorial CO molecules. The P-Fe-P angles are 178.6° (**1a**) and 178.9° (**1**), and the average P-Fe-CO angles are close to 90° (90.02° for **1a** and 89.98 for **1**). All bond lengths are within the range of those for similar complexes of the type $[(CO)_3Fe(PR_3)_2]$.[9]

By using both **1** and **1a**, active systems were obtained in the absence of terpyridine (tpy), but the resulting catalyst system was not stable over a long time period (Table 1, entries 5 and 6). However, in the presence of tpy, a stable system is obtained which shows comparable activity to that of the in situ formed catalyst (Table 1, entries 7 and 8; Figure 2).

As shown in entries 1 and 2 in Table 2, the catalyst activity can be additionally improved by increasing the amine concentration. This observation is in agreement with results obtained for ruthenium complexes, wherein the nature of base influences the catalyst activity.[4c] By applying 1,3-

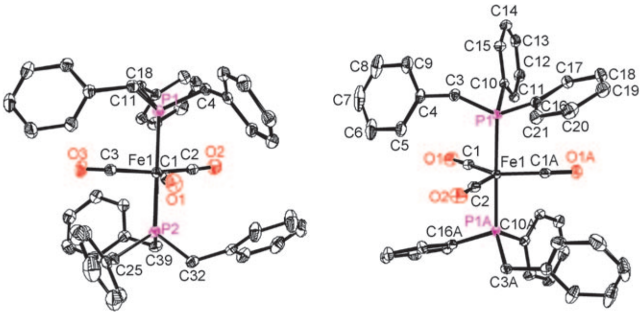

Figure 1. Molecular structure of compound **1** (left) and **1a** (right) in the crystal. The thermal ellipsoids are drawn at 30% probability, and the hydrogen atoms are omitted for clarity.[15]

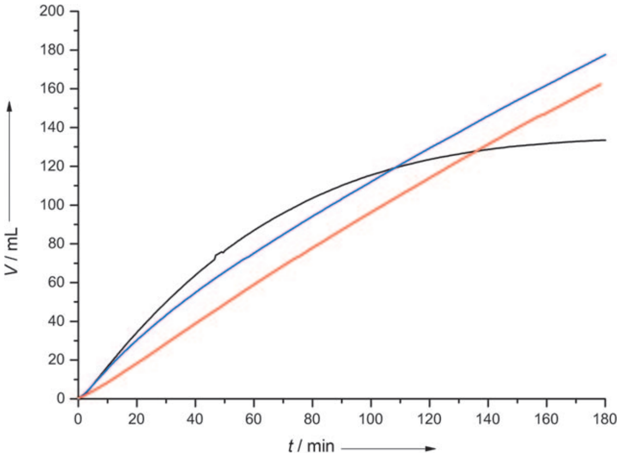

Figure 2. Comparison of gas-evolution experiments with the catalyst **1** (black line) with those of the in situ systems (**1** with 1.0 equiv tpy: blue line; $[Fe_3(CO)_{12}]$, 2 equiv PBn_3, 1.0 equiv tpy: red line). Reaction conditions: 5.0 µmol $[Fe_3(CO)_{12}]$ (15.0 µmol Fe), 5 mL preformed NEt_3/HCOOH (2:5) mixture, 1.0 mL DMF, 60 °C, 3 h, 300 W Xe-light irradiation, no filter. Gas mixture: H_2/CO_2 = 1:1.

Table 2: Influence of base upon the catalyst activity.

Entry[a]	Base	V [mL][b]	TON[b]
1	NEt_3	203 (1033)	138 (702)
2[c]	NEt_3	430 (872)	292 (592)
3	DBU	390 (954)	265 (648)
4	$HexNMe_2$	58	39

[a] Reaction conditions: 10 μmol $[Fe_3(CO)_{12}]$ (30 μmol Fe), 1.0 equiv PBn_3, 1.0 equiv tpy, 5 mL preformed base/HCO_2H (2:5) mixture, 1.0 mL DMF, 60 °C, 3 or 15 h, 300 W Xe-light irradiation, no filter; H_2/CO_2 gas mixture is 1:1; gas volumes detected using an automatic gas burette; qualitative gas analysis using GC methods. [b] Values recorded after 3 h; values in parentheses are those recorded after 15 h. [c] Used NEt_3/HCO_2H (3:4) mixture.

diaza[5.4.0]bicycloundecene (DBU), an increased activity is observed in the first 6 hours of reaction (Table 2, entries 1 and 3); however, under these conditions the catalyst is fully deactivated after 15 hours. *N*,*N*-Dimethyl-*n*-hexylamine ($HexNMe_2$) resulted in only low activity (Table 2, entry 4).

Finally, a solution of HCO_2H/NEt_3 (5:1; 10 mL) was subjected to 20 μmol $[Fe_3(CO)_{12}]$, 1 equivalent PBn_3, and 1 equivalent tpy, and a TON of 1266 (3728 mL gas) was obtained after 51 hours. This represents the highest productivity for any non-noble-metal-catalyzed hydrogen production from formic acid and is one order of magnitude higher than all previously reported catalysts.

After testing the different ligands, there was no clear trends resulting from either electronic or steric parameters. Apparently, the significant difference in activity and stability is not caused by these factors. Unlike PPh_3, PBn_3 can potentially undergo *ortho*-metalation to form a five-membered metallacycle, which could account for the increased stability and activity. To the best of our knowledge *ortho*-metalation of iron(0)/phosphine complexes is only known with 1,2-bis(diphenylphosphine)ethane (dppe) as the ligand.[10] Four-membered metallacycles can be formed thermally and photochemically when either $[Fe(dppe)_2(C_2H_4)]$ or $[Fe(dppe)_2H_2]$ are used as precursors.[11] Such structures can be effectively used for the activation of C(sp)−H bonds.[11a] In the case of PBn_3 *ortho*-metalation could lead to an even more stable five-membered metallacycle, and to substantiate this proposal, we carried out NMR experiments as well as theoretical calculations.[12]

To undergo *ortho*-metalation, a free coordination site at the iron center is needed. The dissociation of either CO or a PBn_3 ligand from the $[Fe(CO)_3(PBn_3)_2]$ complex (**1**) under irradiation leads to the unsaturated complexes **5** and **2**, respectively. In Figure 3 it is shown that the dissociation of CO costs about 10 $kcal\,mol^{-1}$ more in energy than that of PBn_3. However, in both cases the *ortho*-metalated species **4** and **7** are about 10 $kcal\,mol^{-1}$ lower in energy. There are also intermediate states **3** and **6** wherein the hydrogen atom is located between the Fe and the ligand. For species **7** we can predict a coupling constant between the hydrogen atom and both phosphorus nuclei of about 45.9 Hz, as well as a downfield shift of approximately 8 ppm in the ^{13}C NMR spectrum for the C atom beside the carbometalated center of the phenyl ring for **4** and **7**.

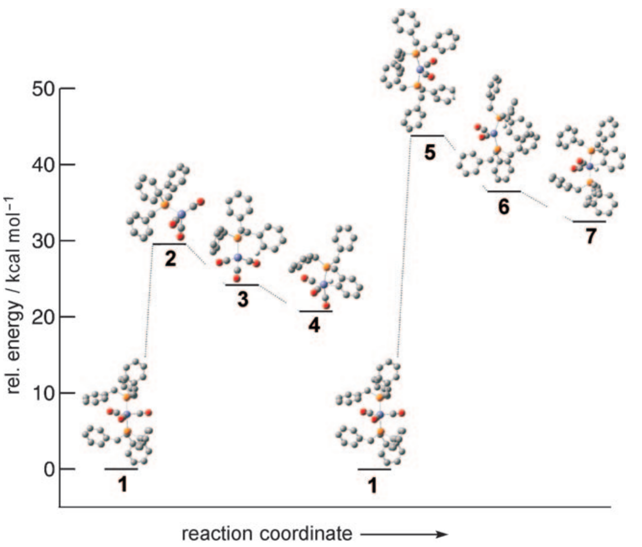

Figure 3. Relative energy for the conversion of $[Fe(CO)_3(PBn_3)_2]$ (**1**) into the metalated species $[HFe(C_6H_4CH_2PBn_2)(CO)_3]$ (**4**) and $[HFe(C_6H_4CH_2PBn_2)(PBn_3)(CO)_2]$ (**7**) via the intermediates $[Fe(PBn_3)_2(CO)_2]$ (**5**) or $[Fe(PBn_3)(CO)_3]$ (**2**).[13,14]

NMR measurements strongly support the formation of metalated species during irradiation of **1** in $[D_7]$DMF. Whereas thermal treatment of **1** at 100 °C did not induce any change in the ^1H, ^{13}C, and ^{31}P NMR spectra, significant changes are obtained under light irradiation with Xe light, thus supporting our hypothesis of metalation: a) Light induces a dissociation of the PBn_3 ligand (observed at $\delta(^{31}P) = -9.3$ ppm in $[D_7]$DMF) or CO leading formally to the fragments $[(CO)_3Fe(PBn_3)]$ (**2**) and $[(CO)_2Fe(PBn_3)_2]$ (**5**). For both fragments *ortho*-metalation of the ligands are energetically favored (Figure 3); b) hydride formation takes place exclusively during irradiation of **1** in $[D_7]$DMF, showing clearly that hydrogen transfer from the ligand to the iron center takes place; c) through ^1H–^{31}P HMQC spectroscopy it was shown that the hydride belongs to the coordinated phosphine;[12] d) the observed H–P coupling constant, $J_{H,P} = 58$ Hz, of the hydride is in acceptable agreement with the calculated H–P coupling constants for **7** ($J_{H,P} = 45.9$ Hz); e) the same hydride signal is observed during the catalytic reactions with formic acid, making it likely that this species plays a key role in the catalytic cycle; f) in the ^{13}CNMR spectrum new signals appear at $\delta = 138$ ppm (shifted downfield by approximately 8 ppm), which is in good agreement with the calculated downfield shifts for carbon atoms that are α to the carbometalated center.[12]

In conclusion, we have developed a new state-of-the-art catalyst system for non-noble-metal-catalyzed decomposition of formic acid into hydrogen and carbon dioxide. The complexes $[Fe(CO)_3(PBn_3)_2]$ (**1**) and $[Fe(CO)_3(PPh_2Bn)_2]$ (**1a**) were synthesized and fully characterized by single-crystal X-ray diffraction. Mechanistic investigations by DFT and NMR spectroscopy indicate the formation of *ortho*-metalated iron species from $Fe(PBn_3)$ fragments, which can account for the higher activity and stability in the presence of PBn_3 compared to PPh_3.

Experimental Section

The reactions were performed in a double-walled thermostatically controlled reaction vessel, which was evacuated and purged with argon six times to remove any other gases. The ligands (1.0 equiv) were added either as powders in a Teflon crucible plus 1 mL of solvent (DMF) or from a freshly prepared stock solution (1 mL DMF). The 5:2 HCO_2H/NEt_3 mixture (5 mL) was then placed in the vessel and the desired temperature was kept constant. The solutions were irradiated with xenon light (300 W) and stirred for at least 20 min until equilibration was attained. The reactions were started by adding the iron complexes (typically 10.0 µmol $[Fe_3(CO)_{12}]$) as solids in Teflon crucibles. The volume of evolved gases was quantitatively measured using automatic gas burettes. In addition, the gases were qualitatively determined by using GC analysis (gas chromatograph HP6890N, carboxen 1000, TCD, external calibration, helium carrier gas). The gas evolution was reproducible to within 1–10%.

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[15] CCDC 784439 (**1**) and CCDC 784440 (**1a**) contain 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.