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Fast and selective homogeneous hydrogenation with nickel(II) phosphane catalysts

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Nickel(II) phosphane complexes are able to hydrogenate oct-1-ene to *n*-octane with high turnover numbers and high selectivities at low temperature and moderate pressure.

From recent research it is known that the active site of the enzyme hydrogenase contains nickel.[1] This enzyme, present in some bacteria, activates molecular hydrogen at atmospheric pressure and room temperature. However, although nickel is widely used as a heterogeneous catalyst for hydrogenation reactions (Raney nickel), homogeneous hydrogenation catalysts containing nickel are scarcely found in the literature.[2] Yet, homogeneous nickel catalysts are known for related reactions like isomerisation, oligomerisation, polymerisation, hydrosilylation and hydrocyanation.[3]

Herein we report on a novel *homogeneous in situ* nickel catalyst for the hydrogenation of linear olefins. In this research nickel(II) acetate in combination with several diphosphane ligands was tested on catalytic activity in the hydrogenation of oct-1-ene (Scheme 1).

In our search for homogeneous nickel hydrogenation catalysts, initially nickel(II) salts in the absence of any ligands were tested. Nickel(II) acetate, without addition of ligand, showed some hydrogenation activity at a reaction temperature of 373 K. It has been reported that nickel(II) acetate in methanol in reductive reaction conditions at elevated temperatures may form colloidal nickel,[4] which is an active, but heterogeneous hydrogenation catalyst. The presence of a black precipitate in the reaction mixture after the hydrogenation reaction at 373 K indicates that also in this case some colloidal nickel was formed. However, this hydrogenation activity drops to zero when the reaction temperature is lowered to 323 K; even after 20 h no hydrogenation activity was observed and no colloidal nickel was formed.

Subsequently, some didentate phosphane ligands were added to nickel(II) acetate, to investigate their influence on catalytic activity.† The results of the hydrogenation reactions are presented in Table 1.

Initially, two simple phosphane ligands, dppe and dppp (for abbreviations see Scheme 1), were used (Table 1, entries 1 and 2). Whereas nickel(II) acetate alone shows some hydrogenation activity at 373 K (probably heterogeneous), the presence of dppe or dppp leads to an unreactive complex. When dppe or dppp is added to the green nickel(II) acetate solution, almost immediately a yellow complex is formed. The fact that the colour of this solution does not change during the hydrogenation experiment and that no black precipitate is observed, indicates that the phosphane ligands prevent the formation of colloidal nickel. As the simple phosphane ligands dppe and dppp did not lead to active hydrogenation catalysts, it was decided to use some more complex phosphane ligands, and methoxyphenyl and cyclohexyl derivatives were selected (Scheme 1).

$R_2P(CH_2)_nPR_2$

Ligand[a]	R	*n*
dppe	Ph	2
dppp	Ph	3
dcpe	*c*-C_6H_{11}	2
dcpp	*c*-C_6H_{11}	3
o-MeO-dppe	*o*-$MeOC_6H_4$	2
o-MeO-dppp	*o*-$MeOC_6H_4$	3
m-MeO-dppe	*m*-$MeOC_6H_4$	2
m-MeO-dppp	*m*-$MeOC_6H_4$	3
p-MeO-dppp	*p*-$MeOC_6H_4$	3

Scheme 1 Structure of the ligands. dppe = 1,2-bis(diphenylphosphino)-ethane, dppp = 1,3-bis(diphenylphosphino)propane, dcpe = 1,2-bis(dicyclohexylphosphino)ethane, dcpp = 1,3-bis(dicyclohexylphosphino)propane, *o*-MeO-dppe = 1,2-bis(di-*ortho*-methoxyphenylphosphino)ethane, *o*-MeO-dppp = 1,3-bis(di-*ortho*-methoxyphenylphosphino)propane, *m*-MeO-dppe = 1,2-bis(di-*meta*-methoxyphenylphosphino)ethane, *m*-MeO-dppp = 1,3-bis(di-*meta*-methoxyphenylphosphino)propane, *p*-MeO-dppp = 1,3-bis(di-*para*-methoxyphenylphosphino)propane.

First, *o*-MeO-dppe was tested in combination with nickel(II) acetate for hydrogenation activity at 373 K in methanol. The formed catalytic species was very active, so that within 15 min, all the oct-1-ene had reacted. Therefore the hydrogenation reaction was performed at a lower temperature of 323 K (Table 1, entry 3). After 1 h the reaction mixture contained, besides *n*-octane and unreacted oct-1-ene, also some isomerisation products, mainly *cis*- and *trans*-oct-2-ene. The propane-bridged analogue *o*-MeO-dppp was also tested on hydrogenation activity in combination with nickel(II) acetate (Table 1, entry 4). With this ligand the activity is increased to 350 turnovers h^{-1}. Furthermore, when ethanol is used as the solvent the activity increased further to 410 turnovers h^{-1} (Table 1, entry 5).

Application of the cyclohexyl ligand dcpe leads to a very active catalyst (Table 1, entry 6). The reaction temperature had to be lowered even further, to 298 K, to be able to follow the reaction course. Even at this low temperature a high turnover number of 460 after 1 h was reached. In contrast to the results obtained with the *ortho*-methoxy ligands the propane-bridged analogue dcpp leads to a somewhat less active catalyst with 350 turnovers h^{-1} (Table 1, entry 7).

In order to establish the homogeneity of the catalysts, the catalytic activity as a function of the amount of catalyst was determined. Only in the case of a homogeneous catalyst is the activity expected to be directly proportional to the catalyst concentration. We performed this test with the *in situ* catalyst formed with nickel(II) acetate and *o*-MeO-dppe; we found that

Table 1 Nickel-catalysed hydrogenation of oct-1-ene[a]†

Entry	Ligand	TON[b]	*T*/K	Solvent
1	dppe	0	373	EtOH
2	dppp	0	373	EtOH
3	*o*-MeO-dppe	220	323	MeOH
4	*o*-MeO-dppp	350	323	MeOH
5	*o*-MeO-dppp	410	323	EtOH
6	dcpe	460	298	MeOH
7	dcpp	350	298	MeOH
8	*m*-MeO-dppe	0	373	MeOH
9	*m*-MeO-dppp	0	373	EtOH
10	*p*-MeO-dppp	0	373	EtOH

[a] *Reaction conditions*: oct-1-ene/Ni = 500, Ni/ligand = 1, [Ni] = 0.005 M, *t* = 1 h, $p(H_2)$ = 50 bar. [b] Turnover number in mol *n*-octane per mol $Ni(OAc)_2$ after 1 h.

the activity of the catalyst increased linearly (correlation coefficient = 0.997) with the catalyst concentration. It is possible that the reaction conditions, dihydrogen, electron-rich phosphine plus an alcohol solvent, can cause reduction of nickel, leading to a heterogeneous catalyst, but even when a non-coordinating, electron-rich phosphine, such as tris(*ortho*-methoxyphenyl)phosphine, is used under identical reaction conditions, no hydrogenation activity is observed. These results, in combination with the observation that pure nickel(II) acetate does not lead to an active catalyst under the reaction conditions, lead to conclusion that genuine homogeneous catalysts are observed here.

The positive effect of the *ortho*-methoxyphenyl and the cyclohexyl groups in the diphosphane ligands on the hydrogenation activity compared to dppe and dppp could be due to either steric or electronic effects. Both the *ortho*-methoxyphenyl group and the cyclohexyl group are weaker π-acceptors than a simple phenyl group. As a consequence the basicity of the phosphorus atoms in the corresponding diphosphane ligands is higher, which will influence the electrophilic nature of the nickel(II) ion. This extra electron density at the metal increases its ability to interact with dihydrogen. Furthermore, *ortho*-methoxyphenyl and cyclohexyl groups are much more bulky than the phenyl group.

In an initial attempt to separate electronic from steric effects of the methoxyphenyl group the *meta* and *para* analogues of these phosphane ligands were also tested for hydrogenation activity in combination with nickel(II) acetate (Table 1, entries 8, 9 and 10). None of the formed complexes showed any hydrogenation activity even at higher reaction temperatures. Only some isomerisation was observed in the case of *p*-MeO-dppp. This indicates that the positive effect of the *ortho*-methoxyphenyl groups on the hydrogenation activity is predominantly steric. It is known that the ligands dppe and dppp can form bis(ligand) complexes with nickel such as in $[Ni(dppe)_2][NO_3]_2$.[5] A positive influence because of steric properties may be explained by a lower probability of the formation of inactive bis(ligand) complexes with the bulkier *ortho*-methoxyphenyl- or cyclohexyl-derived ligands. So far, no X-ray structures of bis(ligand) complexes containing the *ortho*-methoxyphenyl and the cyclohexyl groups in the diphosphane ligands have been reported.

It is assumed that the catalytic cycle for isomerisation at least partly coincides with that of the hydrogenation reaction. With some of the catalysts reported here, a considerable amount of the oct-1-ene is initially isomerised; However, over time the amount of these internal olefins also decreases suggesting that either the catalyst is able to hydrogenate these or isomerisation back to the terminal olefin occurs. Further investigations will concentrate on elucidating the mechanism of the hydrogenation reaction and isomerisation, with these nickel catalysts by variation of the substituents on the phosphane ligand and by changing the reaction conditions.

In conclusion, novel truly homogeneous nickel containing hydrogenation catalysts are described, which show faster and more selective catalytic activity compared to known homogeneous nickel containing hydrogenation catalysts.[2] In the future, a further improved nickel catalyst may replace the more expensive rhodium and ruthenium catalysts which are currently used. Even enantioselective nickel hydrogenation catalysis complexes can be envisaged.

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Notes and references

† In a typical experiment, 0.1 mmol nickel(II) acetate tetrahydrate and 0.1 mmol of the ligand were mixed in 20 ml of dry solvent for 10 min at room temperature under an argon atmosphere. For *o*-MeO-dppe or *p*-MeO-dppp mixing was performed at elevated temperatures and/or for prolonged times, until the ligand was completely dissolved. Solutions containing ligands *o*-MeO-dppp, *m*-MeO-dppe or *m*-MeO-dppp had to be refluxed for 5 h. Then, 50 mmol of oct-1-ene was added to the yellow–orange solution and mixing continued for 5 min. The mixture was transferred into the autoclave, under oxygen-free conditions, and a hydrogen pressure of 50 bar applied. The reaction was initiated by heating the autoclave to the desired temperature. Samples were taken every 15 min over 1 h and were analysed using gas chromatography.

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