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Homogeneous hydrogenation of 1-octene: effect of anion, solvent and ligand on hydrogenation activity and selectivity Crystal structure of the catalyst precursor [Ni(*o*-MeO-dppp)(tfa)$_2$]

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Abstract

The effect of solvent, anion, and amount of ligand on the catalytic hydrogenation of 1-octene by nickel(II) complexes containing the ligands 1,2-bis(di(*ortho*-methoxyphenyl)phosphanyl)ethane (*o*-MeO-dppe) and 1,3-bis(di(*ortho*-methoxyphenyl)-phosphanyl)propane (*o*-MeO-dppp) is reported. Catalysts containing the ligand *o*-MeO-dppe are more sensitive towards variations in solvents and anions than the catalysts containing the ligand *o*-MeO-dppp. The active catalyst precursor complex [Ni(*o*-MeO-dppp)(tfa)$_2$] (tfa = trifluoroacetate) was characterized with X-ray crystallography. The complex has a crystallographic C_2 symmetry; the nickel ion is in a square–planar geometry with two phosphorus donors and two tfa oxygen donors in a *cis* configuration (Ni–P distance 2.1527(4) Å, Ni–O distance 1.9186(10) Å). In reaction mixtures containing *o*-MeO-dppe ligand redistribution takes place, leading to the formation of an inactive bis(ligand) complex. To prevent the ligand redistribution reaction the bulkier ligand 1,2-bis(di(*ortho*-ethoxyphenyl)phosphanyl)ethane (*o*-EtO-dppe) has been synthesized. Even though NMR analysis showed that its nickel complex also is involved in a ligand-redistribution equilibrium, the hydrogenation activity is considerably higher than that of a catalyst containing the ligand *o*-MeO-dppe.

Keywords: Homogeneous catalysis; Hydrogenation; Nickel complexes; Phosphane ligands; Crystal structure

1. Introduction

Recently, we reported that selected nickel(II) diphosphane complexes, containing acetate anions, are able to hydrogenate homogeneously 1-octene to *n*-octane [1]. It appeared that in methanol, the catalytic hydrogenation activity of the nickel(II) catalyst containing the didentate phosphane ligand *o*-MeO-dppp is higher than that of a catalyst containing the ligand *o*-MeO-dppe (Scheme 1). The presence

Abbreviations: tfa, trifluoroacetate; *o*-EtO-dppe, 1,2-bis(di-(*ortho*-ethoxyphenyl)phosphanyl)ethane; *o*-MeO-dppe, 1,2-bis(di-(*ortho*-methoxyphenyl)phosphanyl)ethane; *o*-MeO-dppp, 1,3-bis-(di(*ortho*-methoxyphenyl)phosphanyl)propane

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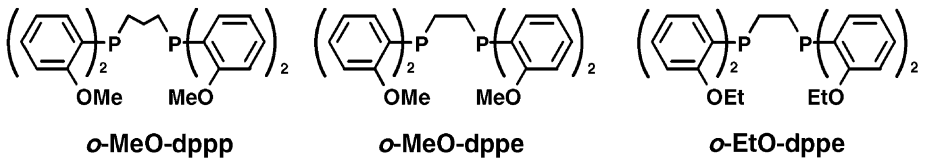
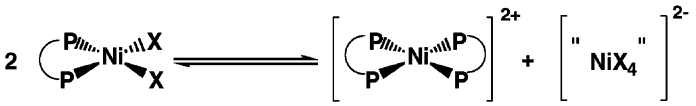


o-MeO-dppp *o*-MeO-dppe *o*-EtO-dppe

Scheme 1.



Scheme 2.

of *ortho*-methoxy groups on the phenyl rings creates so-called hemi-labile ligands [2]. The enhanced enantioselectivity of hydrogenation catalysts containing such methoxy groups has been attributed to the possible metal–oxygen interactions [3].

In an attempt to explain the difference in catalytic activity, a study was undertaken to investigate the nature of species in solution for both *ortho*-methoxy ligands *o*-MeO-dppe [4] and *o*-MeO-dppp [5]. It was found that complexes of the ligand *o*-MeO-dppe are involved in a ligand-redistribution equilibrium, depicted in Scheme 2, in contrast to complexes of the ligand *o*-MeO-dppp. It is foreseen that the redistributed complex is unable to act as a catalyst in the hydrogenation of 1-octene, which is rationalized by the lack of available sites for coordination of the reactants in the cationic unit, whereas the anionic unit containing "naked" nickel, is only expected to yield an active catalyst at higher temperatures, when colloidal nickel particles are known to be formed [6]. In the NMR study of the nickel complexes with the didentate phosphane ligand *o*-MeO-dppe, the redistributed complex was observed in varying amounts, depending on the solvents and anions used [4].

In the present study, the influence of solvent, anion, and amount of ligand on the catalytic hydrogenation of 1-octene in the presence of nickel(II) complexes containing the ligands *o*-MeO-dppe and *o*-MeO-dppp is reported. To study the effect of the steric properties of the ligand on the catalytic hydrogenation, the new ligand 1,2-bis(di(*ortho*-ethoxyphenyl)phosphanyl)ethane (*o*-EtO-dppe) has been synthesized (Scheme 1). These results may give useful insight in the mechanism of the nickel-catalyzed hydrogenation.

2. Experimental

2.1. General procedures

The ^{1}H, ^{31}P and ^{1}H NMR spectra were recorded on a Bruker WM-300 spectrometer at 300.13 and 121.50 MHz, respectively. The ^{1}H and ^{31}P chemical shifts are recorded in δ units relative to TMS (internal) and phosphoric acid (external), respectively.

2.2. Syntheses

2.2.1. General

All the chemicals were reagent grade and used as received or synthesized as described later. To remove peroxides from 1-octene, it was purified by column chromatography (alumina). Reactions were carried out under an inert atmosphere of dry argon or dry dinitrogen gas, unless stated otherwise, by using standard Schlenk techniques. Solvents were degassed prior to use. The syntheses of the ligands *o*-MeO-dppe [4] and *o*-MeO-dppp [7] and the complexes [Ni(*o*-MeO-dppe)X_2] (X = Cl, Br, I, tfa) [4], [Ni(*o*-MeO-dppe)$_2$]Y_2 (Y = tfa and PF_6) [4], [Ni(*o*-MeO-dppp)X_2] (X = Cl, Br, I, trifluoroacetate (tfa)) [5] and [Ni(*o*-MeO-dppp)$(H_2O)_2$]$(PF_6)_2$ [5] have been described elsewhere.

2.2.2. Tris(ortho-ethoxyphenyl)phosphane

This synthesis was performed according to the reported synthesis of tris(*ortho*-methoxyphenyl)phosphane [8]. Starting from 0.2 mol ethoxybenzene, 9.45 g (48% yield) of a white powder was obtained. The mp 113–6 °C. Anal. Calcd. for $C_{24}H_{27}O_3P$

(Fw = 394.5): C, 73.08; H, 6.90. Found: C, 72.96; H, 7.01. MS (ESI): *m/z* 395 $[M + H]^+$. ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.12 (t, 3H, –OCH$_2$C*H*$_3$), 3.97 (q, 2H, –OC*H*$_2$CH$_3$), 6.82 (m, 12H, aromatic protons). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): −34.5 (s).

2.2.3. 1,2-Bis(di(ortho-ethoxyphenyl)phosphanyl)-ethane

This synthesis was performed according to the procedure earlier described for the synthesis of *o*-MeO-dppe [4]. Starting from 30 mmol tris(*ortho*-ethoxyphenyl)phosphane (P(*o*-EtO-Ph)$_3$), 3.4 g (39% yield) of a white powder was obtained. The mp 180–2 °C. Anal. Calcd. for $C_{34}H_{40}O_4P_2$ (Fw = 574.6): C, 71.07; H, 7.02. Found: C, 69.65; H, 6.48. MS (ESI): *m/z* 575 $[M + H]^+$. ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.15 (t, 12H, –OCH$_2$C*H*$_3$), 2.24 (t, 4H, –*CH*$_2$*CH*$_2$–), 3.87 (q, 8H, –OC*H*$_2$CH$_3$), 6.82 (m, 8H, aromatic protons), 7.15 (m, 4H, aromatic protons), 7.26 (m, 4H, aromatic protons). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): −26.18 (s). According to ESI-MS and NMR the ligand is pure; the poor analysis must be explained by the presence of a small amount of mono-substituted ligand or the presence of solvent.

2.3. X-ray crystal structure determination of [Ni(o-MeO-dppp)(tfa)$_2$]

2.3.1. Crystal data

$C_{35}H_{34}F_6NiO_8P_2$, M = 817.27, monoclinic space group *C2/c* (no. 15), a = 17.0119(1), b = 10.9471(1), c = 19.3605(2) Å, β = 98.9729(4)°, V = 3561.40(5) Å^3, Z = 4, T = 150 K, μ = 0.72 mm^{-1}, ρ = 1.525 g/cm^3, crystal size 0.50 mm × 0.50 mm × 0.45 mm.

2.3.2. Data collection and refinement

Orange single crystals were obtained from a dichloromethane/diethyl ether layering. Intensities were measured on a Nonius KappaCCD diffractometer with rotating anode (Mo Kα, λ = 0.71073 Å). The structure was solved with Patterson methods (DIRDIF-97) [9] and refined with the program SHELXL-97 [10] against F^2 of all reflections up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}. Non-hydrogen atoms were refined freely with anisotropic parameters; hydrogen atoms were refined as rigid groups. Because of the crystallographic C_2 symmetry of the molecule, the propyl chain is disordered over two positions. Intensity data of 30,673 reflections were measured, of which 4058 were independent (R_{int} = 0.049). Convergence was reached at $R1$ = 0.0280, $wR2$ = 0.0714, for 3633 reflections with $F_o > 2\sigma(F_o)$; $R1$ = 0.0330, $wR2$ = 0.0739, and S = 1.03 for all reflections and 242 parameters; $R1 = \Sigma\,||F_o| - |F_c||\,/\,\Sigma\,|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0335P)^2 + 4.0809P]$ where $P = (F_o^2 + 2F_c^2)/3$. Residual electron densities of −0.41 and 0.47 eÅ^{-3}. The drawings, structure calculations, and checking for higher symmetry were performed with the program PLATON [11].

2.4. Hydrogenation experiments

Catalytic mixtures were prepared in two methods in a Schlenk tube, either by formation of an in situ mixture or by dissolving an earlier synthesized nickel(II) complex. In a typical in situ experiment, the nickel(II) salt was mixed with the ligand (in 10% excess) in 20 ml of degassed solvent at room temperature until a clear solution was obtained. Also, in the case of the isolated nickel(II) complexes, 20 ml of degassed solvent was added to the complex and the mixture was stirred at room temperature to obtain a clear solution. Sometimes, a clear solution was obtained within 10 min, whereas in some solvents overnight stirring and heating up to 40 °C was needed.

When a clear solution was obtained the substrate, 1-octene, was added and the solution was stirred for another 5 min. Hydrogenation reactions were carried out in a 100 ml Parr stainless steel autoclave equipped with a glass inner beaker, and a motor driven stirrer. The autoclave was evacuated and then filled with argon three successive times, before the prepared solution was introduced via a syringe into the autoclave. The autoclave was then purged with dihydrogen gas for several seconds, before the reaction pressure of dihydrogen was applied. The temperature of the autoclave was controlled by an electronic heating mantle. The autoclave was connected to a recorder to register the pressure during the reaction. The reaction was initiated by activation of the stirrer, and simultaneous activation of the temperature-control unit for reactions at elevated temperatures. After 1 h the autoclave was cooled in an ice-bath and reaction samples were taken, which were stored at −20 °C. In some

cases, biphasic mixtures were obtained after storage at −20 °C, these mixtures were homogenized by the addition of toluene. After dilution with diethyl ether, the samples were analyzed by gas chromatography.

All reported values are the arithmetic means of two or more experiments. Experiments are considered reproducible when the deviation of the obtained results are <10% of the arithmetic mean.

In the hydrogenation experiments, the only side-reaction observed is the isomerization of 1-octene to internal alkenes (*cis*- and *trans*-2-octene, 3-octene and 4-octene). The selectivity reported in the tables is given for the hydrogenation to *n*-octane.

3. Results

3.1. Crystal structure of [Ni(o-MeO-dppp)(tfa)$_2$]

A molecular plot of the complex is given in Fig. 1. Selected distances and angles are given in Table 1. The compound crystallizes in the centrosymmetric space group *C*2/*c*. The coordination geometry around the nickel(II) center is essentially square–planar with two phosphane donors and two tfa oxygen donors in a *cis* configuration. The nickel ion is located on a crystallographic two-fold axis, which is bisecting the O31–Ni1–O31′ and P4–Ni1–P4′ planes. Due to this crystallographic symmetry, the central carbon atom in the propane bridge is disordered. The dihedral angle between the O–Ni–O and P–Ni–P planes does

Table 1
Selected interatomic distances, angles and torsion angles for [Ni(*o*-MeO-dppp)(tfa)$_2$][a]

Ni1-P4	2.1527(4)
Ni1-O31	1.9186(10)
Ni1-O32	2.9604(12)
Ni1-O17	3.5541(12)
Ni1-H26	2.65
P4-Ni1-P4′	96.18(2)
O31-Ni1-O31′	89.29(6)
P4-Ni1-O31	87.29(3)
P4-Ni1-O31′	176.16(3)
O31-Ni1-O32	49.52(4)
Ni1-P4-C11-C12	71.02(12)
Ni1-P4-C21-C22	178.09(11)
Ni1-O31-C30-O32	5.0(2)

[a] Primed atoms at symmetry position: $1-x, y, ((1/2)-z)$.

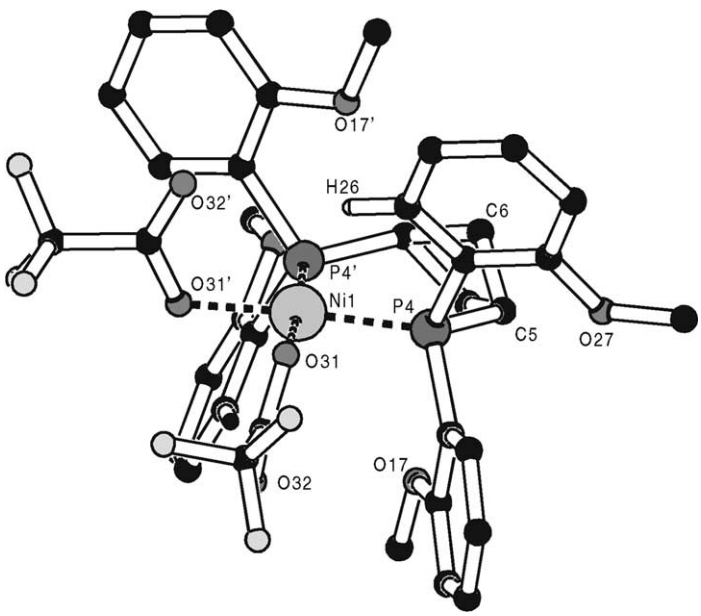


Fig. 1. Pluton [11] plot of [Ni(*o*-MeO-dppp)(tfa)$_2$] with atom-labeling scheme. Hydrogen atoms (except for H26) are omitted for clarity. Symmetry operation: $1-x, y, ((1/2)-z)$.

not differ considerably from zero (2.34(4)°). The Ni–P distances are slightly shorter than in the nickel complexes [Ni(*o*-MeO-dppp)Cl_2] and [Ni(*o*-MeO-dppp)$(H_2O)_2$]$(PF_6)_2$ [5]. The Ni–O31 distance of 1.9186(10) Å is only slightly shorter than the Ni–O distances of the water molecules (1.965(2) and 1.966(2) Å) in [Ni(*o*-MeO-dppp)$(H_2O)_2$]$(PF_6)_2$ [5]. The bite angle of the didentate phosphane ligand is 96.18(2)° in the present compound, which is larger than the bite angle in the other *o*-MeO-dppp complexes (89–91°) [5].

Apart from the strong interactions in the plane of coordination, several weaker interactions are present. The oxygen O32 of the tfa ion is at a distance of 2.9604(12) Å, and the *ortho*-hydrogen atom H26 resides at a distance of 2.65 Å from the nickel(II) center. The electrostatic interaction of the *ortho*-methoxy O17 with the nickel ion is rather weak, as demonstrated by the long distance (3.5541(12) Å) in comparison with the other *o*-MeO-dppp complexes [5].

The tfa is frequently used in homogeneous catalysis as a weakly coordinating anion. So far, crystal structures of complexes containing phosphane ligands and coordinated tfa anions have not been reported. The structures of nickel complexes containing coordinated tfa molecules that have been reported either are high-spin octahedral nickel(II) complexes with nitrogen donor ligands [12], or are low-spin organometallic nickel(II) complexes containing allyl ligands [13].

3.2. Hydrogenation: influence of the solvent

Pure solvents and binary solvent mixtures were used and the results of this study are presented in Tables 2 and 3. In situ mixtures of nickel acetate and a small excess (10%) of ligand were used. The small excess of ligand was used to ensure complete coordination of nickel. The effect of the ligand-to-metal ratio is discussed in Section 3.4.

3.2.1. Pure solvents

In some solvents an in situ complex was not easily formed, as nickel acetate is only soluble in polar solvents, whereas the organic ligands are soluble in relatively nonpolar solvents. Usually, clear solutions were obtained except when acetone was used; in those cases the solutions contained some undissolved material.

In pure methanol, the complex containing *o*-MeO-dppp shows considerable hydrogenation activity at room temperature, in contrast to the complex containing *o*-MeO-dppe (Table 2). At 50 °C, the hydrogenation activity of the latter complex is raised considerably, whereas in the case of *o*-MeO-dppp the hydrogenation activity is only raised by a factor 2. In view of these findings, the reactions in other solvents were carried out at a reaction temperature of 50 °C.

Hydrogenation reactions were carried out in acetonitrile, ethanol and acetone. As a measure of the polarity, the dielectric constant of the solvent is used

Table 2
The effect of different solvents on the hydrogenation of 1-octene using nickel(II) phosphane acetate complexes[a]

Solvent	*o*-MeO-dppp		*o*-MeO-dppe	
	$TON_{overall}$[b]	$S_{n\text{-octane}}$[c]	$TON_{overall}$[b]	$S_{n\text{-octane}}$[c]
MeOH, 25 °C	500	100	Trace	
MeOH, 50 °C	1160	99	400	94
MeCN	170	46	170	0
EtOH	1050	98	870	66
Acetone[d]	Trace		Trace	
Acetone:toluene (1:4 v/v)	Trace		0	
MeOH:CH_2Cl_2 (1:1 v/v)	1480	98	850	75
EtOH:CH_2Cl_2 (1:1 v/v)	1890	86	620	41
n-PrOH:CH_2Cl_2 (1:1 v/v)	1220	60	Trace	
n-BuOH:CH_2Cl_2 (1:1 v/v)	910	44	0	

[a] Reaction conditions: 1-octene:$Ni(OAc)_2$ = 2000, ligand:Ni = 1.1, [Ni] = 1.4 mM, 20 ml solvent, t = 1 h, $p(H_2)$ = 50 bar, T = 50 °C.
[b] Turnover number (moles converted 1-octene per moles $Ni(OAc)_2$ after 1 h).
[c] Selectivity towards *n*-octane (moles *n*-octane per moles converted 1-octene).
[d] Plus 1 ml dichloromethane.

Table 3
The dependence of the hydrogenation of 1-octene on methanol-to-dichloromethane ratio using nickel(II) phosphane acetate complexes[a]

MeOH:CH_2Cl_2	*o*-MeO-dppp		*o*-MeO-dppe	
	$TON_{overall}$[b]	$S_{n\text{-octane}}$[c]	$TON_{overall}$[b]	$S_{n\text{-octane}}$[c]
20:0 (v/v)	1160	99	400	94
15:5 (v/v)	1220	99	610	85
10:10 (v/v)	1480	98	850	75
5:15 (v/v)	1350	92	900	56
3:17 (v/v)	1920	85	530	40
1:19 (v/v)	570	58	Trace	
0:20 (v/v)	0		[d]	

[a] Reaction conditions: 1-octene:Ni(OAc)$_2$ = 2000, ligand:Ni = 1.1, [Ni] = 1.4 mM, 20 ml solvent, t = 1 h, $p(H_2)$ = 50 bar, T = 50 °C.
[b] Turnover number (moles converted 1-octene per moles Ni(OAc)$_2$ after 1 h).
[c] Selectivity towards *n*-octane (moles *n*-octane per moles converted 1-octene).
[d] Not measured because of solubility problems.

(methanol ε = 32.6, acetonitrile ε = 38.8, ethanol ε = 24.3, and acetone ε = 20.7) [14]. Although the dielectric constants of methanol and acetonitrile are comparable, an enormous difference in catalytic activity and selectivity is observed for both ligands in these solvents. The difference in the two solvents of lower polarity, acetone and ethanol, is equally large. Catalytic hydrogenation is observed using the protic solvents ethanol and methanol, whereas in the aprotic solvents acetone and acetonitrile the catalysts are hardly active. The difference in catalytic activity in methanol versus ethanol is not the same for both ligands. Whereas the catalytic activity and selectivity of the *o*-MeO-dppp catalyst are comparable in both solvents, for the *o*-MeO-dppe catalyst in ethanol the catalytic activity increases, however, the selectivity drops significantly.

3.2.2. Binary solvent mixtures

It has been reported that in an acetone:toluene (1:4 v/v) mixture only the mono(*o*-MeO-dppe) complex is present in solution [4]. However, in this solvent

Table 4
The effect of different anions on the hydrogenation of 1-octene using nickel(II) phosphane complexes in a CH_2Cl_2:MeOH mixture (1:1 v/v)[a]

	o-MeO-dppp		*o*-MeO-dppe	
	$TON_{overall}$[b]	$S_{n\text{-octane}}$[c]	$TON_{overall}$[b]	$S_{n\text{-octane}}$[c]
Ni(OAc)$_2$[d,e]	1470	100	1500	90
[NiLCl$_2$][d]	520	100	120	100
[NiLBr$_2$][d]	690	100	240	88
[NiLI$_2$][d]	1220	98	950	68
[NiL(tfa)$_2$][f]	1300	100	trace	
[NiL(H$_2$O)$_2$](PF$_6$)$_2$[f]	2790	100	[g]	
[NiL$_2$](tfa)$_2$[f]	[g]		trace	
[NiL$_2$](PF$_6$)$_2$[f]	[g]		trace	

[a] Reaction conditions: t = 1 h, 20 ml solvent, $p(H_2)$ = 50 bar, T = 50 °C.
[b] Turnover number (moles converted 1-octene per moles Ni(OAc)$_2$ after 1 h).
[c] Selectivity towards *n*-octane (moles *n*-octane per moles converted 1-octene).
[d] 1-Octene:Ni = 2000, [Ni] = 0.9 mM.
[e] Ligand:Ni = 1.1, in situ mixtures.
[f] 1-Octene:Ni = 4545, [Ni] = 0.4 mM.
[g] Complex not available.

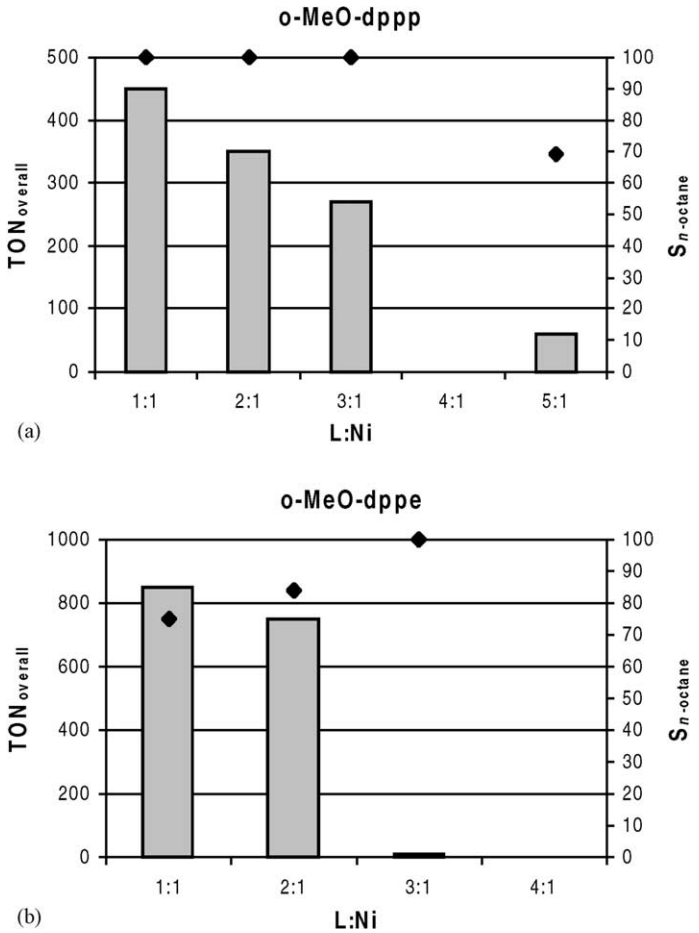


Fig. 2. Schematic representation of the overall turnover number (□) and the selectivity towards *n*-octane (◆) as a function of the nickel-to-ligand ratio for (a) *o*-MeO-dppp (at 25 °C) and (b) *o*-MeO-dppe (at 50 °C). Reactions conditions: 1-octene:Ni$(OAc)_2$ = 2000, [Ni] = 1.4 mM, 20 ml methanol:dichloromethane (1:1 v/v), t = 1 h, $p(H_2)$ = 50 bar. Turnover number is moles converted 1-octene per moles Ni after 1 h.

mixture no hydrogenation activity can be observed for catalysts containing either the ligand *o*-MeO-dppe or *o*-MeO-dppp. The binary solvent mixtures generally give rise to less solubility problems than the pure solvents. However, in a butanol:dichloromethane (1:1 v/v) mixture no clear solution could be obtained with the ligand *o*-MeO-dppe. When, in the case of *o*-MeO-dppp, the solution of butanol:dichloromethane (1:1 v/v) was stirred for a prolonged period, a red precipitate was formed, which was analyzed as [Ni(*o*-MeO-dppp)Cl_2] [5].

The effect of the alkyl group R in a series of CH_2Cl_2:ROH (1:1 v/v) mixtures (R = Me, Et, *n*-Pr, or *n*-Bu) show that, in general, using either of the two ligands both the catalytic activity and selectivity decrease with an increasing size of R, and thus with decreasing polarity of the solvent mixture (Table 2). This drop in the catalytic activity and selectivity is more pronounced in the case of *o*-MeO-dppe.

The addition of small amounts of dichloromethane to the methanol solution does not seem to have a large effect on the hydrogenation activity and selectivity of the catalyst containing the ligand *o*-MeO-dppp (Table 3). However, when the solution contains 75% of dichloromethane the selectivity starts to drop considerably. In the case of *o*-MeO-dppe, the

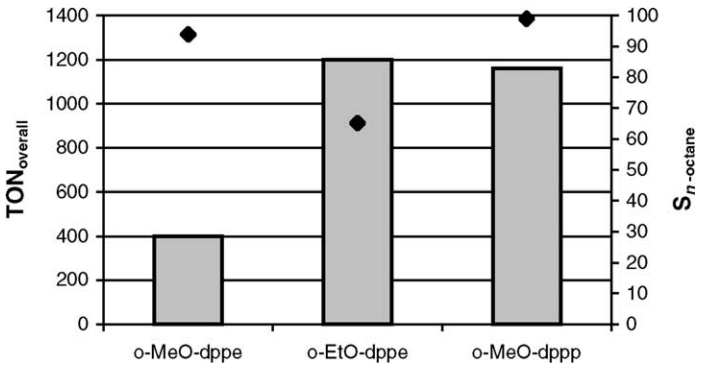


Fig. 3. Schematic representation of the overall turnover number (▭) and the selectivity towards *n*-octane (◆) for three different ligands. Reactions conditions: 1-octene:Ni(OAc)$_2$ = 2000, ligand:Ni = 1.1, [Ni] = 1.4 mM, 20 ml methanol, t = 1 h, $p(H_2)$ = 50 bar, T = 50 °C. Turnover number is moles converted 1-octene per moles Ni after 1 h.

hydrogenation activity reaches a maximum in a 1:1 mixture of methanol and dichloromethane. The selectivity, however, decreases gradually with increasing amounts of dichloromethane. In pure dichloromethane, no catalytic activity is observed at all.

3.3. Influence of the anion

The results collected in Table 4 show that the hydrogenation activity decreases in the order OAc > I > Br > Cl for both ligands. In contrast to *o*-MeO-dppp, for the catalysts containing the ligand *o*-MeO-dppe also an effect on the selectivity is observed. It appears that for catalysts containing the ligand *o*-MeO-dppe hardly any hydrogenation activity is observed with the weakly coordinating anions tfa and PF_6. In the case of *o*-MeO-dppp, however, the complex [Ni(*o*-MeO-dppp)(H_2O)$_2$](PF_6)$_2$ shows a very high hydrogenation activity, whereas the activity of the tfa complex is comparable with the activity of the in situ formed acetate complex.

3.4. Influence of the ligand

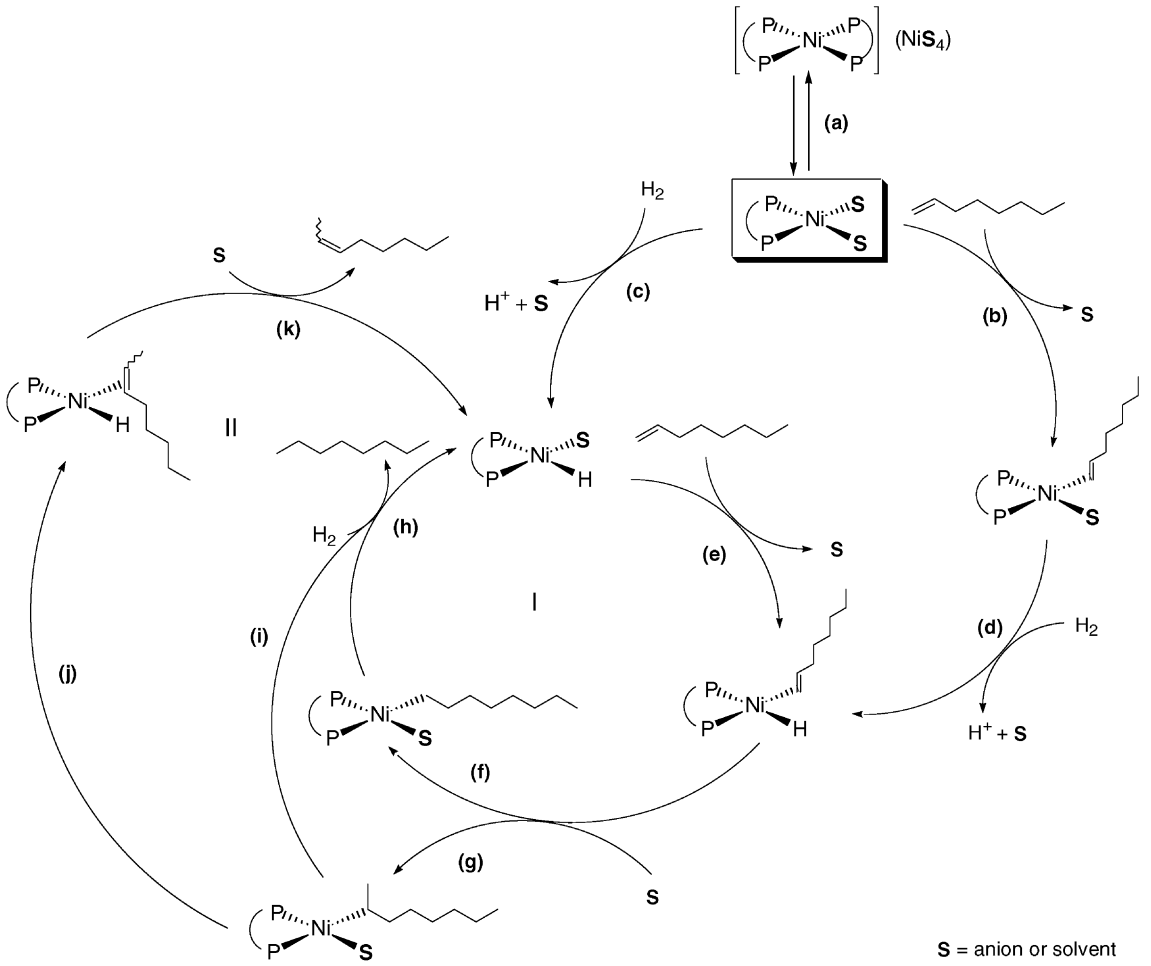
For both ligands the hydrogenation activity in a dichloromethane:methanol (1:1 v/v) mixture hardly changes as the ligand-to-metal ratio changes from 1:1 to 2:1 (Fig. 2). Using *o*-MeO-dppe, the activity decreases enormously when the ligand-to-metal ratio is increased to 3:1. At even higher ligand-to-metal ratios, no activity is observed at all. In the case of *o*-MeO-dppp, the activity decreases more gradually with increasing ligand-to-metal ratios. At a ligand-to-metal ratio of 5:1 still an activity of 77 turnovers is observed; however, the selectivity has dropped considerably.

In Fig. 3, the activity in pure methanol of nickel acetate in combination with the newly synthesized ligand *o*-EtO-dppe is compared to the catalysts formed with either *o*-MeO-dppe or *o*-MeO-dppp. The activity of the new catalyst equals that of the catalyst containing the ligand *o*-MeO-dppp, however, the selectivity is much lower (65% versus 99%).

4. Discussion

4.1. The catalyst

The crystal structure of the catalyst precursor complex [Ni(*o*-MeO-dppp)(tfa)$_2$] shows the nickel ion to be in a square–planar geometry, with both tfa anions coordinated to the metal ion. The axial positions of the nickel ion are partially shielded by weak interactions with an *ortho*-methoxy group of one of the phenyl rings and an *ortho*-hydrogen atom of another. The availability of these axial positions appears to be quite important in the reactivity and selectivity of the nickel complex (see the following paragraphs).



Scheme 3.

The effect of solvent, anion and amount of added ligand on the hydrogenation activity of the complexes is highly dependent on the ligand used. The influence of the investigated parameters is much more pronounced in the case of the ligand *o*-MeO-dppe than with the ligand *o*-MeO-dppp. This confirms that the ligand redistribution reaction that occurs in the *o*-MeO-dppe complexes [4] has a significant influence on the hydrogenation reaction.

In order to separate the influence of the ligand redistribution from other factors, first the effects of the investigated parameters on the *o*-MeO-dppp containing catalyst are discussed. Based on the observations a mechanism is proposed and the influence of the ligand redistribution and the availability of the axial sites in the nickel complex on the hydrogenation activity will be discussed.

4.2. Mechanism

In Scheme 3 the proposed mechanism for the nickel-catalyzed hydrogenation is depicted. In this scheme two possible activation routes are shown: step b, activation via the olefin route,and step c, activation via the hydride route. The proposed actual hydrogenation catalytic cycle (I) is composed by steps e, f and h; the competing isomerization cycle is depicted as cycle II. Also the ligand redistribution equilibrium (step a) is taken into account. However, this equilibrium occurs only in the case of nickel complexes

containing the ligands *o*-MeO-dppe and *o*-EtO-dppe.[1] **S** can be either a solvent molecule or an anion. Steps c, d, h and i involve the activation of dihydrogen. It is assumed that activation of dihydrogen proceeds via heterolytic cleavage leading to a proton and uncoordinated **S** or the alkane RH, and a nickel hydride complex. Homolytic activation or oxidative addition of dihydrogen would involve the formation of a nickel(III) and nickel(IV) species, respectively, which are much less stable [15], and therefore, these routes of dihydrogen activation are considered unlikely.

After activation of dihydrogen and coordination of the olefin migratory insertion leads to either a primary or a secondary nickel-alkyl species, step f or g, respectively. Via hydrogenolysis (step h or i) the hydrogenation cycle can be completed. However, β-H elimination of the secondary nickel-alkyl species (step j) may result in isomerization when the resulting internal olefin dissociates from the complex (step k). Repeated addition and elimination steps will move the double bond along the chain. Ultimately, the obtained isomerization products might also be hydrogenated to the alkane with the nickel(II) catalyst.

In principle all of the described reaction steps are reversible. However, hydrogenolysis of the nickel-alkyl complex (step h or i) may be considered as irreversible, because the reverse of this step involves an unlikely C–H activation.

4.3. Effects related to the hydrogenation reaction: o-MeO-dppp

4.3.1. Solvent effect

The results with binary solvent mixtures indicate that the polarity of the solvent does not notably affect the overall catalytic activity, however, it has an enormous influence on the selectivity of the reaction. In mixtures with lower polarity the rate of β-H elimination appears to be higher than the rate of hydrogenolysis.

It seems that for catalytic hydrogenation activity a protic solvent is required. Aprotic solvents are known to solvate mainly cations, whereas protic solvents can solvate both anions and cations [16]. From Scheme 3 it is clear that solvation of the anion is important during catalytic hydrogenation.

4.3.2. Anion effect

The hydrogenation activity is inversely related to the coordination ability of the anion. A coordinating anion may hinder the coordination of the reactants and, therefore, the hydrogenation activity increases in the order Cl < Br < I ∼ OAc ∼ tfa < PF_6. A direct relationship with the Brönsted basicity of the anion is not found. The activity of [Ni(*o*-MeO-dppp)$(H_2O)_2$]$(PF_6)_2$ is extremely high, which is probably related to the electrophilic nature of the nickel ion; it will react faster with dihydrogen. In a kinetic study it has become clear that the activation of dihydrogen is the rate-determining step in the hydrogenation reaction [17]. The selectivity of the hydrogenation reaction is not affected by the nature of the anion.

4.3.3. Ligand effect

The hydrogenation activity gradually decreases with increasing ligand-to-metal ratios, but the selectivity is not strongly affected. The second ligand on the nickel complex will probably coordinate monodentately, as with the ligand *o*-MeO-dppp a bis(chelate) complex cannot be formed [5]. In this case competition of the reactants with the coordinating abilities of a phosphorus donor atom will decrease the catalytic activity.

4.4. Effects related to the ligand redistribution equilibrium: o-MeO-dppe

4.4.1. General

The additional effects that are observed for *o*-MeO-dppe can be attributed to ligand redistribution [4]. It is not expected this will affect the selectivity of the hydrogenation reaction. However, significant differences in the selectivity of the catalysts containing the ligands *o*-MeO-dppp and *o*-MeO-dppe are observed, and are discussed in Section 4.4.5.

4.4.2. Influence of solvent

The inactivity at room temperature of the complex formed with nickel acetate and *o*-MeO-dppe in methanol confirm that the disproportionated complex

[1] The ^{1}H NMR spectrum of an in situ complex formed by mixing nickel(II) acetate and the ligand *o*-EtO-dppe in deuterated methanol shows a pattern typical for a bis(chelate) complex. Complexes containing the ligand *o*-EtO-dppe can thus be involved in a ligand redistribution equilibrium just as their *o*-MeO-dppe analogues [4].

is unable to act as a catalyst itself. At higher temperatures, however, at least some mono(chelate) complex must be formed, as hydrogenation activity is observed. The addition of the apolar substrate 1-octene may shift the ligand redistribution equilibrium partly towards the mono(chelate) complex (step a).

When decreasing the polarity of protic solvents or solvent mixtures the hydrogenation activity increases. However, after a maximum in hydrogenation activity, the hydrogenation activity drops as more apolar solvent is added. In the more apolar solvent mixtures the species **S**, solvent or more likely the anion, is more tightly bound to the nickel atom and no catalytically active species can be formed.

4.4.3. Influence of anion

As is observed for the ligand *o*-MeO-dppp the hydrogenation activity increases with less coordinating abilities of the anion (Cl < Br < I < OAc). However in the case of *o*-MeO-dppe, the use of the more weakly coordinating anions, tfa and PF_6, lead to an inactive catalyst. From the inactivity of these catalysts (in situ and preformed complexes), it appears that even in the presence of the olefin and at higher temperatures the bis(chelate) complexes are not converted into a catalytically active mono(chelate) complex. These observations confirm that the conversion of the bis(chelate) into the mono(chelate) complex is assisted by the anion, as has been shown with NMR studies [4].

The catalytic activity of the in situ catalyst formed from nickel(II) acetate and the ligand *o*-MeO-dppe appears to be dependent on the concentrations used (TON = 850 and 1500 for [Ni] = 1.4 and 0.9 mM, respectively). As this significant difference in activity is not observed when the ligand *o*-MeO-dppp is used, it may be related to the ligand redistribution reaction. It is likely that in a more dilute solution less bis(chelate) complex will be formed, so that a larger number of the nickel ions may participate in the catalytic hydrogenation.

4.4.4. Influence of ligand

Up to a 2:1 ligand-to-metal ratio no major effect on the hydrogenation activity is observed. This observation can be explained using two different equilibria. When the ligand-to-metal ratio is 1, the catalyst will be involved in a ligand-redistribution equilibrium (Scheme 2). When using a ligand-to-metal ratio of 2 or higher, the catalyst will be involved in an equilibrium of dissociation of the second phosphane ligand. The fact that the hydrogenation activity is not severely affected by the addition of one extra equivalent of ligand suggests that in each case the equilibrium lies on

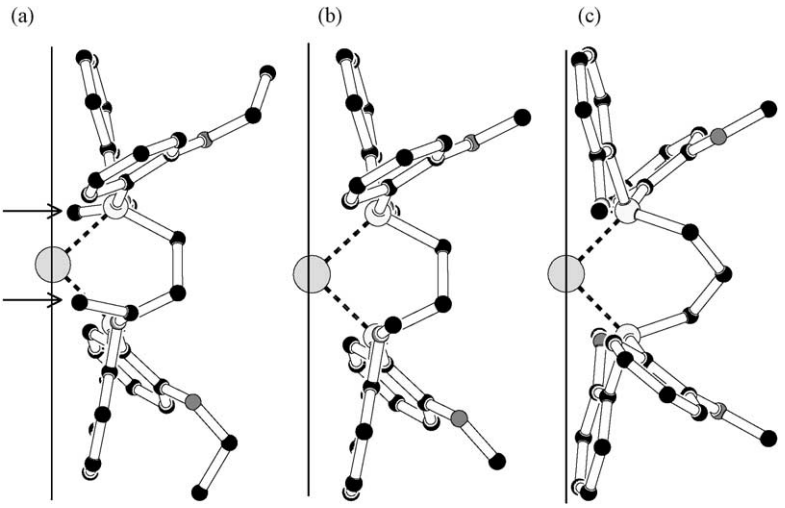


Fig. 4. Top view of nickel complexes containing the ligands (a) *o*-EtO-dppe, (b) *o*-MeO-dppe, and (c) *o*-MeO-dppp. For clarity, the other coordinating donor atoms are omitted. The ethoxy groups in the proximity of a hypothetical second coordinating ligand are indicated with an arrow. The part (a) was created artificially using the X-ray structural data of [Ni(*o*-MeO-dppe)I_2][5] by changing the methoxy groups into ethoxy groups.

the side of the bis(chelate) complex; only a small part is present as the catalytically active mono(chelate) complex. When using a ligand-to-metal ratio of 3 or higher only the bis(chelate) complex will be present in solution and no hydrogenation activity is observed.

NMR studies have shown that the complex containing the ligand *o*-EtO-dppe is also involved in a ligand-redistribution equilibrium (see footnote 1). However, the ethoxy groups may still help in more rapid formation of the catalytically active mono(chelate) complex from the bis(chelate) complex. The steric effect of the ethoxy groups is illustrated in Fig. 4 (compare Fig. 4a and b).

4.4.5. Selectivity

The selectivity of a catalyst containing the ligand *o*-MeO-dppe is always lower than that of a catalyst containing the ligand *o*-MeO-dppp. Isomerization can only occur in case of 2,1-insertion of the olefin in the nickel-hydride bond (step g). The bulkiness of the *o*-MeO-dppp ligand can either hinder the formation of the secondary alkyl species (step g) or the subsequent β-H elimination (step j). Both reactions require more space at the equatorial positions of the nickel complex than the hydrogenolysis of the primary alkyl species (step h). The larger bite angle of the ligand *o*-MeO-dppp as compared to *o*-MeO-dppe implies more steric crowding in the plane of coordination (compare Fig. 4c and b), giving a likely explanation for the higher selectivities that are obtained with the former complex.

This is in agreement with the observation that the selectivity for hydrogenation drops from 94 to 65% when the ligand *o*-EtO-dppe is used instead of *o*-MeO-dppe. The side-on coordination of dihydrogen at an axial position of the nickel ion, which is assumed to precede heterolytic cleavage [18], will be hindered in a larger extent by the bulkier ethoxy group than by the somewhat smaller methoxy group (compare Fig. 4a and b).

5. Summary and conclusion

The availability and accessibility of axial versus equatorial coordination sites determines which reaction, isomerization or hydrogenation, is catalyzed by the nickel(II) phosphane complexes. The factors influencing the availability of these coordination sites are solvent, anion and amount and type of ligand. The presence of a protic solvent was found to be essential in order to observe catalytic activity, as it is needed for the solvation of the anions. The accessibility of the coordination sites for substrate and dihydrogen is determined by the nature of the ligand.

The importance of the accessability of the equatorial coordination sites is demonstrated by the fact that catalysts containing the ligand *o*-MeO-dppe are more sensitive towards variations in solvents and anions than the catalysts containing the ligand *o*-MeO-dppp. Ligand redistribution of the former catalyst precursor takes place and leads to the formation of an inactive bis(ligand) complex. Determination of the actual concentration of this inactive complex may provide valuable insight in the intrinsic activity of the catalyst containing the ligand *o*-MeO-dppe.

In an attempt to prevent the formation of the bis(chelate) complex the sterically more hindered ligand *o*-EtO-dppe was synthesized. The presence of an ethoxy group instead of a methoxy group indeed increases the hydrogenation activity with a factor three. NMR analysis, however, showed that the complex containing the ethoxy-substituted ligand is also involved in a ligand-redistribution equilibrium. It is likely that to completely prevent the occurrence of the ligand-redistribution equilibrium a sterically more demanding alkoxy group, like O^iPr or O^tBu, has to be introduced on the phosphane ligand.

6. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-167499. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (internatioal): +44-1223/336-033, e-mail: deposit@ccdc.cam.ac.uk).

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