

5 Nickel

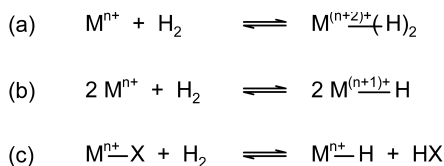
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5.1 Introduction

Nickel is frequently used in industrial homogeneous catalysis. Many carbon–carbon bond-formation reactions can be carried out with high selectivity when catalyzed by organonickel complexes. Such reactions include linear and cyclic oligomerization and polymerization reactions of monoenes and dienes, and hydrocyanation reactions [1]. Many of the complexes that are active catalysts for oligomerization and isomerization reactions are supposed also to be active as hydrogenation catalysts.

The choice of nickel as a homogeneous hydrogenation catalyst is self-evident if one considers Nature. The hydrogenase enzymes make use of the abundantly available transition metals nickel and iron for the activation of dihydrogen or the reduction of protons. The nickel-containing hydrogenase enzyme is not able to hydrogenate organic substrates, but it can activate dihydrogen at atmospheric pressure and ambient temperatures [2]. Dihydrogen oxidation in living cells is coupled to the reduction of electron acceptors such as oxygen, nitrate, sulfate, carbon dioxide and fumarate, whereas proton reduction (dihydrogen evolution) is an essential element of pyruvate fermentation or the disposal of excess electrons. Studies of either *para*- to *ortho*-hydrogen conversion or H_2/D^+ (or D_2/H^+) exchange reactions indicate that in the hydrogenase active site dihydrogen is activated *via* a heterolytic pathway, forming a hydride and a proton, as shown schematically in Scheme 5.1 [2]. The rational design and synthesis of structural and functional models for hydrogenases [3], as well as their characterization and reactivity studies, might contribute to the development of new catalysts for practical use in, for example, fuel cells, as has been expertly described by Cammack et al. [4]. The advantage of the use of inexpensive nickel over costly metals such as rhodium or ruthenium is evident.

Despite the fact that Nature uses nickel for the activation of dihydrogen, and that Raney-Ni is one of the oldest and the most important heterogeneous hydrogenation catalysts, very few nickel complexes are known to catalyze the homoge-



Scheme 5.1 Different modes of dihydrogen activation.

(a) Oxidative addition, forming a metal dihydride species;
 (b) homolytic activation, forming two metal monohydride species;
 (c) heterolytic splitting, forming a metal hydride species and a proton.

neous hydrogenation reaction. In this section, a brief overview will be provided of mononuclear nickel complexes, which have been reported to catalyze homogeneously the hydrogenation of various olefins. Many of the reported nickel-containing hydrogenation catalysts are of the Ziegler type (i.e., a nickel salt in combination with a reducing agent such as trialkylaluminum), and in many cases it is questionable whether the reported complexes yield really homogeneous hydrogenation catalysts or that the observed catalytic hydrogenation activity is due to formation of colloidal (heterogeneous) nickel particles [5].

5.2

Coordination Chemistry and Organometallic Aspects of Nickel

5.2.1

Nickel–Hydride Complexes

The existence of hydride complexes of nickel has long been recognized, with the first reports of these compounds relying mainly on the evidence of $^1\text{H-NMR}$ investigations. The number of X-ray structures containing at least one nickel–hydride bond is rather limited, and the reported structures include a relatively large number of organometallic clusters. Only a limited number of mononuclear or dinuclear structures possibly relevant for hydrogenation catalysis have been reported. These complexes typically contain electron-donating phosphane ligands with cyclohexyl, isopropyl or tertiary-butyl groups at phosphorus. The synthesis of the nickel hydride complexes is usually achieved by reaction of nickel(II) halide complexes with the mild reducing agents such as HBMe_3^- and BH_4^- , or by addition of H^+ to a nickel(0) complex.

An interesting nickel–hydride complex with a biologically relevant ligand arising from enzyme modeling has been reported by the group of Holm [6]. Reaction of the complex $[\text{Ni}(\text{NS}_3)\text{Cl}]^+$ ($\text{NS}_3 = \text{tris}(t\text{-butylsulfanylethyl})\text{amine}$) with NaBH_4 results in the trigonal bipyramidal complex $[\text{Ni}(\text{NS}_3)\text{H}]^+$; the presence of the hydride was confirmed by a high-field $^1\text{H-NMR}$ resonance at -37.75 ppm. The latter complex reacts reversibly with ethene to form the ethyl complex, and it catalyzes the isomerization of 1-hexene [6]. A similar complex has been reported with the tripo-

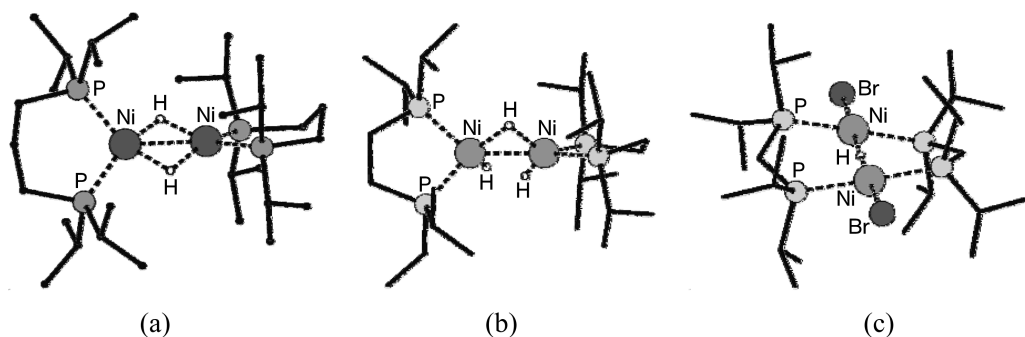


Fig. 5.1 Projection of hydride complexes: (a) $[\text{Ni}(\text{dipp})_2(\mu\text{-H})_2]$ [15]; (b) $[\{\text{HNi}(\text{dippe})\}_2(\mu\text{-H})]^+$ [16]; (c) $[\text{Ni}_2\text{Br}_2(\text{dippm})_2(\mu\text{-H})]$ [17].

dal phosphorus ligand tris(2-diphenylphosphanylethyl)amine, but in this case substoichiometric amounts of hydride were found to be present in the complex [7].

Using monodentate phosphane ligands, only a few square-planar nickel(II) complexes have been reported, containing a hydride coordinated *trans* to a halide ion (based only on NMR evidence) [8], a phenolate group [9], an imine nitrogen [10], or a tetrahydridoborate anion [11]. The structures show significant distortion from the ideal square-planar geometry due to the bulky phosphane ligands. The hydride is visible in the $^1\text{H-NMR}$ spectra around -25 ppm as a triplet resulting from the coupling with two *cis* phosphane donors.

The use of chelating didentate phosphane ligands with an ethyl or propyl bridge often results in the formation of dinuclear nickel complexes with two bridging hydrides [12–15]. The complexes are readily formed by the reaction of the corresponding mononuclear nickel dichloride complex with mild reducing agents such as HBMe_3^- or HBEt_3^- . In the resulting complexes of general formula $[\text{P}_2\text{Ni}(\mu\text{-H})_2]$, the metal ion is formally nickel(I) with a nickel–nickel bond length of 2.4 \AA . A projection of the structure of $[\text{Ni}(\text{dipp})_2(\mu\text{-H})_2]$ is shown in Figure 5.1 (a) (dipp = 1,3-bis(diisopropylphosphanyl)propane). Despite earlier predictions and theoretical calculations, the dinuclear core is nonplanar; the complexes are diamagnetic, showing the hydride resonance as a quintet around -10 ppm [12–15]. Bach et al. have studied the reactivity of the complex $[(\text{dbpe})\text{Ni}(\mu\text{-H})_2]$ (dbpe = $t\text{Bu}_2\text{PCH}_2\text{CH}_2\text{P}t\text{Bu}_2$) with deuterium gas; scrambling was observed resulting in the formation of the monodeuteride and dideuteride complexes [14]. The $^{31}\text{P-NMR}$ spectrum of the complex $[(\text{dbpe})\text{Ni}(\mu\text{-H})_2]$ shows a singlet at $+94.6$ ppm; when a spectrum is recorded in an H_2 atmosphere it shows an additional singlet at $+108$ ppm which has been tentatively ascribed to a mononuclear nickel(II) dihydride complex, or to a nickel(IV) tetrahydride complex as a result of oxidative addition of dihydrogen, and which would be intermediates in the scrambling process [14].

The reaction of $[\text{Ni}(\text{dippe})\text{Br}_2]$ (dippe = 1,2-bis(diisopropylphosphanyl)ethane) with NaBH_4 results in the formation of a dinuclear trihydride complex $[\{\text{HNi}$

(dippe)}₂(μ-H)⁺ (see Fig. 5.1 b) [16]. The structure shows a bridging hydride at a bent angle as well as a Ni–Ni bond with a distance of 2.3 Å. The complex is diamagnetic and displays one quintet at –13.4 ppm, indicating rapid interconversion of the bridging hydride with the terminal hydrides. The structure can be regarded as a protonated form of the dihydrides described above, but attempts to deprotonate the complex have failed, even using a strong base [16].

The small bite-angle ligands dcpm (bis(dicyclohexylphosphanyl)methane) or dippm (bis(diisopropylphosphanyl)methane) yield dinuclear nickel complexes of formula [Ni₂X₂(μ-P₂)₂(μ-H)] (X=halide) with one hydride bridging the two nickel centers [17, 18]. The ligands in these complexes are not chelating, but are binding two nickel ions. The compounds are mixed-valent, containing a nickel(I) and a nickel(II) ion. The complexes are therefore paramagnetic and for [Ni₂Cl₂(μ-dcpm)₂(μ-H)] a *g*-value of 2.139 at room temperature was reported [18]. The complex [Ni₂Cl₂(μ-dcpm)₂(μ-H)] is bent, with a Ni–H–Ni angle of 128° and a Ni–Ni distance of 2.9 Å [18], whereas the complex [Ni₂Br₂(μ-dippm)₂(μ-H)] (see Fig. 5.1 c) is nearly planar with a Ni–H–Ni angle of 178° and a Ni–Ni distance of 3.2 Å [17].

A mononuclear nickel hydride complex with three N-heterocyclic carbene ligands has been reported; the compound was formed by oxidative addition of an imidazolium salt to the Ni(0) bis(carbene) complex [19]. The hydride signal of this nickel(II) complex appears at –15 ppm.

Recently, the crystal structure of a nickel(II) complex with a tridentate silyl ligand has been reported [20]. The structure in the solid state shows an η²-(Si–H) binding to nickel, with a Ni–H distance of 1.47 Å; NMR spectra of the complex in solution at –80°C suggest the formation of a nickel(IV) hydride species through oxidative addition of the silyl-hydrogen to nickel [20].

5.2.2

Nickel–Alkene and Nickel–Alkyl Complexes

A large number of (mostly zero-valent) nickel–alkene complexes has been reported. Although these complexes have not been recently reviewed, their general properties and structures were expertly described in 1982 [21]. A complete overview of the reported nickel–alkene and nickel–alkyl complexes is beyond the scope of this section, in which a selection of nickel–alkene and nickel–alkyl complexes is described, mostly related to possible intermediates in hydrogenation catalysis.

The reaction of [Ni(ethene)₃] with a hydride donor such as trialkyl(hydrido)-aluminate results in the formation of the dinuclear anionic complex [{Ni(ethene)₂]₂H][–] [22]. The nickel(0) centers in this complex are in a trigonal planar environment of two ethene molecules and a bridging hydride ion, with the ethene carbons in the plane of coordination. The two planes of coordination within the dinuclear complex are almost perpendicular to each other, and the Ni–H–Ni unit is significantly bent, with an angle of 125° and a Ni–Ni distance of 2.6 Å [22].

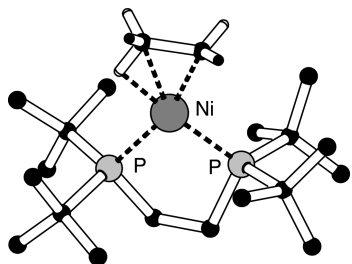


Fig. 5.2 Projection of [Ni(dbpe)(ethyl)] [23].

Protonation of (diphosphane)nickel(0)–ethene complexes with $\text{HBF}_4 \cdot \text{OEt}_2$ results in the formation of the corresponding cationic three-coordinate nickel(II)–alkyl complexes, in which a β -agostic hydrogen is present [23]. Figure 5.2 illustrates the structure of [Ni(dbpe)(ethyl)] with an agostic Ni–H distance of 1.64 Å [23]. For these nickel complexes, β -elimination and alkene rotation appeared to be slow on the NMR timescale at temperatures below 27 °C. NMR spectroscopy at 20 °C revealed a multiplet at –1.24 ppm for the three protons at the β -carbon, whereas at –100 °C a broad signal at –5.8 ppm is assigned to the agostic hydrogen [23].

In contrast, the fluxionality of neutral three-coordinate nickel(II)–alkyl complexes with β -diketiminato ligands is described in a recent publication [24]. The β -agostic complexes undergo facile β -elimination and reinsertion resulting in a mixture of primary and secondary nickel(II)–propyl complexes [24]. The corresponding four-coordinate, square-planar complexes with an additional nitrogen-donor ligand do not show β -agostic interactions in the solid state. In solution, however, dissociation of the nitrogen-donor ligand readily occurs and in the NMR spectra resonances are observed that are due to a β -agostic hydrogen interaction of the coordinated alkyl group [25]. Similarly, the neutral (acetylacetonato)(triphenylphosphane)nickel(II)–ethyl complex does not show agostic interactions in the square-planar solid-state structure, whereas in solution scrambling of the alkyl protons is observed [26]. In another recent report a remarkably stable dinuclear nickel(II)–hexyl complex has been reported; the compound does not show any agostic interactions, neither in the solid state nor in solution [27].

5.2.3

Mechanistic Aspects of Hydrogen Activation

For catalytic hydrogenation the activation of a dihydrogen molecule, the binding of an alkene, and the formation of a metal–alkyl intermediate are the most crucial aspects of a plausible catalytic mechanism. Support for a nickel–hydride mechanism in the oligomerization of ethene by nickel complexes with a chelating phosphorus–oxygen ligand was obtained through the crystallization of a complex trapped with triphenylphosphane [28]. The proton NMR spectrum of this complex shows the hydride resonance at –24.85 ppm as a double doublet due to the two *cis* phosphorus atoms [28].

Protonation mechanisms of nickel complexes and the relevance to hydrogenases, as well as to industrial catalysts, have recently been reviewed [29]. The huge interest in the possibilities of a hydrogen economy, based on the cheap and sustainable generation of H₂, and the clean and efficient oxidation of H₂ in fuel cells has given impetus to the research for functional models of hydrogenases. In the search for active functional models for [NiFe] hydrogenases, nickel complexes are tested on hydrogenase activity and three types of reactivity can be distinguished: 1) H₂/D⁺ exchange (scrambling); 2) activation of H₂ (oxidation to H⁺); and 3) reduction of H⁺ to H₂. For functional models of the [NiFe] hydrogenases the first two activities are of importance.

Bis(diphosphane)nickel complexes have been reported to show heterolytic splitting of dihydrogen [30]. The complex [Ni(PNP)₂](BF₄)₂, in which PNP is the ligand Et₂PCH₂N(Me)CH₂PEt₂, possesses both hydride and proton acceptor sites. When dihydrogen gas is passed through a solution of [Ni(PNP)₂]²⁺ in acetonitrile or dichloromethane, the solution bleaches during formation of the hydride species [HNi(PNHP)(PNP)]²⁺, in which one of the central nitrogen atoms of the ligands is protonated. In the ¹H-NMR of the complex [HNi(PNHP)(PNP)]²⁺ at low temperatures, two resonances are observed at -15.2 and 7.4 ppm, that have been assigned to the hydride and the NH-proton, respectively. The hydride and the NH-proton undergo rapid intramolecular exchange with each other and with protons in solution [30].

The structures and reactivity of the nickel complexes described above seem to indicate that, for nickel-containing hydrogenation catalysts, heterolytic activation of dihydrogen may be the most likely mechanistic pathway. The nickel-hydride complexes are stabilized by the presence of electron-donating phosphane ligands, making the nickel complexes with these ligands the most likely candidates for active homogeneous hydrogenation catalysts.

5.3

Hydrogenation Catalysis

5.3.1

Ziegler Systems

The so-called Ziegler-type catalysts have been studied rather extensively. This type of catalyst is formed by treating a transition-metal salt with a reducing agent. The most frequently used reducing agents include trialkylaluminum, alkylaluminum chlorides, alkali metals, LiAlH₄, and NaBH₄. The mixtures yield dark, air-sensitive solutions that appear homogeneous to the eye, but most likely contain colloidal metal [5]. Ziegler-type catalysts made from cobalt or nickel salts with triethylaluminum can be used for the hydrogenation of benzene to cyclohexane under rather mild conditions (155 °C, 10 bar). In a typical patent example, benzene is hydrogenated to cyclohexane (99% conversion) with more than 2500 turnovers after 1 h, using a catalyst prepared from a mixture of nickel and

zinc octoates and excess triethylaluminum [31]. A process has been developed by Institut Français du Pétrole [32].

Ziegler-type hydrogenation catalysts have been used for the hydrogenation of vegetable oils [33, 34], cyclohexadienes [35], and butadiene rubbers [36–38]. Under rather mild (1 bar H₂, 40 °C) conditions (substituted) 1,4-cyclohexadienes can be hydrogenated selectively to the cyclohexenes in yields of up to 80%; trace amounts of benzene were detected as a result of disproportionation reactions [35]. The active catalyst was prepared from [Ni(acac)₂] (Hacac = acetylacetonate), Et₃Al₂Cl₃ (10 equiv. to Ni) and PPh₃. The activity is rather low, and with a substrate:catalyst ratio (SCR) of 100 complete conversion is reached after 6 to 28 h. Isomerization of the substituted cyclohexadienes occurred, and a mechanistic pathway involving η^3 -allyl coordination of the substrate was proposed. Dihydrogen activation was proposed to occur via oxidative addition [35].

Recent investigations into the hydrogenation of rubbers include catalytic systems prepared from nickel(II) 2-ethylhexanoate or nickel(II) acetylacetonate activated with triisobutylaluminum [36], triethylaluminum [38], or butyl lithium [37, 38]. Large amounts of co-catalysts (initiator) are necessary. Hydroxyl-containing polybutadienes were hydrogenated at low H₂ pressures, affording the saturated polymers with full retention of the OH functionality [38]. Again, the activity of the catalysts is rather low, with SCRs of approximately 20 having been used.

5.3.2

Nickel Complexes of Oxygen- or Nitrogen-Containing Ligands

Catalytic homogeneous hydrogenation of cyclohexene has been claimed for simple systems such as nickel(II) acetylacetonate [39] or a nickel–chloride complex with two monodentate amines [40]. The latter complex was used as comparison for a heterogeneous catalyst obtained by impregnation of the complex on γ -alumina [40]. SCRs of 100 were used at 30 atm. H₂ and temperatures up to 100 °C, resulting in conversions of only 20–35% after 1 h.

Nickel complexes of simple tetradentate ligands containing nitrogen- and oxygen-donor atoms have also been investigated for their catalytic activity in homogeneous hydrogenation [41–43]. The complex [Ni(saloph)] (saloph=bis(salicylidene)phenylenediamine) has been reported to catalyze the hydrogenation of cyclohexene to cyclohexane and cyclooctene to cyclooctane at a moderately high dihydrogen pressure of 60 bar and a temperature of 50 °C [42]. The catalyst is more reactive in the hydrogenation of cyclohexene than in the hydrogenation of cyclooctene, the turnover frequency (TOF) being 13 h⁻¹ and 7 h⁻¹, respectively (SCR 100, t=5 h, in ethanol). The reaction is suggested to proceed *via* the high-valent [Ni^{IV}(saloph)(H)₂] species, which supposedly is formed through the oxidative addition of dihydrogen to the divalent [Ni(saloph)] complex [42]. It has been claimed that encapsulation of the analogous nickel complex [Ni(salen)] (salen=bis(salicylidene)ethylenediamine) in zeolite Y also results in a homogeneous catalyst for hydrogenation reactions [44]. The hydrogenation of 1,5,9-cyclodode-

catriene has been investigated using similar salen-type nickel complexes under rather harsh conditions (150 °C, 50 bar), but giving rather low activities (TOF < 14 h⁻¹) [41]. In a recent study, nickel complexes of similar tetradentate ligands derived from pyrrole 2-carboxaldehyde and various diamines were used as catalysts in the hydrogenation of phenylacetylene [43]. The activity of these systems is also rather low, and complete conversion was not even reached after 24 h (SCR 150, at 40 °C and 1 bar). Also in this case activation of dihydrogen is believed to proceed via oxidative addition to give a Ni(IV) dihydride intermediate [43].

[Ni(acac)₂] has been reported to be an active catalyst for the hydrogenation of cyclohexene to cyclohexane in methanol at moderate pressures and high temperature. At 100 °C and a H₂ pressure of 30 bar, a TOF of 450 h⁻¹ is reported (SCR 1000, t=1 h, in methanol). From a study including pretreatment of the catalyst under a nitrogen atmosphere, it was concluded that alkene coordination precedes hydrogen activation [39]. [Ni-(acac)₃] has been used for the catalytic hydrogenation of unsaturated fatty acids and esters [45]. No hydrogenation activity is observed at temperatures below 100 °C. After an induction period of 3 h, methyl linolenate can be hydrogenated with a TOF of 10 h⁻¹ (SCR 10, t=1 h, 100 °C, 7 bar, in methanol). It is quite likely that the actual catalyst is heterogeneous, as an induction period is needed and black precipitates are formed during the hydrogenation reaction.

5.3.3

Nickel Complexes of Triphenylphosphane

The tetrahedral nickel complexes [NiX₂(PPh₃)₂] (X=Cl, Br, or I) have been reported to show catalytic activity in the hydrogenation of linear, cyclic, terminal, and sterically hindered olefins; a summary of the reported activities in the hydrogenation of various substrates is provided in Table 5.1 [46–50]. The catalytic activity of the different halide complexes in the hydrogenation of methyl linolenate decreases in the order I>Br>Cl, but also when the iodide complex is used the activities remain extremely low, even at elevated temperatures and pressures [46]. Selective hydrogenation of polyunsaturated compounds to monounsaturated compounds is observed, as well as migration of the double bond and the isomerization of *cis*- to *trans*-alkenes. Nonconjugated dienes are assumed to be converted into conjugated dienes through migration of the double bonds. Subsequently, these conjugated dienes are hydrogenated to monoenes. Monoolefins are hardly further hydrogenated. The isomerization reaction was found not to occur in the absence of dihydrogen. Therefore, it was suggested that both the hydrogenation and isomerization reaction proceed *via* a monohydride species and that dihydrogen is activated via a heterolytic pathway [46].

Similar low activities were found in the hydrogenation of 1-octene [47]. The use of [Ni(PPh₃)₂I₂] in the hydrogenation of norbornadiene resulted in considerable amounts of nortricyclene, *via* transannular ring closure, whereas 1,5-cyclooctadiene yielded bis-cyclo-[3.3.0]oct-2-ene. According to these authors, the re-

Table 5.1 Hydrogenation of several substrates in the presence of the nickel complex $[\text{Ni}(\text{PPh}_3)_2\text{I}_2]$.^{a)}

Entry	Substrate	$p\text{H}_2$ [bar]	T [°C]	TOF ^{b)}	Main product	Reference
1	1,5,9-cyclododecatriene	78.5	175	165	cyclododecene	50
2	1,5,9-cyclododecatriene	50	100	1	cyclododecene	49
3	methyl linoleate	40	90	2	methyl oleate	46
4	1,3-cyclooctadiene	50	100	8	cyclooctene	49
5	1,5-cyclooctadiene	50	100	9	cyclooctene ^{c)}	49
6	2,5-dimethyl-1,5-hexadiene	50	100	7	2,5-dimethyl-2-hexene	49
7	2,5-dimethyl-2,4-hexadiene	50	100	8	2,5-dimethyl-2-hexene	49
8	isoprene	50	100	0		49
9	norbornadiene	50	100	29	nortricyclene ^{d)}	49
10	methyl oleate	40	90	0		46
11	methyl <i>cis</i> -9, <i>cis</i> -15-octadecadienoate	40	90	trace	monoene	48
12	1-octene	1	20	trace	<i>n</i> -octane	47

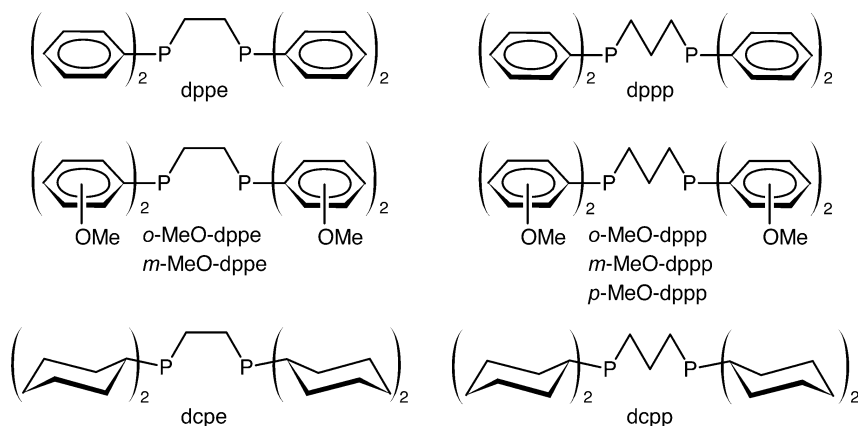
- a) Reaction conditions for entry 1: SCR=100, t =30 min, no solvent added; entries 2, 4–9: SCR=15 (59 for entry 8), t =1 h (30 min for entry 9), in acetic acid; entries 3, 10, 11: SCR=5 (9 for entry 11), t =3 h, in benzene.
- b) Turnover frequency in mol converted substrate per mol Ni per hour, calculated from data in [46–50].
- c) Transannular ring closure was also observed.
- d) *Via* transannular ring closure, nortricyclene is further hydrogenated to norbornane.

sults suggested the involvement of a η^3 -allyl-nickel intermediate in the catalytic cycle [49]. Kinetic studies have been undertaken for the hydrogenation of 1,5,9-cyclododecatriene to cyclododecene, using the catalyst $[\text{Ni}(\text{PPh}_3)_2\text{I}_2]$ under rather harsh conditions (155–175 °C, 80 bar) [50]. It was proposed that a monohydride–nickel complex is the active species, and dihydrogen activation was proposed to proceed via oxidative addition [50].

5.3.4

Nickel Complexes of Didentate Phosphane Ligands

The catalytic activity of nickel(II) acetate in combination with a number of chelating phosphane ligands in the hydrogenation of 1-octene has been studied extensively during the past decade [51–56]. It was found that *in-situ*-prepared mixtures of nickel(II) acetate with the electron-donating ligands *o*-MeO-dppe, *o*-MeO-dppp, dcpe, or dcpp (see Scheme 5.2) achieved quite high activities in the hydrogenation of 1-octene, the nonoptimized catalytic systems showing turnover numbers (TONs) of up to 460 per hour at 25 °C and 50 bar [51]. In



Scheme 5.2 Structure of the ligands used. dppe: 1,2-*bis*(diphenylphosphanyl)ethane; *o*-MeO-dppe: 1,2-*bis*(di(*o*-methoxyphenyl)phosphanyl)ethane; dcpe: 1,2-*bis*(dicyclohexylphosphanyl)ethane; *m*-MeO-dppe: 1,2-*bis*(di(*m*-methoxyphenyl)phosphanyl)ethane; dppe: 1,2-*bis*(diphenylphosphanyl)ethane; dppp: 1,3-*bis*(diphenylphosphanyl)propane;

o-MeO-dppp: 1,3-*bis*(di-*o*-methoxyphenylphosphanyl)propane; dcpp: 1,3-*bis*(dicyclohexylphosphanyl)propane; *m*-MeO-dppp: 1,3-*bis*(di(*m*-methoxyphenyl)phosphanyl)propane; *p*-MeO-dppp: 1,3-*bis*(di(*p*-methoxyphenyl)phosphanyl)propane.

contrast, use of the simple ligands dppe or dppp resulted in inactive systems; the results are summarized in Table 5.2 [51].

In a first attempt to separate electronic from steric effects of the *ortho*-methoxy group, the *meta* and *para* analogues of the methoxy-substituted ligands were also tested for hydrogenation activity. None of these showed any hydrogenation activity, however, seemingly indicating that the positive effect of the *ortho*-methoxy group should be attributed mainly to steric effects [51].

In order to explain the differences in catalytic activity of nickel compounds containing the various ligands, the behavior of the nickel complexes in solution was investigated in more detail, for which NMR spectroscopy appeared to be a valuable tool [54]. Using ^1H - and $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopy, the behavior of the complexes has been studied in several solvents. It appeared that, in solutions, the nickel complexes of the ligand *o*-MeO-dppe are involved in ligand-exchange reactions; the mono(ligand) complexes $[\text{Ni}(\textit{o}\text{-MeO-dppe})\text{X}_2]$ are in equilibrium with bis(ligand) complexes $[\text{Ni}(\textit{o}\text{-MeO-dppe})_2]^{2+}$ and “naked” (solvated) nickel ions $[\text{NiX}_4]^{2-}$ (see Scheme 5.3) [54]. The exact nature of the species “ NiX_4^{2-} ” is dependent on the solvent and the anions; in coordinating solvents it may exist as $[\text{Ni}(\text{solvent})_6]^{2+}$. The position of the equilibrium appeared to be highly dependent on the anion X and the solvent used. In a polar solvent in combination with weakly coordinating anions, only the bis(ligand) complex was observed, whereas in an apolar solvent in combination with coordinating anions only the mono(ligand) complex was present. From these studies it appeared that the differences in catalytic hydrogenation activity of nickel(II) acetate in combi-

Table 5.2 Nickel-catalyzed hydrogenation of 1-octene.^{a)}

Entry	Ligand	TOF _{1-octene} ^{b)}	S _{n-octane} ^{c)}	[Ni] [mM]	SCR
At 25 °C					
1	dppe	0		1.8	1000
2	dppp	2	100	1.8	1000
3	<i>o</i> -MeO-dppe	8	100	1.4	2000
4	<i>o</i> -MeO-dppp	500	100	1.4	2000
5	dcpe	2000 ^{d)}	98	3.6	500
6	dcpe	1740	80	1.4	2000
7	dcpp	360	97	3.6	500
At 50 °C					
8	dppe	0		1.8	1000
9	dppp	0		1.8	1000
10	<i>o</i> -MeO-dppe	400	94	1.4	2000
11	<i>o</i> -MeO-dppp	1160	99	1.4	2000
12	dcpe	1990	83	1.4	2000
13	<i>m</i> -MeO-dppe ^{e)}	0		3.6	500
14	<i>m</i> -MeO-dppp ^{e, f)}	0		3.6	500
15	<i>p</i> -MeO-dppp ^{f)}	10	0	3.6	500

a) Reaction conditions: Ni:ligand ratio=1, t=1 h, p_{H₂}=50 bar, in 20 mL methanol.

b) Turnover number in mol converted 1-octene per mol Ni(OAc)₂ after 1 h.

c) Selectivity towards *n*-octane (mol *n*-octane per mol converted 1-octene).

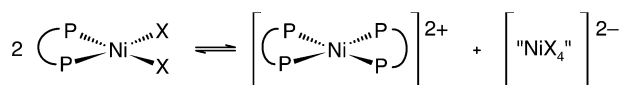
d) Complete conversion after 15 min.

e) No clear solution could be obtained after mixing nickel(II) acetate and the ligand.

f) Reaction performed in ethanol.

All data taken from [57].

nation with dppe or *o*-MeO-dppe could not be rationalized by the assumption that the bulkier ligand would prevent the formation of inactive bis(ligand) complexes. A comparison of the behavior of the nickel complexes of the ligand *o*-MeO-dppe with the unsubstituted analogue dppe showed that the latter ligand was more readily oxidized [54]. The source of the oxygen was unknown; as the experiments were carried out in an inert atmosphere the oxidation seemed to be related to the nickel(II) center, as observed previously [58]. It has been reported earlier that Pd(OAc)₂ is able to oxidize tertiary phosphanes [59]. This possibility of oxidation was found to play a major role in the case of the nickel complexes of the propane-bridged ligands *o*-MeO-dppp and dppp, as for both of these ligands the formation of bis(ligand) complexes is not possible, but only the substituted ligand *o*-MeO-dppp yields an active catalyst [53]. Prevention of oxidation of the phosphorus atom by the *ortho*-methoxy group is most likely due to steric effects; nickel(II) acetate in combination with *p*-MeO-dppp did not



Scheme 5.3 Schematic representation of the ligand-exchange equilibrium.

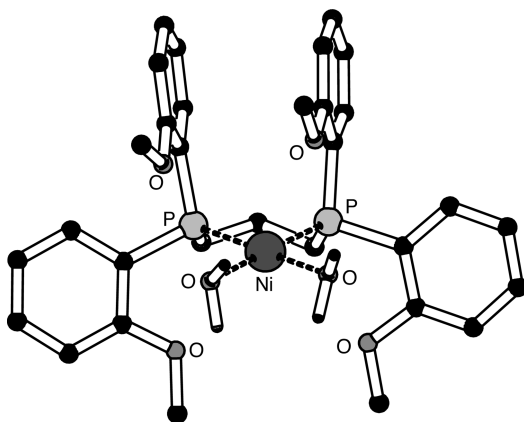


Fig. 5.3 Projection of $[\text{Ni}(o\text{-MeO-dppp})(\text{H}_2\text{O})_2]^{2+}$.

yield an active hydrogenation catalyst [51], and $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopy showed that also in this case the ligand is rapidly oxidized [54].

The inability to form a *bis*(ligand) complex with the ligand *o*-MeO-dppp is most likely due to a combination of the large bite angle caused by the propylene-bridge in the ligand, and the rather small ionic radius of the nickel(II) ion. Attempts to synthesize a *bis*(ligand) complex using the ligand *o*-MeO-dppp were unsuccessful. Instead, an unprecedented low-spin nickel complex containing two coordinated water molecules was formed – that is the complex $[\text{Ni}(o\text{-MeO-dppp})(\text{H}_2\text{O})_2](\text{PF}_6)_2$ (Fig. 5.3) [53]. This complex yields a highly active and selective hydrogenation catalyst, with a TOF of 2800 h^{-1} in the hydrogenation of 1-octene [55]. The impossibility to form a *bis*(ligand) complex might be the most important reason for the considerably higher hydrogenation activity of catalysts based on this ligand, compared to those based on *o*-MeO-dppe [53].

The catalytic activity of nickel(II) complexes of didentate phosphane ligands containing *ortho*-methoxy phenyl, *ortho*-ethoxy phenyl or cyclohexyl groups in the hydrogenation of 1-octene has been studied in more detail [55, 56]. The only observed side reaction in the hydrogenation of 1-octene is the isomerization to internal alkenes. The factors which influence the availability and accessibility of the coordination sites in the catalytically active species are solvent, anion, and amount and nature of ligand. The influence of these factors has been investigated using catalysts containing *o*-MeO-dppp, as these are not prone to ligand-exchange equilibria [55]. The presence of a solvent that is both polar and protic has been found to be essential in order to observe catalytic activity. This catalytic

activity is furthermore inversely related to the coordination ability of the anion. In the case of *o*-MeO-dppe, the catalyst is not active at all at a ligand-to-metal ratio higher than 2. In the case of *o*-MeO-dppp, the catalytic activity gradually decreases with increasing ligand-to-metal ratio. At a ratio of 5:1 an activity of 77 turnovers after 1 h is still observed, though the selectivity for hydrogenation has fallen considerably (70%). Although the ligand-exchange equilibrium occurs, the nickel complexes containing the ligands *o*-MeO-dppe and *o*-EtO-dppe still yield active hydrogenation catalysts. The presence of the more bulky ethoxy groups instead of the methoxy groups increases the hydrogenation activity by a factor of three, with the TOF rising from 400 h⁻¹ to 1200 h⁻¹; the selectivity for *n*-octane, however, is decreased from 99 to 65% [55]. The type of ligand merely influences the accessibility of the axial or equatorial coordination sites for the reactants, and hence the selectivity towards the hydrogenated product *n*-octane [55]. With the ligand dcpe, very active hydrogenation catalysts are obtained; at 50 °C and 50 bar H₂, TONs of up to 3000 h⁻¹ have been reached, although also in this case the selectivity was decreased to 88% [56].

The kinetics of the nickel-catalyzed hydrogenation of 1-octene have been studied using nickel(II) acetate in combination with the ligand *o*-MeO-dppp [52]. The effects of temperature and dihydrogen pressure, as well as the influence of nickel and substrate concentrations have been studied (T = 30–60 °C, p_{H₂} = 30–60 bar, [Ni] = 0.35–2.81 mM, [1-octene] = 0.98–3.91 M, ligand:Ni ratio = 1.1 in a mixture of dichloromethane and methanol). The kinetic study resulted in the surprisingly simple rate law: $r = k_{\text{cat}}[\text{Ni}][1\text{-octene}]p_{\text{H}_2}$. These kinetic data are consistent with a mechanism in which the terminating hydrogenolysis step of the nickel-alkyl complex is the rate-determining step of the catalytic cycle with all preceding steps at equilibrium. The first-order dependence in the nickel concentration indicates that dinuclear nickel complexes with bridging hydrides are not present during catalysis, and that thus only mononuclear nickel complexes are present [52]. This absence of dinuclear species is remarkable, as these dinuclear complexes are known for a number of didentate phosphane ligands (see Section 5.2.1). The first-order dependence of the substrate was confirmed by the results with other substrates, as the hydrogenation rate was seen to depend strongly on the nature of the substrate. The results for some different substrates are listed in Table 5.3 [52]. The rate of hydrogenation of the internal alkene cyclooctene was much lower than that of the terminal alkene 1-octene. The hydrogenation of ethene was found to be very rapid, with an estimated TOF of 9000 h⁻¹; this is quite unusual, as ethene is not hydrogenated by the generally very active Wilkinson's catalyst [60].

The homogeneous nature of the catalysts is confirmed by the linear dependence of the catalytic activity on the concentration of nickel(II). Only in the case of a truly homogeneous catalyst is the activity expected to be directly proportional to the catalyst concentration. In the case of the formation of nanoclusters, larger agglomerates – and, therefore, a comparatively lower number of active sites – will be formed at higher concentrations of the nickel salt. Furthermore, a sigmoidal curve for the rate of consumption of substrate has been proposed

Table 5.3 Different substrates in the homogeneous hydrogenation catalyzed by *in-situ* mixtures of Ni(OAc)₂ and *o*-MeO-dppp.^{a)}

Entry	Substrate	TOF ^{b)}	SCR	Main product
1	1-octene	1480	2000	<i>n</i> -octane
2	ethene ^{c)}	9000	2000	ethane
3	cyclooctene	30	400	cyclooctane
4	1,7-octadiene	30	1000	1-octene
5	styrene	0	200	
6	1-octyne	0	250	

a) Reaction conditions: [Ni]=2.5 mM (before substrate is added), t=1 h, p_{H₂}=50 bar, T=50 °C, in 20 mL dichloromethane/methanol (1:1, v/v).

b) Turnover is mol converted substrate per mol nickel in 1 h.

c) T=40 °C and t=10 min.

All data taken from [52].

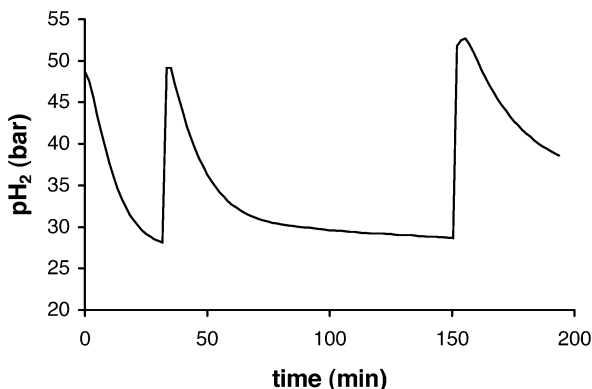


Fig. 5.4 Dihydrogen pressure drop of the hydrogenation of 1-octene using an *in-situ*-formed catalyst containing Ni(OAc)₂ and the ligand *o*-MeO-dppe. After 30 and 150 min, fresh 1-octene is added to the reaction mixture and the H₂ pressure is reset to 50 bar. (Reproduced from [57])

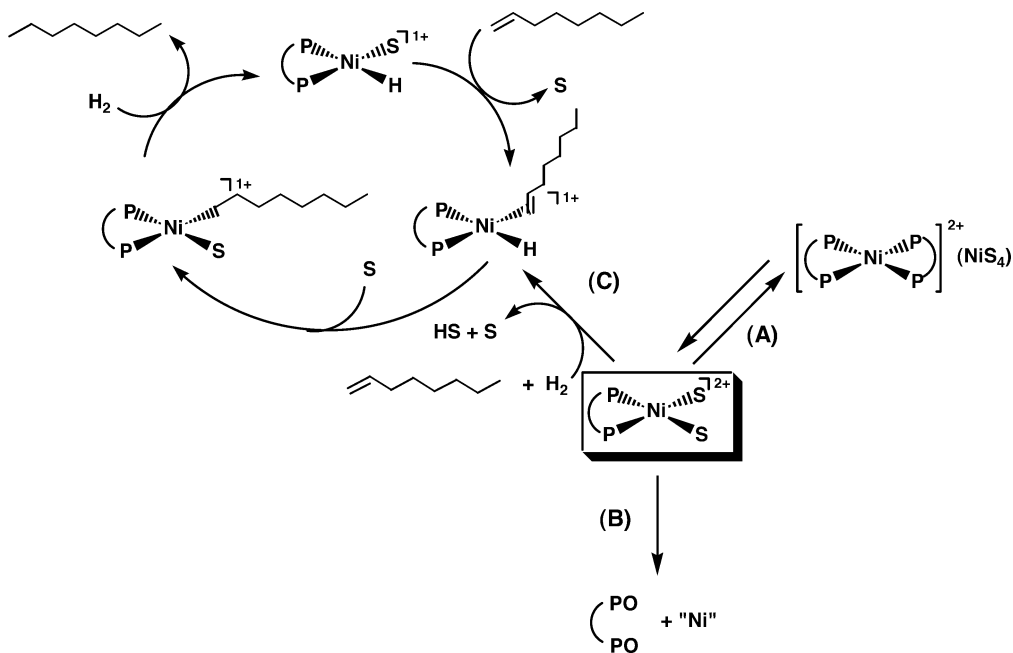
as being characteristic for the nanocluster formation reaction [5]. For the nickel(II) catalysts with didentate phosphane ligands the hydrogenation reaction starts immediately without any induction period (Fig. 5.4) [57]. In addition, it is possible to regenerate the catalysts from the reaction mixtures after the hydrogenation experiments. These results – in combination with the observation that pure nickel(II) acetate does not lead to an active catalyst under the applied reaction conditions (50 °C) and the excellent reproducibility of the results – lead to conclusion that the reported nickel(II) complexes of didentate phosphane ligands yield truly homogeneous hydrogenation catalysts.

5.4 Concluding Remarks

Many Ziegler-type catalytic systems, in addition to a few mononuclear nickel complexes of nitrogen- or oxygen-containing ligands, have been reported as being homogeneous hydrogenation catalysts for a number of substrates. In most of these cases, it is doubtful whether the reported nickel complexes really yield homogeneous hydrogenation catalysts; it is more likely that catalytic hydrogenation activity is due to formation of colloidal (heterogeneous) nickel particles. Despite the recent report of a nickel(IV) hydride species [20], the assumption that dihydrogen activation in these catalytic systems would proceed via oxidative addition remains dubious.

Nickel(II) complexes with the correct choice of a didentate phosphane ligand do yield very active homogeneous hydrogenation catalysts. It has been found that nickel complexes with chelating diphosphane ligands may be involved in three different processes, namely ligand-exchange reactions, ligand oxidation, and the actual hydrogenation reaction (see Scheme 5.4).

The larger bite angles of the C_3 -bridged ligands preclude the ligand-exchange equilibrium, the ionic radius of the nickel(II) ion being too small to accommo-



Scheme 5.4 Three processes in which nickel diphosphane complexes can be involved under catalytic hydrogenation conditions. (A) ligand exchange; (B) oxidation; and (C) hydrogenation of 1-octene. For simplicity, the reac-

tion steps are not depicted as equilibria and the isomerization reaction has been omitted. In this scheme, S depicts a solvent molecule, but it might also be an anion.

date two of these didentate ligands in a square-planar geometry. Considering the C₂-bridged ligands, only dcpe (see Scheme 5.2) has a ligand cone that is large enough to prevent coordination of a second didentate ligand. It is assumed that the nickel(II) ion catalyzes the oxidation of tertiary phosphane ligands. This oxidation appeared to be very rapid in the case of the unsubstituted ligands dppe and dppp, whereas it is relatively slow for *o*-MeO-dppe and *o*-MeO-dppp. Most probably, the electronic properties of the ligand influence the oxidation sensitivity of the ligand in the presence of nickel.

If the ligand-exchange reaction, as well as oxidation of the ligand, could be prevented, then the formation of highly active hydrogenation catalysts with simple diphosphane ligands might be possible. Consequently, the bulk application of inexpensive, nickel-containing homogeneous hydrogenation catalysts might come within reach.

Abbreviations

SCR substrate:catalyst ratio
 TOF turnover frequency
 TON turnover number

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