

Catalyst Deactivation by β -Hydride Elimination: Olefin and Alkyne Insertion into Arenido–Nickel(II) Bonds

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Square planar arenido-(triphenylphosphane)nickel(II) complexes (**3**) containing a N,O-chelate ligand are catalysts for the carbon monoxide/ethene copolymerisation reaction. Pathways for catalyst deactivation have been elucidated by investigating the reactions of such complexes with aliphatic unsaturated compounds like olefins and alkynes. We have shown that the double or triple bond, respectively, inserts into the nickel–carbon bond followed by β -hydride elimination resulting in aryl-substituted olefins and allenes, which

have been identified by means of GC/MS. The remaining nickel forms a bis(N,O-chelate ligand)nickel complex, the crystal structure of which has been determined. The nickel atom is coordinated in a square-planar manner by two ligands. Additional coordination of two neighbouring complexes via their nitrile groups completes the coordination of the nickel to a distorted octahedron and forms a two-dimensional metal-organic framework (MOF).

Introduction

The Shell Higher Olefins Process (SHOP) is one of the most important catalytic processes of industrial relevance performed with nickel complexes.^[1,2] The worldwide production capacity amounts to more than 10^6 t/a forming linear α - and internal olefins of a chain length between C₈ and C₂₀. SHOP includes oligomerisation of ethene as well as isomerisation of olefins and olefin metathesis. The oligomerisation of ethene is performed with the nickel catalyst **1** (see Figure 1).

Ethylene polymerisation can be achieved with similar nickel catalysts, e.g. with complexes comprising N,O-chelate ligands instead of a P,O-ligand, like the ones described by Brookhart with an anilinetropone ligand (**2**, Figure 1).^[3]

The SHOP catalysts and the anilinetropone complexes of Brookhart show structural similarity to the nickel complexes **3a** and **3b** described in this work (Figure 2) and perform similar reactions like insertion of olefins and successive β -hydride elimination, which will be discussed below. The complexes discussed here contain a N,O-chelate ligand and were found to catalyse – unlike the SHOP catalysts – the copolymerisation of ethene and carbon monoxide to yield polyketones.^[4]

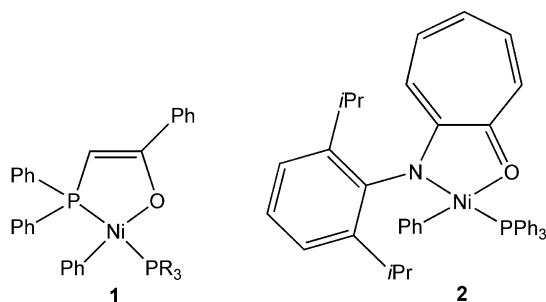


Figure 1. SHOP catalyst **1** and the ethene polymerisation catalyst **2** studied by Brookhart.

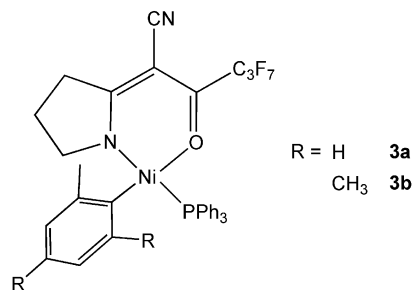


Figure 2. Nickel catalysts active in the copolymerisation reaction of ethene and carbon monoxide.

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lost, nickel complexes could provide a low cost alternative. The nickel complexes shown here are the best ones to date in terms of efficiency to catalyse the synthesis of polyketones. In order to increase the efficiency and to understand the reaction we varied the substituents on the N,O-chelate ligand.^[12] To inhibit decomposition, which occurs during the catalysis, and thus to prolong the lifetime of the catalyst it is of vital interest to investigate the pathways of decomposition.

The reactions of the complexes **3a** and **3b** with aliphatic olefins and alkynes in the absence of carbon monoxide and the products thereof will be discussed in this work.

Results and Discussion

Complexes **3a** and **3b** (Figure 2) react with unsaturated compounds such as aliphatic olefins and alkynes. For our investigation we used 1-heptene, 1-hexene, 2-hexyne, 2-heptyne as well as cyclopentene and cyclohexene and elucidated the reaction pathway leading to the formed products. In all cases the yellow solution of the complexes **3a** and **3b** dissolved in the mentioned unsaturated compounds turned cloudy and colourless with time. The reaction of the complexes **3a** and **3b** with 1-heptene and 1-hexene, respectively, is finished within days and with 2-hexyne and 2-heptyne within hours at ambient temperature.

Characterisation of the Precipitated Reaction Products

The whitish precipitate formed was characterised by IR spectroscopy and mass spectrometry and turned out to be a mixture of the bis(N,O-chelate ligand) nickel complex NiL_2 (**5**) (Scheme 1), triphenylphosphane and triphenylphosphane oxide, respectively. The identity of NiL_2 (**5**) was confirmed independently by synthesising it in 93% yield from nickel(II) bromide and 4,4,5,5,6,6,6-heptafluoro-3-oxo-2-[pyrrolidin-(2Z)-ylidene]hexanenitrile,^[12] the N,O-chelate ligand HL (**4**), in the presence of a base (Scheme 1).

We assume that in the reaction of the complexes **3a** and **3b** with olefins and alkynes NiL_2 (**5**) is most likely formed via a nickel-hydride intermediate resulting from a β -hydride elimination (see below).

NiL_2 (**5**) is a highly insoluble paramagnetic compound the crystal structure of which was determined by X-ray diffraction studies (Figure 3). The complex NiL_2 (**5**) crystallises in the centrosymmetric, orthorhombic space group *Pbca*, with the nickel being the centre of symmetry. The nickel(II) atom is coordinated primarily in a square planar manner by two N,O-chelate ligands. The coordination sphere is completed by two nitrile functions of two neighbouring complexes resulting in a distorted octahedral environment. By this axial interaction of the nitrile nitrogen to an adjacent nickel centre a two-dimensional “metal-organic framework” is formed (see Figure 4). The polymeric structure consists of layers, which are composed of combs of four nickel centres each as depicted in Figure 4. The distance between two consecutive planes of nickel atoms corresponds to the half of the cell constant *c*, *c*/2 = 10.015 Å. Each comb of the framework is incompletely filled with two perfluorinated side chains of the ligands, resulting in a

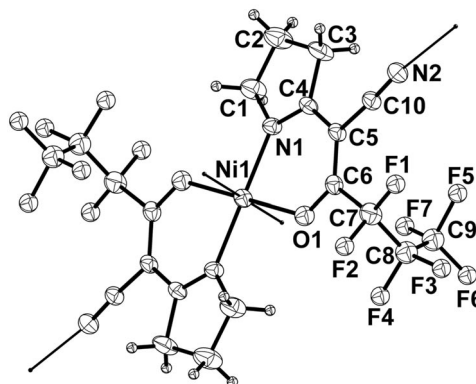
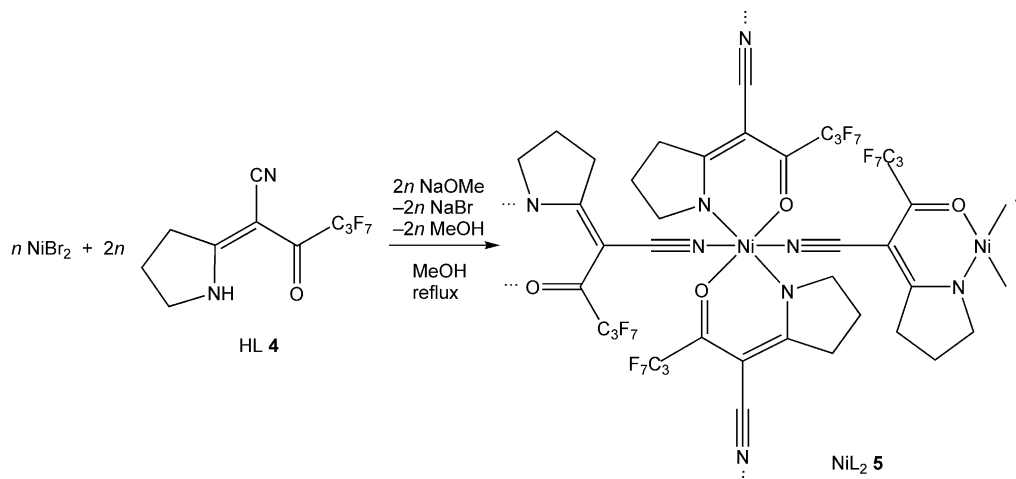


Figure 3. Molecular structure of complex NiL_2 (**5**), only basal coordination plane shown. All but the fluorine atoms (arbitrary radius) are shown at 50% probability level.



Scheme 1. Synthesis of the bis(N,O-chelate ligand)-nickel complex NiL_2 (**5**).

rhombic shape with the angles being 105.88° and 74.12°, respectively. The axial Ni–nitrile bond length (2.11 Å) is significantly longer than distances for such bonds documented in the literature. A bis(N,O-chelate ligand)-nickel complex, with the N,O-chelate ligand being an α -iminoketone, and two acetonitrile ligands in *trans*-position exhibits a Ni–NC bond length of 2.05 Å.^[13] The distance of the Ni–N bond in [Ni(MeCN)₆]²⁺ ranges from 2.07 to 2.08 Å with various counteranions.^[14,15] The coordination bond between nitrogen and nickel is the only position in this framework, which is flexible enough to be adjusted. Apparently, to achieve the required space for the two C₃F₇ chains in the comb of the framework the bond between nickel and the nitrogen atom of the nitrile group is elongated.

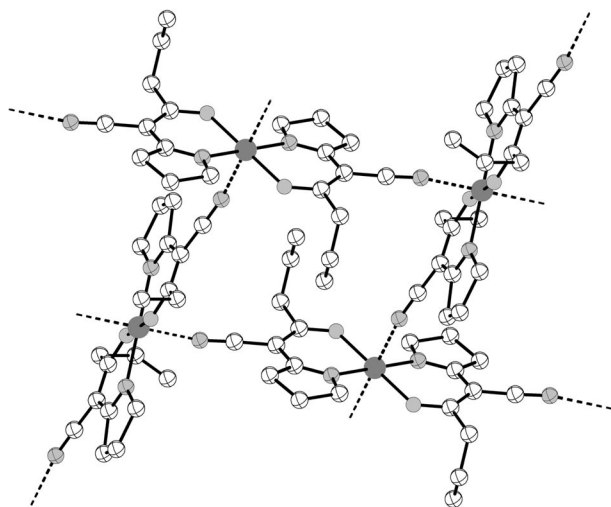


Figure 4. Perspective view of four units of NiL₂ (**5**). Hydrogen and fluorine atoms are omitted for clarity (arbitrary radius of all atoms).

The formation of this two-dimensional coordination polymer explains why NiL₂ (**5**) is only soluble in strong donor solvents like dmso.

Figure 4 shows the square-planar coordination planes of four adjacent complex molecules with coplanar Ni atoms in the polymer. The planes intersect nearly rectangularly at ca. 82.35°.

The IR spectrum of NiL₂ (**5**) supports the findings of the crystal structure. The absorption of the C≡N stretching vibration at 2238 cm^{−1} is remarkable as it is shifted to higher frequencies compared to 2212 cm^{−1} in the corresponding vibration in the free ligand. The C≡N stretching vibration of **3a** also amounts to only 2216 cm^{−1}. This confirms a coordination via the nitrogen atom of the nitrile group to the nickel centre of a neighbouring complex as a coordination at the nitrile group results in a higher stretching frequency.^[16] The crystal structure shows that the C≡N bond length in NiL₂ (**5**) is significantly longer than the one in **3a** (see Table 1).

In the literature the crystal structure of a similar bis-ligand copper(II) complex is documented, with the N,O-chelating ligand being 3-oxo-3-phenyl-2-(pyrrolidine-2-ylidene)-propanenitrile.^[17] Like NiL₂ (**5**), the compound forms a

Table 1. Selected interatomic distances [Å] and angles [°] in NiL₂ (**5**) and **3a**.^[4]

	NiL ₂ (5)	3a
Ni(1)–N(1)	2.031(4) Å	1.926 Å
Ni(1)–O(1)	2.034(3) Å	1.918 Å
Ni(1)–N(2)C(10)	2.108(4) Å	–
N(2)≡C(10)	1.143(6) Å	1.135 Å
Angle of the planes of adjacent molecules of the complex	82.35°	–
Bite angle N(1)–Ni(1)–O(1)	91.96(13)°	91.13°

two-dimensional coordination polymer, making up combs of four copper centres with a coordination of the nitrile group to an adjacent copper centre.

Characterisation of the Reaction Products in the Solution

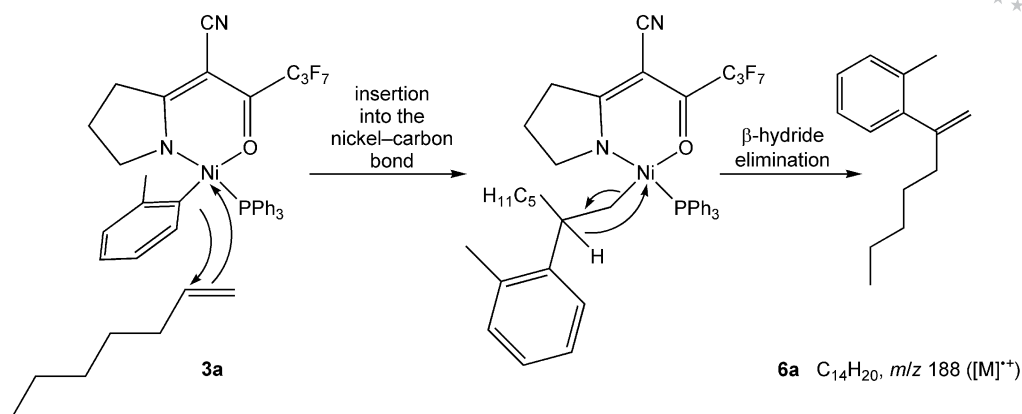
The products of the reaction of **3a** and **3b** with cyclic (cyclopentene and cyclohexene) and non-cyclic (1-heptene, 1-hexene, 2-hexyne and 2-heptyne) unsaturated compounds were analysed with GC/MS.

In the case of 1-heptene, 1-hexene, 2-hexyne and 2-heptyne we found that β -hydride elimination through insertion of the unsaturated compound into the arenido–nickel bond takes place at ambient temperature. This was proved by the β -hydride elimination products found in the GC/MS spectra. This is similar to the SHOP oligomerisation where ethene is repeatedly inserted into the nickel–hydride bond, which is formed in a first step. The α -olefin is then likewise released via β -hydride elimination.^[1,2] In contrast to the SHOP process our catalysts **3a** and **3b** are deactivated by β -hydride elimination after the first insertion of a higher olefin.

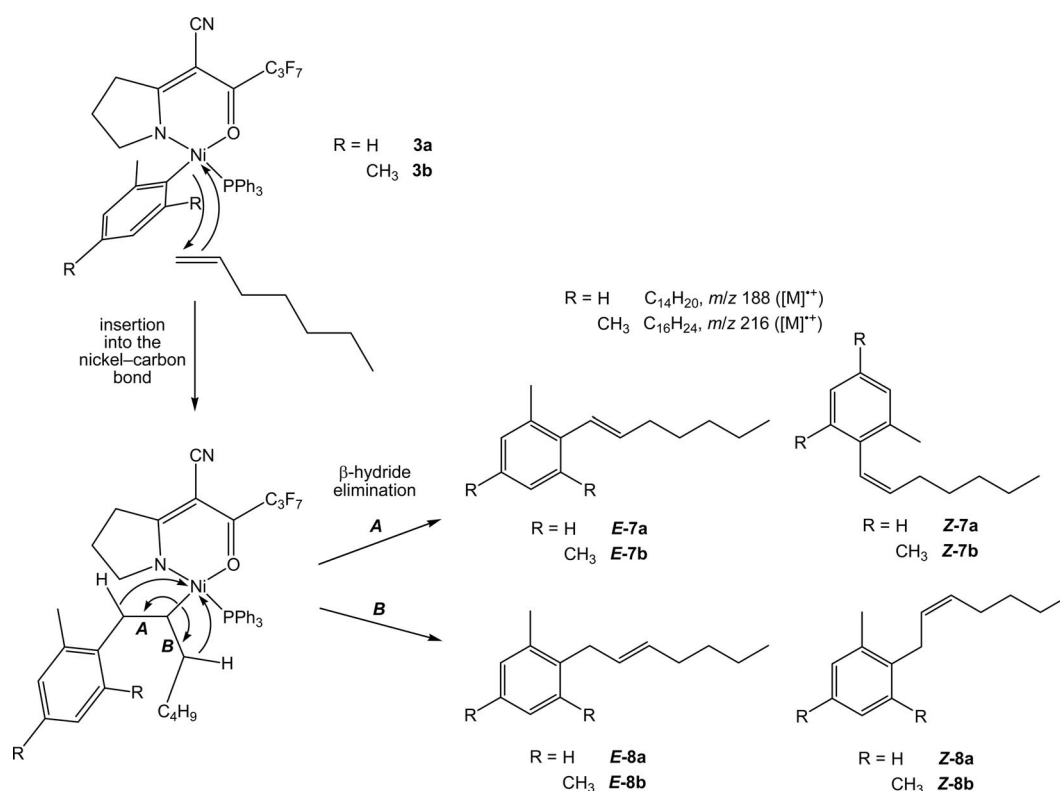
The insertion of ethene into **3a** has been investigated as well. Here we also find the β -hydride elimination product, 2-methyl styrene, showing a mass spectrum with the molecular ion m/z 118 ([M]⁺). However, if **3a** is reacted with 70 bar of ethene at room temp., the polymerisation of ethene is significantly faster than the β -hydride elimination so that polyethylene is produced in high yields.

For 1-heptene, according to the pathway depicted in Schemes 2 and 3 five isomers are possible depending on how the olefin is orientated towards the nickel centre and the arenido ligand before inserting into the nickel–carbon bond. 1-Heptene can bind to nickel with C-1 (Scheme 2) or C-2 (Scheme 3). After olefin insertion β -hydride elimination can occur in two different ways, denoted **A** and **B** in Scheme 3. Of the five isomers one contains a terminal double bond (**6a**) and two have an internal double bond (**7a**, **7b** and **8a**, **8b**), the latter showing *E/Z* isomerism.

In the case of the 2-toluenido complex **3a** all of the five proposed isomers were found in the gas chromatogram and identified by means of EI mass spectra. These isomers appear in the gas chromatogram with different retention times (see Supporting Information) and they all show mass spectra with the molecular ion m/z 188 ([M]⁺). Four of the EI



Scheme 2. Mechanism of the β -hydride elimination with 1-heptene, insertion of the double bond resulting in a bond to the nickel atom via C-1.



Scheme 3. Mechanism of the β -hydride elimination with 1-heptene, insertion of the double bond resulting in a bond to the nickel atom via C-2, all possible isomers are shown (“a” isomers originate from the reaction with complex **3a**, “b” isomers from the reaction with complex **3b**).

spectra differ only in the intensity of the fragments, while the fifth shows a different fragmentation pattern. We assume that this EI spectrum belongs to **6a**, while the other four spectra can be related to the other isomers, **E-7a**, **Z-7a**, **E-8a** and **Z-8a**. The reasons for this will be discussed below.

Although the isomers **7a** and **8a** vary in the position of the double bond in the alkyl chain, their EI spectra show an identical fragmentation pattern, differing solely in the intensity of the fragments. This allows no correlation of the isomers to the spectra. This phenomenon is well docu-

mented in the literature.^[18] In 1969 Gerrard and Djerassi investigated the EI mass spectra of a series of isomeric phenylheptenes and found that they exhibited double bond mobility upon electron impact and therefore all isomers showed nearly identical mass spectra. The examined 1-phenylheptenes underwent skeletal and hydrogen rearrangements; for instance, the base peak $[M - C_4H_9]^+$ of these spectra results from a rearrangement of the molecule ion including a 1,3-hydrogen shift. For this reason the spectrum of **7a** does not show a peak for $[M - C_5H_{11}]^+$, also evident for the rearrangement process.

Hence the four β -hydride elimination products of **3a** with 1-heptene, **E-7a**, **Z-7a**, **E-8a** and **Z-8a**, are distinctly characterised by very similar EI mass spectra, all with a molecular ion m/z 188 ($[M]^+$) and a base peak $m/z = 131$, $[M - C_4H_9]^+$, resulting from an allyl or an alkyl cleavage. The fragmentation in the EI spectrum of **7a** and **8a** is consistent with the EI mass spectrum of 1-phenylhept-1-ene.^[19]

The EI mass spectra of the β -hydride elimination products of **3b** with 1-heptene, **7b** and **8b**, can be interpreted analogously. Fragmentation pattern and mass differences are identical.

The EI mass spectrum of the isomer **6a** (see Scheme 2) shows a different fragmentation pattern, also with a molecular ion m/z 188 ($[M]^+$), but a base peak of $m/z = 132$, which is evoked by a McLafferty rearrangement and corresponds to $[M - C_4H_{10}]^+$. The fragmentation conforms to the EI spectrum of 2-phenylhept-1-ene.^[20]

The GC/MS analysis of the reaction of **3a** with 1-heptene shows that all five possible isomers **6a**, **E-7a**, **Z-7a**, **E-8a** and **Z-8a** are formed, as discussed above. The reaction of the mesitylenido complex **3b** with 1-heptene yields only two of the five possible isomers.

It is probably the steric hindrance of the arenido ligand that inhibits the reaction pathway shown in Scheme 2 and leads to the formation of only one pair of *E/Z* isomers through the pathway of Scheme 3. The influence of the second *ortho*-methyl group would also account for the slower decomposition of the mesitylenido complex **3b** in comparison to the 2-toluenido complex **3a**. Which of the two *E/Z* isomer pairs is formed (**7b** or **8b**) cannot be stated as there is no apparent reason which rotamer could be favoured.

To unambiguously approve the aforesaid findings, we conducted the same experiment using 1-hexene instead of 1-heptene. We found all five corresponding isomers from the reaction with **3a** and two corresponding isomers from the reaction with **3b**, as expected.

Triphenylphosphane in Excess Does Not Inhibit β -Hydride Elimination

Fast β -hydride elimination counteracts the polymerisation of olefins. Added triphenylphosphane might prolong the lifetime of the catalyst by suppressing β -hydride elimination or it might prolong the lifetime of the nickel-hydride species to allow the repeated insertion of olefins. Different effects of added triphenylphosphane are documented in the literature. According to Brookhart^[21] added triphenylphosphane has no influence on the polymerisation of ethene with catalyst **2**, while Grubbs^[22] states that additional triphenylphosphane suppresses the polymerisation with nickel complex **9** (Figure 5).

Additional experiments with excess triphenylphosphane added to the reaction of complexes **3a** and **3b**, respectively, with 1-heptene were carried out. In both cases the corresponding β -hydride elimination products were formed, regardless of the amount of triphenylphosphane present. Apparently an excess of triphenylphosphane has no influence

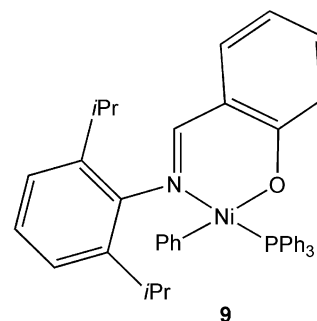


Figure 5. Ethene polymerisation catalyst **9** studied by Grubbs.^[22]

on the insertion of 1-heptene into the nickel–carbon bond nor on the β -hydride elimination. This is in favour of an associative mechanism in which the complex and the coordinating olefin react to an intermediate five-coordinate species before the olefin inserts into the arenido–nickel bond.

One of the referees of this article has pointed out that we cannot exclude a dissociative mechanism with the N,O-chelate ligand acting as a hemilabile ligand.^[23] During this pathway one donor function of the anionic and rather rigid N,O-chelate ligand would reversibly unblock a coordination site to which the incoming olefin can coordinate. In case of a dissociation of the O-donor function the olefin would be coordinated *trans* to the arenido ligand and the complex would still have to isomerise to allow insertion into the arenido–nickel bond.

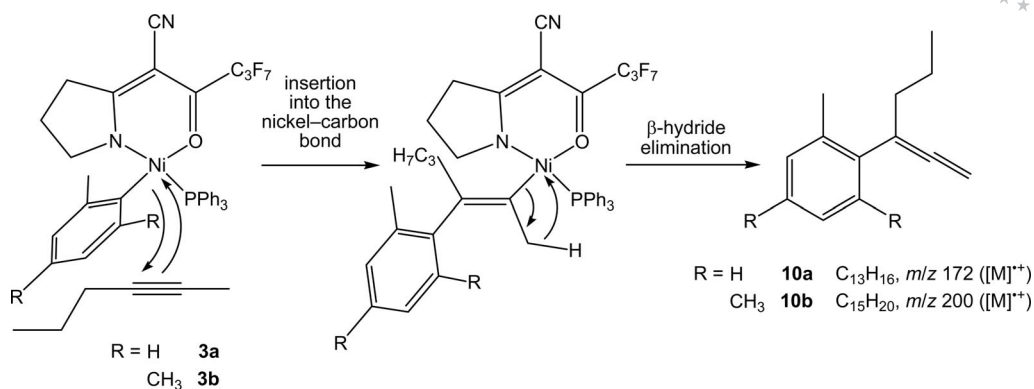
Heinicke has reported on related catalytically active nickel(II) complexes with anionic P,O-chelate ligands *in lieu* of our N,O-ligand. With trimethylphosphane a catalytically five-coordinate nickel complex of type $[NiMe(PMe_3)_2-(P,O)]$ ^[24] could even be prepared and structurally characterised.

Reaction of Complexes **3a** and **3b** with Alkynes Leads to the Formation of Allenes

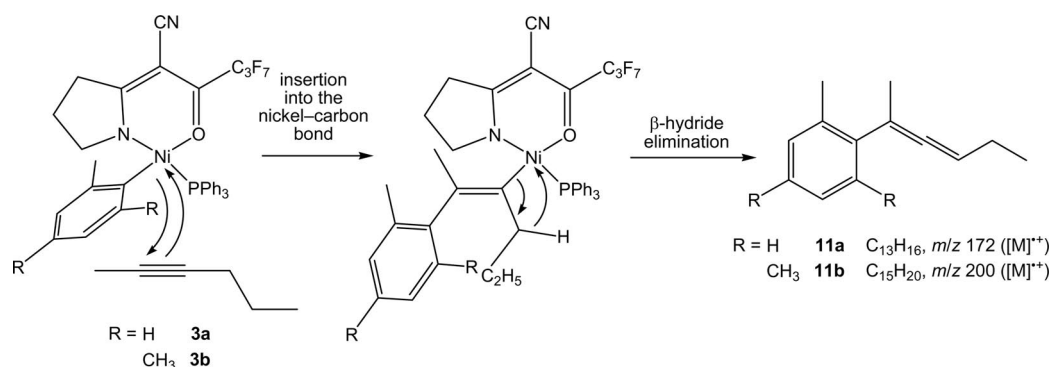
Complexes **3a** and **3b** react likewise with 2-hexyne. The insertion of alkynes into nickel(II)-arenido bonds is described in the literature, although only with sterically demanding alkynes, which do not show β -hydride elimination.^[25,26] The formation of allenes through β -hydride elimination has been reported on silver(111) surfaces where allyl moieties are activated to afford 1,2-propadiene.^[27]

Analogously to the mechanistic pathway of the reaction with 1-heptene described above the alkyne can be inserted into the nickel–carbon bond in two different ways (see Schemes 4 and 5), forming two isomeric allenes. If the 2-hexyne molecule binds with atom C-2 to the nickel atom, as depicted in Scheme 4, a terminal allene (**10a**, **10b**) is formed. On the contrary, according to Scheme 5 an internal allene is generated, with *R/S* enantiomers (**11a**, **11b**), when binding occurs at atom C-3.

Both isomers are found in the gas chromatogram of **3a** with 2-hexyne (**10a** and **11a**) as well as in the gas chromatogram of **3b** with 2-hexyne (**10b** and **11b**) and were identified by their EI mass spectra.



Scheme 4. Mechanism of the β -hydride elimination with 2-hexyne, insertion of the triple bond resulting in a bond to the nickel atom via C-2.

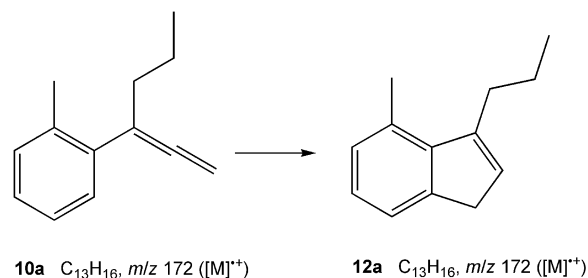


Scheme 5. Mechanism of the β -hydride elimination with 2-hexyne, insertion of the triple bond resulting in a bond to the nickel atom via C-3.

The EI mass spectra characterise all four isomers distinctly. The EI spectrum of isomer **10a** shows a molecular ion of $m/z \, 172 \, ([\text{M}]^{+})$ with the base peak of $m/z = 129$ resulting from $[\text{M} - \text{C}_3\text{H}_7]^{+}$. Consistent with this spectrum is the EI mass spectrum of **10b**, which is only shifted by the mass of two methyl groups to a molecular ion $m/z \, 200 \, ([\text{M}]^{+})$. The EI mass spectrum of **11a** also has a molecular ion of $m/z \, 172 \, ([\text{M}]^{+})$. Here the base peak $m/z = 143$ is evoked by the fragment $[\text{M} - \text{C}_2\text{H}_5]^{+}$. The spectrum of **11b** is in accordance with this spectrum. The parent compound 2-phenyl-2,3-hexadiene causes a similar EI spectrum.^[28]

The reaction of the 2-toluenido complex **3a** with 2-hexyne leads to a further product with an EI spectrum very similar to the one of isomer **10a**, which only differs in the intensity of the fragments. This product is absent in the reaction of **3b** in 2-hexyne as is evident from the comparison of the two gas chromatograms. Especially the intensity of the molecular ion $m/z \, 172$ in this spectrum is a lot higher indicating a more stable molecule than **10a**. This can be explained by a rearrangement of **10a** to **12a** as shown in Scheme 6.

Such rearrangements are long since documented in the literature.^[29–31] This rearrangement cannot occur with the β -hydride elimination product of the mesitylenido complex **3b**, as in **10b** the *ortho* position of the aryl substituent is



Scheme 6. Rearrangement of **10a**.

blocked by a methyl group. A possible mechanistic explanation could be a metal-catalysed cycloisomerisation of the allene **10a**. This could take place through activation of the distal π -bond of the allene by coordination of the electrophilic nickel(II) present in the solution, followed by an *endo* attack of the nucleophilic aromatic ring and formation of the product through protodemetalation of the intermediate.^[32] The EI spectrum of **12a** is consistent with the EI mass spectrum of 1-propyl-3*H*-indene.^[33]

The reaction of 2-heptyne with the complexes **3a** and **3b**, respectively, lead to products corresponding to the ones with 2-hexyne. The EI spectra of the β -hydride elimination products (Figure 6) thereof are in accordance with the β -

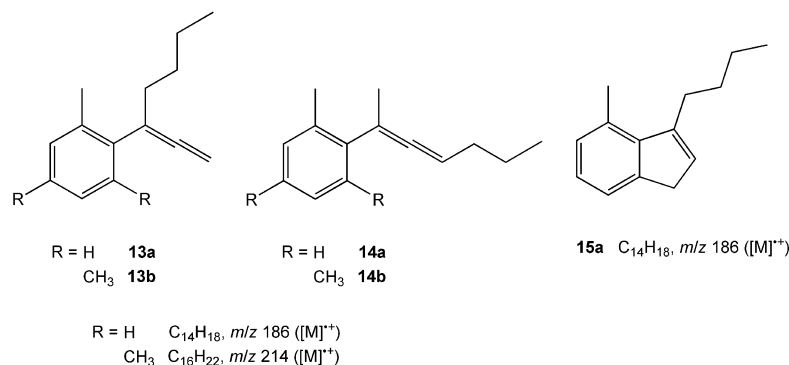


Figure 6. Isomers found in the reaction of 2-heptyne with the complexes **3a** and **3b**, respectively.

hydride elimination products of 2-hexyne, just shifted by one CH_2 unit. Also the ratio of the intensities in the gas chromatograms are very alike.

Apart from the β -hydride elimination products we also found 2-methylphenol and 2,4,6-trimethylphenol as consequence of a different reaction mechanism. The alcohols of the arenido ligand are probably formed by oxidative cleavage of the nickel–carbon bond. This reaction is rather slow and when the experiments in 1-heptene are carried out under nitrogen, the oxidative pathway is suppressed to a large extent. According to the gas chromatograms the main reaction pathway is the β -hydride elimination. The β -hydride elimination with 2-hexyne is so much faster that the oxidative cleavage of the nickel–carbon bond is not observed.

We also performed the experiment with cyclopentene and cyclohexene, respectively, to see whether β -hydride elimination can be suppressed when using cyclic olefins. A precondition for β -hydride elimination is the roughly coplanar orientation of the metal, the α and the β carbon atom as well as the hydrogen atom that is to be eliminated. This orientates the β -H close to the metal.^[34] A look at the intermediate after the insertion of 1-heptene into the nickel–carbon bond (see Scheme 2) shows that the hydrogen atoms in β -position can easily be brought into a conformation suitable for β -hydride elimination (Figure 7, **16**). If the insertion of cyclopentene or cyclohexene takes place, a conformation that allows β -hydride elimination is difficult to achieve (Figure 7, **17**) therefore a potential insertion product would be more stable towards β -hydride elimination.

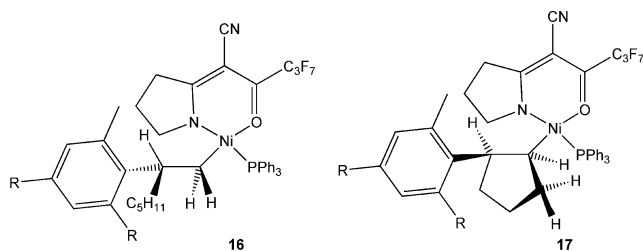


Figure 7. Conformation of the intermediate after the insertion of the olefin into the nickel–carbon bond (**16** 1-heptene, **17** cyclopentene) suitable for β -hydride elimination.

No sign of β -hydride elimination was found for the reaction of the complexes **3a** and **3b** with cyclopentene and cyclohexene. Instead of β -hydride elimination products we only found the arenido ligand in 2-methylphenol and 2,4,6-trimethylphenol, respectively, which suggest an oxidative cleavage of the nickel–carbon bond. In fact the decomposition of the complexes took much longer in the absence of oxygen or did not take place at all.

It is probably the steric demand or the steric rigidity that hinders the insertion of the cycloolefins and the β -hydride elimination.

In a further experiment an excess of cyclopentene was added to complex **3a**, dissolved in deuteriated benzene, and the reaction was monitored for several weeks with NMR spectroscopy. Neither the ^1H NMR nor the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum gave a hint for insertion of cyclopentene into the nickel–carbon bond. Therefore according to these NMR experiments an insertion of cyclopentene does not take place.

Conclusions

Both complexes **3a** and **3b** are air-stable in solid state and do not decompose in toluene solution for several days, or under heating to reflux for several hours, respectively. They react relatively fast with olefins and alkynes. The reaction of **3a** and **3b** with 1-heptene and 1-hexene, respectively, is completed within days and with 2-hexyne and 2-heptyne within hours at ambient temperature. We have shown that 1-heptene, 1-hexene, 2-hexyne and 2-heptyne insert into the nickel–carbon bond of the square-planar nickel(II) complexes described here and subsequently form β -hydride elimination products comprising several isomers. The products of the insertion of 1-heptene and 1-hexene lead to olefins, while the products of the insertion of 2-hexyne and 2-heptyne produce allenes. Although β -hydride elimination is widely known as a decomposition pathway of organo transition metal complexes the formation of allenes through β -hydride elimination has only been described to occur on silver(111) surfaces.^[27]

The resulting nickel-hydride species decomposes to form the bis(N,O-chelate ligand)nickel complex **NiL₂ (5)**, the crystal structure of which has been determined. Upon ad-

dition of excess triphenylphosphane to the reaction with 1-heptene the β -hydride elimination following the insertion into the nickel–carbon bond is not suppressed. The stability of the complexes in solution significantly increases from the 2-toluenido complex to the mesitylenido complex by at least an order of magnitude when exposed to air as well as under inert conditions.

Compared to our complexes the SHOP catalyst **1** is able to form a stable nickel-hydride intermediate, which is necessary for a repeated insertion of olefins. Complexes **3a** and **3b** do not repeatedly insert higher olefins as no stable nickel-hydride complex is formed, the latter being a precondition for oligomerisation. The observed β -hydride elimination apparently takes place much faster than the insertion of the olefins. However, the nickel complexes **3a** and **3b** are catalytically active in the strictly alternating copolymerisation of carbon monoxide and ethene.^[4] Obviously here the insertion of CO is much faster than the β -hydride elimination. We assume that catalyst deactivation i.e. the termination of the copolymerisation reaction is the result of a β -hydride elimination.

Experimental Section

General Procedures: Infrared spectra were recorded on a FT-IR Bruker IFS 66 spectrometer. EI-MS data and FAB-MS spectra were recorded on a Finnigan MAT 8200 in a 3-nitrobenzylalcohol matrix. GC/MS spectra were determined on a Thermo Finnigan Trace GC-Ultra Trace DSQ comprising a column of 15 m length with 0.25 mm in diameter and a DB5MS phase. Injection temperature was 220 °C, column temperature increased starting at 50 up to 250 °C with 20 °C min⁻¹. %Area is listed as intensity of the signal in the gas chromatogram. One-dimensional NMR spectra were recorded at room temperature, proton and ³¹P NMR spectra on a Bruker Avance DRX 200 spectrometer. Unless otherwise stated chemicals were purchased from commercial sources, used as received and dried and degassed by standard methods. 4,4,5,5,6,6,6-Heptafluoro-3-oxo-2-[(2Z)-pyrrolidin-2-ylidene]hexanenitrile^[12] (**4**) and the complexes **3a**^[4] and **3b**^[35] were prepared according to literature procedures.

Bis{4,4,5,5,6,6,6-heptafluoro-3-oxo-2-[(2Z)-pyrrolidin-2-ylidene]hexanenitrilo}nickel(II) (5): Nickel(II) bromide (0.44 g, 2.0 mmol), 4,4,5,5,6,6,6-heptafluoro-3-oxo-2-[(2Z)-pyrrolidin-2-ylidene]hexanenitrile (**4**) (1.2 g, 4.0 mmol) and sodium methoxide (0.20 g, 4.0 mmol) are dissolved in 50 mL of methanol and refluxed until the solution is clear and light green. The solvent is removed under reduced pressure and the remaining solid is stirred in water overnight. After filtration 1.24 g of a slightly violet solid were obtained (93%). IR (KBr disk): $\tilde{\nu}$ = 2985, 2883 (νC–H aliphatic), 2238 (νCN), 1622 (νCO), 1555 (νC=C), 1432 (δC–H aliphatic), 1207 (νC–F) cm⁻¹. MS (EI): *m/z* (%) = 665 (14) [M]⁺, 664 (68) [M – H]⁺, 495 (13) [M – C₃F₇H]⁺, 362 (16) [M – C₁₀H₆N₂OF₇]⁺, 304 (17) [M – C₁₀H₆N₂OF₇Ni]⁺, 192 (24) [M – C₁₃H₇N₂OF₁₄]⁺, 135 (100) [M – C₁₃H₆N₂OF₁₄Ni]⁺. MS (FAB⁺): *m/z* (%) = 665 (< 1) [M]⁺, 460 (6), 329 (34), 307 (100), 289 (60). C₂₀H₁₂F₁₄N₄NiO₂ (665.06): calcd. C 36.12, H 1.82, N 8.43; found C 36.1, H 1.8, N 8.3.

The magnetic moment μ_{eff} = 3.1 BM was determined in methanolic solution by a standard Evans setup.

Crystals were obtained via slow diffusion in a u tube. A u tube with a diameter of 12 mm and a length of 200 mm was filled with methanol up to one third and frozen with liquid nitrogen. On one side a methanolic solution of nickel(II) bromide (0.2 mmol, 0.04 g) and on the other side a methanolic solution of **4** (0.400 mmol, 0.125 g) and triethylamine (0.4 mmol, 0.04 g) were added. After approx. three weeks violet crystals had formed on the bottom of the u tube.

Crystal data for C₂₀H₁₂F₁₄N₄NiO₂ were collected with Stoe-CCD diffractometer at 293 K (graphite-monochromated Mo-K α radiation, λ = 0.71073 Å) *M* = 665.05, orthorhombic centrosymmetric space group *Pbca*, *a* = 9.664(2) Å, *b* = 12.797(3) Å, *c* = 20.029(4) Å, *V* = 2477.1(10) Å³, 28156 reflections measured, *R*(int) = 0.0403, 2167 unique reflections, 1809 observed reflections [*I* > 2σ(*I*)], 187 parameters, 9 restraints, *R*₁ [*I* > 2σ(*I*)] = 0.0695, *wR*₂ (all reflections) = 0.1281, shift/su_{max} = 0.048, completeness (2θ_{max} = 50°): 0.99.5%, $\delta\rho_{\text{max}}$ = 0.908 e Å⁻³.

CCDC-752362 contains 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.

General Procedure for the Reaction of Complexes 3a and 3b with Unsaturated Compounds: 70 mg of the complex **3a** or **3b**, respectively, were dissolved in degassed olefin or alkyne (8 mL), under nitrogen and stirred until the solution became colourless and cloudy. The precipitate was separated from the solution by centrifugation and dried in vacuo. The solution was kept under nitrogen before recording the GC/MS spectra.

The reaction with excess triphenylphosphane was carried out as described above, except that 5 equiv. triphenylphosphane was added to the reaction mixture.

NMR Experiment with Cyclopentene: 3a (29.8 mg, 0.0417 mmol) was dissolved in degassed [D₆]benzene (0.6 mL) under nitrogen in a NMR tube and degassed and dried cyclopentene (0.1 mL, 1 mmol) was added. The reaction was monitored during four weeks.

Supporting Information (see also the footnote on the first page of this article): GC and MS data of all reaction products and β -hydride elimination products.

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