

Tuning of nickel 2-phosphinophenolates – catalysts for oligomerization and polymerization of ethylene

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Abstract

This short personal account summarizes recent work concerning the syntheses and structural aspects of neutral and cationic (organo)nickel and (organo)palladium 2-phosphinophenol(ate) complexes and catalysts for the oligo- or polymerization of ethylene. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

Phosphinoenolate nickel chelate catalysts, invented more than two decades ago, have found large scale industrial applications in the shell higher olefins process [1] and also considerable academic interest [2,3]. The recent discovery of novel nickel chelate polymerization catalysts with high tolerance to water and functional groups has opened a renaissance of the research in this field [4–10]. The interest for cationic nickel catalysts [11] was stimulated by the selectivity of cationic nickel diimine catalysts for branched polyethylenes [5]. Our investigations with 2-phosphinophenols **1** as ligands, originally used as building blocks for —P=C—O— [12] and other phosphorus heterocycles [13], started after the mid ninetieths. The structural similarity of nickel phosphinophenolate and phosphinoenolate complexes along with the wider possibilities to substitute phosphinophenols, the aromatic stabilization of the enol form and increased rigidity as compared to phosphinoenols

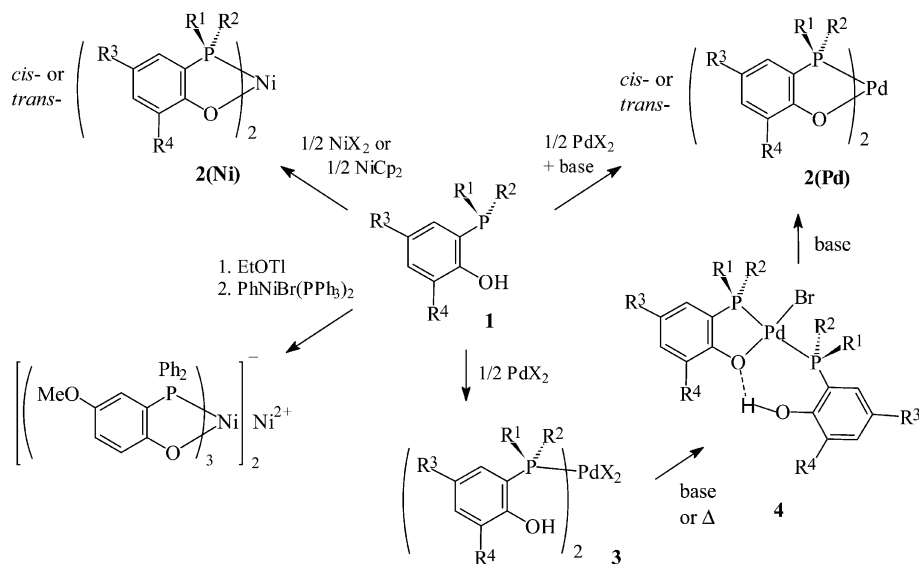
prompted us to study the oligo- and polymerization of ethylene with neutral and cationic nickel and palladium phosphinophenol(ate) chelate catalysts.

2. Nickel bis(phosphinophenolate) complexes

Nickel(II) and palladium(II) salts are known to form bis($\text{P} \cap \text{O}^-$ -chelate) complexes **2** (Scheme 1) [14–24]. While intermediate nickel complexes could not be detected and isolated, *trans*-Pd(2-phosphinophenol)₂X₂ **3** and *trans*-Pd(phosphinophenolate-P,O)(phosphinophenol) halides **4** or μ -O-bridging Pd(phosphinophenolate-P,O) di- or tetramers are reported as isolable intermediates and are characterized by crystal structure analyses [21,24,25]. Organometallic nickel compounds and Ni(0) complexes also like to form nickel (II) bis($\text{P} \cap \text{O}^-$ -chelates), even with less than two equivalents of phosphinophenols, but usually stepwise. This was observed for nickelocene [15,19] reacting via isolable cyclopentadienylnickel phosphinophenolates. With Ni(PMe₃)₄ a Ni(0)phosphinophenol tris(trimethylphosphine) complex was obtained while air oxidation produced Ni(II)

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Scheme 1.

bis(P ∩ O[−]-chelates) [26]. In polymerization experiments with in situ formed Et₂PC₆H₄OH/Ni(COD)₂ catalysts using a small catalyst to ethylene ratio, the respective nickel bis(P ∩ O[−]-chelate) was detected in the mother liquor after the reaction ceased [10]. This means that the bis(P ∩ O[−]-chelates) are a spent form of the catalyst and catalytically inactive. That the simple bis(P ∩ O[−]-chelates) may not be the only spent form is suggested by the recently reported formation of μ-O bridging dimer chloropalladium phosphinophenolate complexes, characterized by crystal structure analyses [25]. This (P ∩ O[−]-chelate)-type was discussed as spent form of nickelphosphinoenolate catalysts [27] but not yet detected for nickelphosphinophenolates. Recently we observed a linear trinuclear μ-O bridging nickel phosphinophenolate complex, consisting of two *fac*-nickel tris(phosphinophenolate) units coordinating a central nickel cation, the first example of nickel(II) phosphinophenolates with (distorted) octahedral nickel atoms. It was obtained by reaction of thallium 2-diphenylphosphino-4-methoxyphenolate, formed in situ from TIOEt and the respective phosphinophenol, with PhNiBr(Ph₃P)₂ in THF without removal of the ethanol liberated in the first step. Since the reaction of the same phosphinophenol with nickelocene in THF yields the common nickel *cis*-bis(P ∩ O[−]-chelate) complex, the unusual trinuclear structure was probably caused by the presence of triphenylphosphine and equimolar amounts of EtOH and stepwise complex formation via phenylnickel and subsequently ethoxynickel phosphinophenolate phosphine complexes, possibly supported by the higher basicity of the phenolate oxygen atom in *trans*-position to the 4-methoxy group [22]. This shows that particularly in the presence of phosphine additives and/or alcohols, the deactivation paths may be different and furnish further, presently unknown complex types.

The electronic preference for *cis*-configuration of the square planar nickel(II) and palladium(II) bis(phosphinophenolates) with P and O atoms each in *trans*-position is found for the basic P-dialkyl- as well as for P-diphenylphosphino derivatives but can be easily counterbalanced by steric factors. Bulky substituents on P favor the *trans* structure. Thus, diethylphosphino and isopropylphenylphosphino groups induced *cis*-, diisopropyl- like di-*tert*-butylphosphino groups *trans*-configuration. Dicyclohexylphosphino and *tert*-butylphenylphosphino groups adopt an intermediate position and may prefer *cis*- or *trans*-configuration dependent on the molecular environment (crystal or solution), the solvent or substituents at the phenolate backbone. The easy change of the configuration, e.g., simply by solution of *trans*-[Ni(*c*Hex₂PC₆H₄O)₂] in CDCl₃ [21] or *cis*-[Ni(*t*BuPhP-4,6-*t*Bu₂C₆H₄O)₂] in THF [26], shows that despite the P ∩ O[−]-chelate ligands act as “spectator ligands”, forming the stable backbone of SHOP-type catalysts, the kinetic stability of the bis(P ∩ O[−]-chelate) complexes is limited even at room temperature. However, the isomerization is slow in comparison to the processes causing the fluxional behavior of hemilabile 2-phosphinophenolether [28] or related P ∩ O chelates [29].

3. Organonickel phosphinophenolate complexes and catalysts

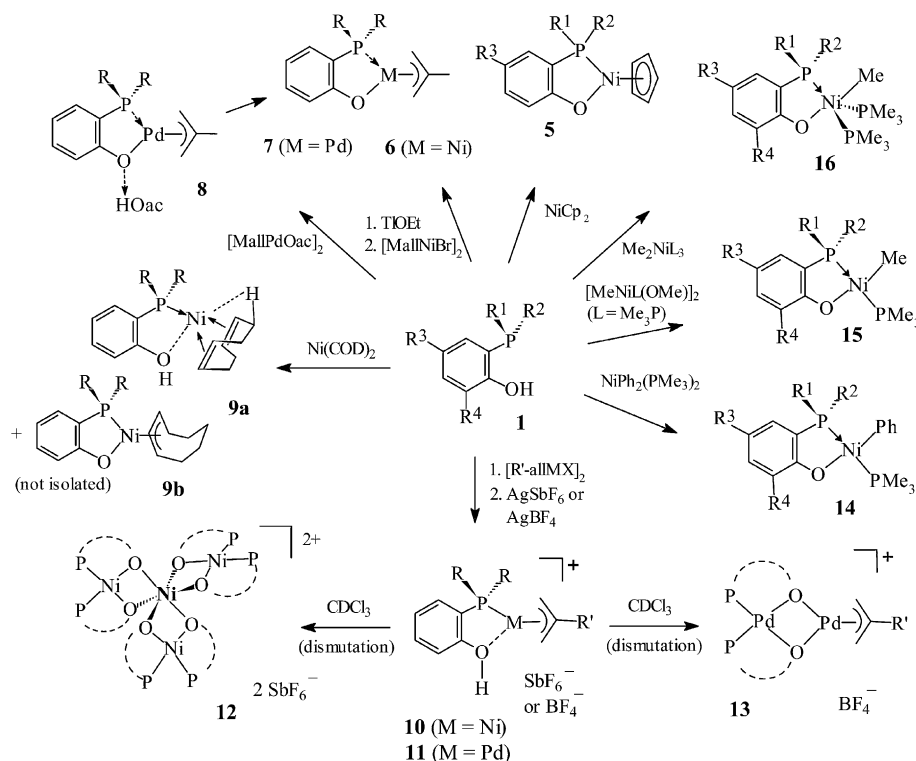
3.1. Synthesis and catalytic screening of single component catalyst precursors

DTA investigations of single component SHOP-catalysts have shown that nickelhydride phosphino-enolates,

generated by thermolysis of organonickel phosphinolenates, are catalytically active and supposed to start the chain growth [2]. This inspired investigations on organonickel phosphinophenolates. Cyclopentadienyl-nickel phosphinophenolates **5** (Scheme 2) were obtained from nickelocene and one equivalent of phosphinophenol [15,19]. However, they do not catalyze the oligo- or polymerization of ethylene, even at quite high temperature (140 °C) [19]. Differential thermoanalysis indicated cleavage of cyclopentadiene only above 180 °C while the latter decompose already at 130 °C [2]. Therefore, methallylnickel phosphinophenolates **6** have been synthesized and investigated. Methallylnickel diphenylphosphinophenolate starts to decompose above 50 °C while the dicyclohexylphosphino derivative is more stable with a DTA maximum at 120 °C. Correspondingly the former becomes catalytically active around 70 °C, the latter only at 110–120 °C [10]. Methallylpalladium phosphinophenolates **7**, obtained by high-vacuum sublimation of the respective acetic acid conjugates **8**, are stable even at 200 °C and thus catalytically inactive [30]. Catalysts generated in situ from 2-phosphinophenols and equimolar amounts of Ni(COD)₂ behave similarly as **6**. Multinuclear NMR studies of the precatalyst solution, formed from 2-diphenylphosphinophenol and Ni(COD)₂ at room temperature, gave evidence of two components, the major being a nickel(0) phosphinophenol complex **9a** with agostic interactions to the olefin ligand and the minor being

an allyl type complex **9b** with a phosphorus resonance very similar to that of the methallylnickel complex. The catalyst formation is connected with isomerization of the COD ligand as only the free 1,3-isomer was detectable by ¹³C NMR, and this seems to stabilize the catalyst [10]. The catalytic properties in the polymerization of ethylene are similar to those of the corresponding methallylnickel complexes **6** with respect to the activation temperature, conversion, selectivity and molecular weight distribution, so that identical catalyst species and similar resting states may be assumed.

Cationic methallyl nickel and allylpalladium phosphinophenol complexes with weakly or non-coordinating anions are much less stable, particularly in solution. The Ni species **10** decomposes in CDCl₃ solution within an hour, the Pd species **11** with BF₄⁻ anion within a day, while solid **11** (BF₄⁻) decomposes only on heating. **11** with SbF₆⁻ anion allowed to grow single crystals from THF/hexane and was found to be a cationic Pd(P ∩ OH-chelate) complex with hydrogen bridging bond to THF. The solution ¹³C NMR spectra, however, are indicative rather for a free OH group. The chemical shift of the ¹³C(O) nucleus is nearly identically with that in the phosphinophenol itself. Only the downfield shift of the OH proton resonance in the complex as compared to the ligand gives evidence of interactions with the metal ion [30]. The decomposition of **10** and **11** in CDCl₃ solution led to novel cationic μ-O-bridging complexes **12** and **13**, probably by dismutation and cleavage of



Scheme 2.

Ni(SbF₆)₂ and Pd(BF₄)₂, respectively. By lack of more suitable ligands the Ni(II) or Pd(II) *cis*-bis(P ∩ O[−]-chelates) act here as bidentate ligands towards the central octahedral nickel(II) or square-planar palladium(II). This was shown by crystal structure analyses. The tetranuclear nickel complex **12** is highly stable, even under non-inert conditions, while the dinuclear Pd-allyl complex **13** decomposes already on recrystallization with liberation of the respective palladium(II) *cis*-bis(P ∩ O[−]-chelate) [31].

The first single component organonickel(II) phosphinophenolate precatalysts studied in the oligomerization of ethylene have been phenylnickel phosphinophenolate phosphine complexes **14**, obtained by the “ylide method” from *o*-benzochinone-2-ylidene-triphenylphosphorane, Ni(COD)₂ and PR₃. This includes the migration of a phenyl group from phosphorus to nickel and is so far restricted to the formation of the diphenylphosphino species [32,33]. Recently, we found a general access to **14**, including dialkylphosphino or phenoxy-substituted derivatives, by reactions of **1** with diphenylnickel bis(trimethylphosphine) which is easily available from two equivalents of phenyllithium and NiCl₂ in the presence of two PMe₃ [34]. Methylnickel(II) phosphinophenolate phosphine complexes **15** were synthesized by reaction of **1** with the dimeric methylmethoxynickel(trimethylphosphine) while reaction with dimethylnickel tris(trimethylphosphine) furnished methylnickel(II) phosphinophenolate bis(trimethylphosphine) complexes **16**, which in the crystal possess nearly ideal trigonal bipyramidal structure [20]. Both, the phenyl- as well as the methylnickel phosphinophenolate complexes **14–16**, behave as single-component precatalysts for the oligomerization of ethylene. The chain lengths of the products are much shorter than those obtained with catalysts of type **6** or **9** while the high selectivity for linear α -olefins is preserved [20,33,34].

3.2. Ligand screening and tuning

The similar catalytic properties of single component precatalysts **6** and in situ generated precatalysts **9** allowed to carry out the catalyst screening by the much easier available catalysts of type **9**, simply formed by reacting the ligand to be tested with Ni(COD)₂ in an equimolar ratio. All P-tertiary and P-secondary as well as some phenoxy-substituted primary 2-phosphinophenols probed were active ethylene polymerization catalysts, usually also their trimethylsilylethers [10] and carboxylic acid esters (as oligomerization catalysts) [35], but 2-phosphinophenol alkylethers, 2-phosphinoanilines or 2-hydroxy-2'-phosphino-1,1'-diaryls did not form oligo- or polymerization catalysts. This gives evidence that the formation of a nickel P ∩ O[−]-chelate complex of medium size is a precondition for catalytic properties [10].

A 2:1 molar ratio of **1**:Ni(COD)₂ leads to inactive bis(P ∩ O[−]-chelates) and a lack of ligand (<1:1) to partial deposition of inactive black nickel while a slight excess of **1** (1.1–1.2:1) like phosphine additives (see below) stabilizes the catalyst and increases the TON and even the reaction rate but diminishes strongly the molecular weights of the products [36].

Catalyst formation needs reasonable heating from room to the reaction temperature in the presence of ethylene, in particular PH-functional 2-phosphinophenols. Injection of the precatalyst solutions at 80 °C to ethylene-toluene solutions causes low turnover numbers or inactivity and immediate deposition of black nickel. The activation temperature for 2-diphenylphosphinophenol/Ni(COD)₂ catalysts is about 70 °C, for alkylphenylphosphino- and dialkylphosphinophenol/Ni(COD)₂ catalysts it is somewhat higher, up to 120 °C for 2-di-*tert*-butylphosphinophenol. The conversion of ethylene by the 2-diphenylphosphinophenol/Ni(COD)₂ catalyst is higher at 80 °C than at 100 °C except for a lower ethylene to catalyst ratio, probably due to partial catalyst decomposition. As expected, the molecular weights decrease with increasing reaction temperature. To estimate the influence of P- and phenoxy substituents for ligand tuning, most screening experiments were run at normalized conditions (batch reaction with 100 μ mol catalyst in 20 mL toluene solution, p_{start} 50 bar, bath temperature 100 °C). It was found that the weight average molecular weights of the polyethylenes obtained with precatalysts **9** of the type 2-R₂PC₆H₄OH/Ni(COD)₂ increase roughly in the order R = Ph < Et \approx *t*Bu < *i*Pr < *c*Hex, illustrated by some examples compiled in Table 1. This indicates a superposition of two opposing effects, an increase of M_w with growing basicity of the phosphino group but decrease with increasing steric demand of the P-alkyl groups. The polydispersity M_w/M_n rises in the order R = Et \approx *c*Hex < *i*Pr < *t*Bu. With the exception of the *c*Hex₂P catalyst this corresponds to increasing Tolman angles (Et₂PPh, *i*Pr₂PPh, *c*Hex₂PPh, *t*Bu₂PPh θ_1 = 136°, 155°, 162°, 170° [37]).

Methyl, *tert*-butyl or methoxy substituents in 4- or 6-position of the phenolate group usually cause strongly diminished molecular weights of the polymers while catalyst life time and turnover numbers are usually increased, in particular with two *tert*-butyl groups in 4- and 6-position. Secondary and in case of 4,6-*tert*-butyl or 4-methoxy groups even primary *o*-phosphinophenols give polymerization catalysts if the components are heated sufficiently slowly in presence of ethylene (20 min until 100 °C). 4-Methoxy groups cause here strongly increased M_w values (up to 812.000) of the polymers [38] in contrast to the behavior of P-tertiary catalysts. The high polydispersity and bimodal molecular weight distribution might be attributed to mixing problems. The selectivity for mainly linear α -olefins is maintained in

Table 1
Influence of P-substituents

M_w (R)	Ph	<i>t</i> Bu	Et	<i>i</i> Pr	<i>c</i> Hex
2-R ₂ P-C ₆ H ₄ OH/Ni(COD) ₂ catalysts					
M_w^a	5510	14020	21800	25840	58930
M_n^a	4430	2330	7940	6230	26500
M_w/M_n^a	1.2	6.0	2.8	4.1	2.2
Conversion ^a	66	94	84	40	72
M_w^b		29920	25140	38400	97500
M_n^b		7270	9230	13100	32040
M_w/M_n^b		4.1	2.7	2.9	3.0
Conversion ^b		25	98	59	51
M_w (R)	Ph ^A	<i>i</i> Pr ^B	Ph ^A	<i>i</i> Pr ^A	
2-RHP-C ₆ H ₄ OH/Ni(COD) ₂ catalysts					
4-R'	Me	Me	MeO	MeO	MeO
M_w^A	16360	18040	696800	812600	812600
M_n^A	8100	13760	7230	9500	9500
M_w/M_n^A	2.0	1.3	96.3 ^C	85.5 ^C	85.5 ^C
conversion ^A	75	50	71	94	94

^a 100 °C, p_{start} 50 bar.^b 80 °C, p_{start} 50 bar, for R = Et 70 °C, p_{start} 30 bar.^A 80 °C, p_{start} 50 bar.^B 140 °C, p_{start} 40 bar.^C Bimodal molecular weight distribution.

all phosphinophenolate catalysts though the content of branched products is slightly increased in case of P-dialkyl-, in particular dicyclohexylphosphino substituted catalysts.

3.3. Influence of solvents and additives

The frequently insufficient conversion of ethylene in the presence of **9** due to short living time of the catalysts in toluene can be overcome by stabilizing additives or solvents (Table 2). These are either π -donors or Lewis bases which interact with the free coordination site without to block it for coordination of ethylene. The time-averaged occupation of the coordination site by the additive or solvent on account of ethylene coordination diminishes however the polymerization rate, as shown by the slower pressure decrease in presence of hexene, DMF or ethers (Fig. 1). Except in case of 1-hexene also the molecular weights decrease roughly in this order,

Table 2

Influence of solvents on the polymerization of ethylene in the presence of 2-Ph₂PC₆H₄OH (or 2-*c*Hex₂PC₆H₄OH*)/Ni(COD)₂ (each 100 μ mol, 20 mL solvent, 100 °C)

Solvent	Conversion	TON
Toluene/1-hexene (1:1)	99	5700
DMF	94	3020
DME	96	3850
THF	66	3420
THF/H ₂ O (19:1)*	69*	1500*
THF/H ₂ O (1:1)*	40*	1530*
Toluene/H ₂ O (19:1)	30	1400
EtOH, CH ₃ CN, CH ₃ COOEt, hexane	0	

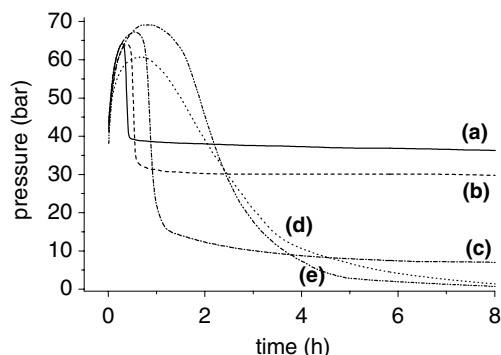


Fig. 1. Pressure–time plots of the batch polymerization of ethylene with 2-diphenylphosphinophenol/Ni(COD)₂ (each 100 μ mol, 20 mL solvent, 100 °C) in: (a) toluene, (b) THF, (c) DME, (d) DMF and (e) 1-hexene.

suggesting that the rate of insertion and termination or the ratio of these rates is less influenced by O-donor solvents. It should be noted that water is tolerated by phosphinophenol-Ni(COD)₂ catalysts, in particular in mixture with THF and better by dicyclohexyl- than by diphenylphosphinophenolate nickel catalysts. In THF the reaction rate is increased by addition of water and the TON decreases only at larger portions of water, mainly when the phosphinophenol or the catalyst partly precipitate. For better water soluble derivatives good suitability for suspension polymerization in toluene–water or olefin–water systems may be expected [10].

In the presence of 1-hexene or other α -olefins, also esters with more than one CH₂ between ester and vinyl group, we not only observed slower polymerization of ethylene, but also some random copolymerization, and

the molar masses exceed in some samples those of polyethylenes obtained in toluene with the same catalyst. Using the α -olefins as solvents the incorporation of α -olefin is low in case of the 2-diphenylphosphinophenol/ $\text{Ni}(\text{COD})_2$ catalyst, roughly 3 to 10 branches per chain, but markedly larger in case of the 2-dicyclohexylphosphinophenol/ $\text{Ni}(\text{COD})_2$ catalyst, estimated to about 10–20 branches per chain. To illustrate this, the ^{13}C NMR spectrum of the random copolymer with 1-undecenoic acid ethyl ester is shown (Fig. 2) [39]. The strong signals for the side groups and the branching methine groups distinguish clearly from the weak signals for characteristic carbon atoms of the main

chain like C2, C3 or C $_n$ which is connected to the final olefinic group.

Finally, it shall be mentioned that 2-phosphinophenol/ $\text{Ni}(\text{COD})_2$ derived catalysts can also be used for the oligomerization of ethylene. By combination with non-functionally substituted tertiary phosphines of suitable basicity and Tolman angle they can be tuned to give linear oligomers in the range C4–C10, C4–C20, soft waxes or low melting linear polyethylenes. Also oligomers with higher contents of isoolefins can be produced. Some examples are presented in Table 3 [36]. Very similar effects were shown by use of single component phenylnickel [33] or methylnickel phosphinophenolate

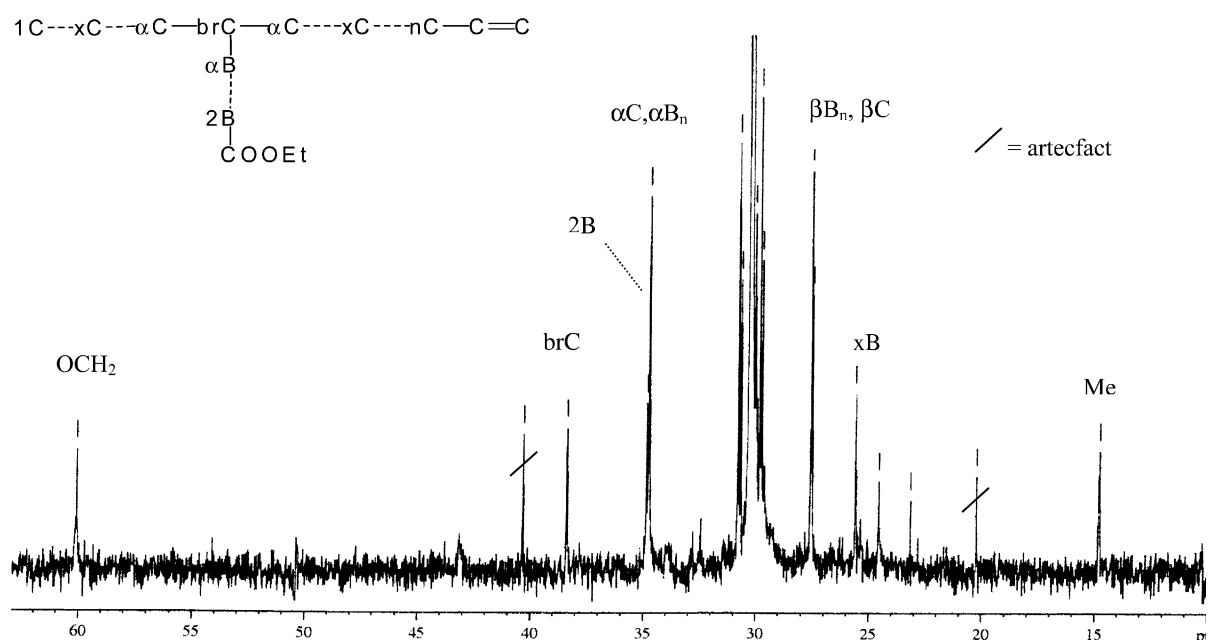


Fig. 2. ^{13}C NMR spectrum of random polyethylene-co-polyundecenoic acid ethyl ester, obtained with the $c\text{Hex}_2\text{PC}_6\text{H}_4\text{OH}/\text{Ni}(\text{COD})_2$ catalyst.

Table 3
Effect of phosphine additives on the oligomerization of ethylene by catalysts of type 9

Additive	C_2H_4 g conversion (%)	TON ($\text{mol} \cdot \text{mol}^{-1}$)	TOF_{max} ($\text{mol} \cdot \text{mol}^{-1} \text{h}^{-1}$)	Products (g)	Properties: m.p. ($^\circ\text{C}$) molar mass (g mol^{-1})
–	12.6 (50–66)	2250–2960	8000–23000	HDPE (6.0–8.1)	m.p. 124–126 M_{NMR} 1300–2000
Me_3P	11.3 (70)	2800	300	Butenes (>3.8) Liq. oligomers (1.5)	90% lin. α -olefins
Et_3P	16.0 (72)	3600	1600	Butenes (>4.8) Liq. oligomers (6.8)	95% lin. α -olefins
Cy_3P	15.0 (77)	3560	16000	PE wax (11.1)	m.p. 112–115 M_{NMR} 840
Ph_3P	14.6 (95)	4950	28000	Gas C $_4$ and C $_6$ (2.5) Liq. oligomers (2.8) Wax (8.6)	95% lin. α -olefins
$p\text{Tol}_3\text{P}$	10.1 (>99)	3600	8000	Butenes (>1.1) Liq. oligomers (5.8)	45% lin. α -olefins
$m\text{Tol}_3\text{P}$	13.0 (99)	4600	4000	Butenes (1.8) Liq. oligomers (4.7) Wax (6.4)	60% lin. α -olefins
$o\text{Tol}_3\text{P}$	13.7 (51)	2500	12000	HDPE (6.5)	m.p. 124–125 M_{NMR} 1900–2100

phosphine precatalysts [20], which differ only by the lack of liberated COD which may compete with phosphine and ethylene in the solution for the free coordination site of the catalyst.

The oligomer composition can be tuned not only by the type of the phosphine additive but also by its content relative to the phosphinophenol and metal. As shown for catalysts formed from 2-diphenylphosphinophenol, triphenylphosphine and $\text{Ni}(\text{COD})_2$, lower oligomers are favored by an increased content of triphenylphosphine which surprisingly does not block the catalyst. The behavior of 2-dicyclohexylphosphinophenol/triphenylphosphine/ $\text{Ni}(\text{COD})_2$ catalysts, however, is different [36].

3.4. Mechanism of the oligopolymerization of ethylene in presence of neutral nickel(II) phosphinophenolate catalysts

The ligand screening has shown that the nickel catalyst requires a stable $\text{P} \cap \text{O}^-$ -chelate backbone. The good correlation of decomposition and catalyst activation temperatures for the methallylnickel phosphinophenolates suggests that the catalytic process is started by formation of hydridonickel phosphinophenolates.

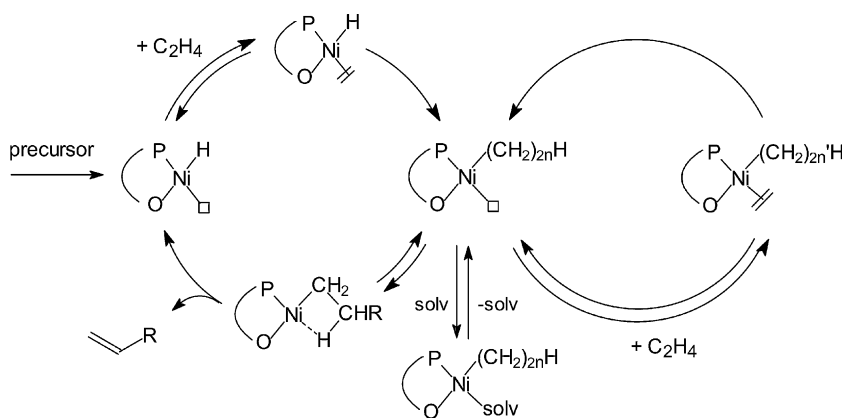
To get further support for this assumption, direct activation by hydrides was investigated. It was found that mixtures of 2-diphenylphosphinophenol, $\text{NiCl}_2 \cdot \text{DME}$ and sodium hydride as well as mixtures of nickel bis(2-diphenylphosphinophenolate), $\text{NiCl}_2 \cdot \text{DME}$ and sodium hydride in toluene produce catalysts which convert ethylene slowly to even somewhat higher molecular weight polymers with almost the same selectivity. This shows up how the catalyst lifetime can be prolonged and that the air stable nickel(II) bis($\text{P} \cap \text{O}^-$ -chelate) complexes can be applied for catalyst generation. The slow reaction rate is probably due to generation of the catalyst at the surface of the least soluble component, the in part considerably higher conversion to a continuous catalyst generation [10]. Dialkylphosphinophenolate

nickel catalysts cannot so easily be prepared with hydrides. This requires long induction periods and heating with NaH up to 130 °C. A little productive diethylphosphinophenolate nickel catalyst could also be generated from the respective bis($\text{P} \cap \text{O}^-$ -chelate) and triethylsilane at 120 °C. Efficient oligomerization catalysts are formed, however, even in case of the somewhat less reactive nickel bis(dicyclohexylphosphinophenolate), by reaction with butyllithium. Trapping of the liberated lithium phosphinophenolate by excessive $\text{NiCl}_2 \cdot \text{DME}$ increased the molecular weight but by far not to the value observed with the respective precatalyst of type **9**. Attempts to generate the catalysts by addition of MAO have not been successfully, possibly by stabilization of the bis($\text{P} \cap \text{O}^-$ -chelates) via μ -O-bridging coordination.

The formation of catalysts by means of hydrides supports the assumption of Ni-hydrides as initial catalysts at the begin of the chain growth reaction, the activation by *n*-BuLi is in line with the easy insertion of ethylene into the Ni–C(alkyl) bond. Considering also the effects of solvents and phosphine additives a mechanism according to Scheme 3 is proposed to explain the experimental results obtained with neutral nickel phosphinophenolate catalysts [10].

3.5. Behavior of cationic organonickel and organopalladium phosphinophenol complexes

Cationic methallyl nickel and allylpalladium phosphinophenol complexes with non-coordinating anions, **10** and **11**, respectively, are much less stable in solution than the corresponding neutral complexes and are highly active in the oligomerization of ethylene. In presence of **10** the oligomerization starts already at room temperature during pressurizing and proceeds quantitatively without external heating. The products are isomer mixtures of lower olefins, C4–C8 for the 2-diphenylphosphinophenol Ni catalyst, C4–C10 for the 2-dicyclohexylphosphinophenol Ni catalyst. GC analysis of



Scheme 3.

Table 4
Composition of the C6-fraction in the oligomerization of ethylene with **10**

Olefin	R = Ph (%)	R = <i>c</i> Hex (%)
3-Methyl-pentene-1	Trace	1.1 (2.8)
1-Hexene/2-methylpentene-1	0.1 (0.4)	1.0 (2.6)
2-Ethylbutene-1	5.6 (20.1)	19.5 (50.3)
<i>trans</i> -Hexene-3	2.3 (8.3)	3.0 (7.7)
<i>cis</i> -Hexene-3		
<i>trans</i> -Hexene-2	6.1 (22.0)	7.3 (18.8)
<i>trans</i> -3-methylpentene-2	3.2 (11.5)	1.6 (4.1)
<i>cis</i> -hexene-2	1.5 (5.4)	2.3 (5.9)
<i>cis</i> -3-methylpentene-2	9.0 (32.4)	3.0 (7.7)

the C6-fraction (Table 4) revealed mainly branched olefins and internal double bonds in case of linear olefins. The Pd complex **11** (BF_4^-) is somewhat less active and needs heating at 70–80 °C to produce mainly butene isomers.

The completely different selectivity as compared to the oligomerization by neutral nickel 2-phosphinophenolate catalysts and the similar product composition observed with the cationic nickel catalyst **10**, [methallylnickel(PPh_3)]⁺ PF_6^- (C_4 2.5/68.4/29.1, C_6 26.8, C_8 2.3 mass%) or [mesitylnickel(PR_3)]⁺ PF_6^- complexes with non-functional PR_3 ligands [28] suggest a different mechanisms and that the role of the oxygen atom in the cationic catalyst solutions is limited more or less to a place-holder function, stabilizing the catalyst as is typically for hemilabile transition metal complex catalysts [29]. The labile O-coordination destabilizes the Ni–C bond and allows much faster insertions, even insertion of 1-butenes, which gives rise to branched olefins, in particular 2-ethyl-butene-1 and small amounts of 3-methyl-pentene-1. The formation of butenes-2 and hexenes-2 or -3 may also be explained in this way, but the formation of larger amounts of 3-methyl-pentene-2, probably by catalytic isomerization of 2-ethyl-butene-1 and 3-methyl-pentene-1, accounts also for a considerable contribution of metal- or proton-catalyzed double bond migrations to the thermodynamically more stable internal olefins. Evidence for such reactions was obtained by the double bond isomerization of 1-hexene and *cis*-hexene-2 by heating in presence of **10** [30].

4. Summary and conclusions

Organonickel phosphinophenolate complexes can be synthesized by reaction of 2-phosphinophenols with diorganonickel, organonickel halide or organonickel-methoxy compounds. Provided easy formation of a nickel hydride, either by direct β -elimination or by β -elimination after insertion of ethylene, the compounds are precatalysts for the polymerization or, in presence

of a monodentate phosphine, for the oligomerization of ethylene. Catalytically active organonickel phosphinophenolate precatalysts can easily be formed in situ with $\text{Ni}(\text{COD})_2$. The catalysts can be tuned by suitable substituents or additives to synthesize linear polyethylene or ethylene oligomers with various molecular weight ranges. Also isoolefin oligomers are available, either by suitable additives (*m*- ToI_3P or *p*- ToI_3P) or use of cationic methallylnickel phosphinophenol precatalysts. In presence of α -olefins branched random copolymers can be made. The branching is low (3–20 per 1000 C atoms) but can be tuned within its limits by the P-substituents. Some catalysts are quite tolerant towards several donor solvents and even water and thus offer the possibility to develop water soluble derivatives for suspension polymerization or two-phase oligomerization. All the experimental observations fit in case of neutral nickel phosphinophenolate catalysts with a mechanism analogously to that proposed for the oligomerization in the SHOP process: necessity of a ligand that forms stable P,O-nickel chelates, initial generation of a hydride complex, retardation of the chain growth reaction by competitive solvent or additive interactions and strong influence on the chain lengths by the P-substituents via the *trans*-effect to β -hydrogen atoms of the growing chain. For cationic nickel phosphinophenol catalysts the selectivity is lower due to weak O-coordination and unselective insertion of α -olefins as well as to proton or metal catalyzed double bond isomerization reactions.

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