2-Phosphanylphenolate Nickel Catalysts for the Polymerization of Ethylene

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Abstract: The previously unknown methallylnickel 2-diorganophosphanylphenolates (R=Ph, *c*Hex) were synthesized and found to catalyze the polymerization of ethylene. To explore the potential for ligand-tuning, a variety of P-alkyl- and P-phenyl-2-phosphanylphenols was synthesized and allowed to react with [Ni(cod)$_2$] (cod = 1,5-cyclooctadiene) or with NiBr$_2$·DME and NaH. The complexes formed in situ with [Ni(cod)$_2$] are generally active as ethylene polymerization catalysts with all the ligands tested, whereas the latter systems are inactive when 2-dialkylphosphanylphenols are applied. M_w values, ranging from about 1000 to about 100000 g mol^{-1}, increase for various R$_2$P groups in the order $R{=}Ph < Et \approx tBu < iPr < cHex$, while aryloxy substituents usually diminish the molecular weights. Increasing basicity of P- or aryloxy substituents usually leads to increasing turnover numbers. The polymers are high density polyethylene (HDPE) with low methyl and sometimes low long-chain branching. Investigation of the influence of the solvent shows that the catalysts are stabilized by some oxygen-containing Lewis bases as well as by olefins. The catalysts are tolerant to water, in particular the 2-dicyclohexylphosphanylphenolate nickel catalyst, which in THF–water (1:1) gives HDPE with $M_w = 39000$, $M_n = 14500$ g mol^{-1}. Additives of tetrahydrothiophene or pyridine do not inhibit the catalyst, but decrease the reaction rate and the molecular weight of the polymers.

Keywords: chelates • homogeneous catalysis • nickel • O,P ligands • polymerization

Introduction

Late transition-metal chelate catalysts, initially applied in the Shell higher olefin process (SHOP),[1] are presently experiencing a renaissance through the use of modified phosphanylenolate, iminophenolate, bulky diimine, or tridentate diimine chelate ligands.[2–5] A particular advantage of some of these catalysts is their tolerance of polar and functional groups and even water, which poison the traditional Ziegler–Natta and metallocene catalysts with the exception of a recently reported encapsulation of the catalytic centers by prepolymerization.[6] 2-Diphenylphosphanylenolate nickel complexes [Ni($Ph_2P\cap O$)(R)(PR$_3$)], which usually oligomerize ethylene[1] are known to give polymers in nonpolar solvents such as hexane[7,8] or in the presence of phosphane scavengers.[8] Similarly, high molecular weight polyethylene is formed with phenylnickel $Ph_2P\cap O^-$ P-ylide catalysts in cyclohexane.[9] Recently it was found that bulky substituents at the enolate group[10] or use of cationic phosphanylacetophenone $P\cap O$–nickel catalysts[11] increase the activity as polymerization catalysts, and that sulfonated phenylnickel diphenylphosphanylenolate phosphane catalysts allow the formation of low molecular weight polyethylene in water/toluene (95:5).[12,13] In a preliminary study we found that catalysts formed in situ from 2-(alkylphenylphosphanyl)phenols and [Ni(cod)$_2$][14] (cod = 1,5-cyclooctadiene) give linear polyethylenes with higher yields and molecular weights than 2-diphenylphosphanylphenolate catalysts.[9a,15] Similar effects were observed in the oligomerization of ethylene with various P-substituted 2-phosphanylphenolate methylnickel phosphane complexes[16] and might be attributed to the higher basicity at phosphorus. Considering the superior catalytic properties of the recently reported *N*-basic salicylaldimine nickel catalysts,[4] related with phosphanylphenolate catalysts by a C=N

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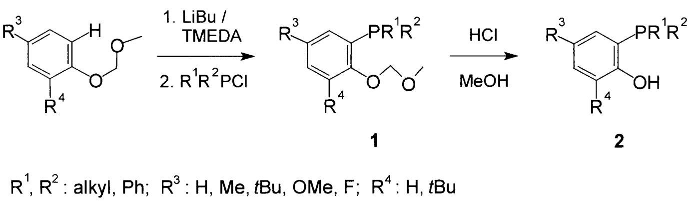
fragment instead of phosphorus, we synthesized a variety of 2-phosphanylphenols with different substituents at phosphorus and the phenol backbone and investigated the polymerization of ethylene under varied conditions, with single-component and with in situ generated nickel 2-phosphanylphenolate catalysts.[17] We present here the results obtained with neutral *P*-tertiary phosphanylphenolate nickel catalysts including the influence of polar additives or solvents.



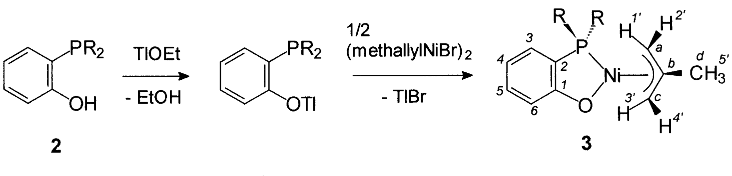
Scheme 1. Synthesis of 2-phosphanylphenols **2** via MOM ethers **1**. (The substitution pattern is assigned by a four-letter code index, representing the substituents at the phosphorus center followed by the substituents in 4- and in 6-position of the phenoxy group: **H** hydrogen, **M** methyl, **E** ethyl, **I** isopropyl, **B** *tert*-butyl, **C** cyclohexyl, **P** phenyl, **O** methoxy, **F** fluoro.).

Results and Discussion

Synthesis of new ligands: 2-Phosphanylphenols are accessible by various routes such as nickel-catalyzed arylation of triarylphosphanes and subsequent cleavage of an aryl group,[18,19] reaction of 2-lithio-lithiumphenolates with chlorophosphanes,[20] metalation of 2-bromophenylphosphinites with sodium,[21] or orthometalation of phenylmethoxymethylethers and coupling with chlorophosphanes, followed by acidic cleavage of the methoxymethyl (MOM) protecting group. The latter procedure, introduced by Rauchfuss,[22] was used to synthesize several novel representatives (Scheme 1) with various substituents at phosphorus and the phenol backbone. However, limitations of this widely applicable procedure arose from insufficient selectivity of the orthometallation in 2- or 3-methoxy or in dimethoxyphenylmethoxymethyl ethers,[17a] from acid-mediated P–C bond cleavage of PH derivatives during deprotection[17a] and from steric hindrance of substitution by tBu_2PCl.[17b] Prolonged heating with the latter furnished exclusively $(tBu_2P)_2$ instead of the substitution product which is available by coupling with 2-lithioanisol and subsequent ether cleavage.[23]

The novel phosphanylphenols were characterized by elemental analyses, and NMR data confirmed their structure. The general properties of 2-phosphanylphenols have been described recently.[20]

Synthesis of methallylnickel phosphanylphenolate complexes: η^3-Allyl- or η^5-cyclopentadienylnickel diphenylphosphanylenolate P$\cap$O-chelate complexes are known to catalyze the oligomerization of ethylene. The reaction starts at 40 or 130 °C, when the unsaturated hydrocarbon ligand is cleaved off.[1,24] η^5-Cyclopentadienylnickel 2-phosphanylphenolate P$\cap$O-chelate complexes, however, do not catalyze this reaction up to 140 °C. As shown by differential thermal analysis (DTA), they are thermally more stable and lose cyclopentadiene only at 180–200 °C.[14a] This prompted us to study representatives of the hitherto unknown η^3-allylic nickel phosphanylphenolates. The methallyl complexes $\mathbf{3_{PPHH}}$ and $\mathbf{3_{CCHH}}$ were obtained from $\mathbf{2_{PPHH}}$ and $\mathbf{2_{CCHH}}$, respectively, by metallation with thallium ethanolate and subsequent reaction of the sparingly soluble thallium salts with methallyl nickel bromide in THF (Scheme 2).



Scheme 2. Synthesis of η^3-methylallylnickel 2-phosphanylphenolates $\mathbf{3_{PPHH}}$ and $\mathbf{3_{CCHH}}$.

The diphenylphosphanyl species $\mathbf{3_{PPHH}}$ starts to decompose above 40 °C without a sharp decomposition temperature and is sensitive to air. The dicyclohexylphosphanyl complex $\mathbf{3_{CCHH}}$ is more stable to thermal degradation and air. It melts at 135–138 °C, displays small mass loss in the region 60–140 °C, and decomposes rapidly only above 160 °C. The NMR spectra are not altered after exposure of solid $\mathbf{3_{CCHH}}$ to air. The structure of the complexes was eluci-

Abstract in German: *Die bislang unbekannten Methallylnickel 2-diorganophosphanylphenolate (R = Ph, cHex) wurden dargestellt und als Einkomponentenkatalysatoren der Ethylenpolymerisation charakterisiert. Um Möglichkeiten des Ligand Tuning zu erkunden wurden eine Reihe von P-Alkyl- und P-Phenyl-2-phosphanylphenolen synthetisiert und mit [Ni(1,5-cod)$_2$] oder NiBr$_2$·DME und NaH umgesetzt. Die mit [Ni(cod)$_2$] in situ gebildeten Komplexe sind generell als Polymerisationskatalysatoren für Ethylen aktiv während die Systeme mit NiBr$_2$·DME und NaH im Falle von 2-Dialkylphosphanylphenolen inaktiv sind. Die M_w-Werte reichen von ca. 1000 bis 100 000 g mol^{-1} und steigen bei unterschiedlichen R$_2$P-Resten in der Reihenfolge R = Ph < Et ≈ tBu < iPr < cHex während Aroxy-Substituenten die Molekulargewichte zumeist vermindern. Zunehmende Basizität von P- oder Aroxy-Substituenten führt im allgemeinen zu größeren Umsatzzahlen. Bei den Polymeren handelt es sich um HDPE mit niedrigem Gehalt an Methyl- oder Langkettenverzweigungen. Die Untersuchung des Lösungsmitteleinflusses zeigt eine Stabilisierung der Katalysatoren durch einige sauerstoffhaltige Lewis-Basen sowie durch Olefine. Die Katalysatoren sind gegenüber Wasser tolerant, insbesondere der 2-Dicyclohexylphosphanylphenolat Nickelkatalysator, der in THF-Wasser (1:1) HDPE mit M_w = 39 000, M_n = 14 500 g mol^{-1} liefert. Zugaben von Tetrahydrothiophen oder Pyridin führen nicht zur Inhibierung des Katalysators, sondern bewirken Abnahme der Reaktionsgeschwindigkeit und der Molekulargewichte der Polymeren.*

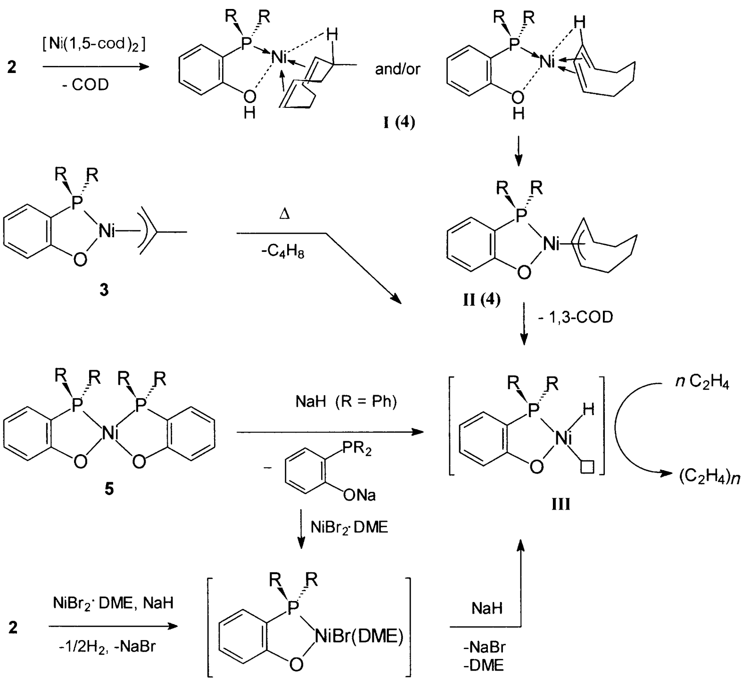
dated by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. Chemical shifts and coupling constants are in accordance with P∩O-chelate and η^3- methallyl coordination at nickel. The chelate nature of $\mathbf{3_{PPHH}}$ and $\mathbf{3_{CCHH}}$ can be seen from the ^{13}C coordination chemical shifts of C1 ($\Delta\delta = 22.8$, 17.8) and the increased P–C coupling constants of C2 ($^1J = 50.6$, 42.4 Hz) as well as from the ^{31}P coordination chemical shifts ($\Delta\delta = 58.2$, 78.1) characteristic for 2-phosphanylphenolate nickel chelate complexes.[14,16,17,25,26] The methallyl carbon nuclei C_a ($\delta_a =$ 43.9 (s), 38.6 ppm (d, $J_{P,C} = 6.0$ Hz)) of the Ni–C bond located *trans* to the oxygen atom and the protons H-*1′* and H-*2′* at C_a (CH-COSY) display considerable upfield shifts in comparison to the signals of C_c ($\delta_c = 70.6$ (d, $J_{P,C} = 22.6$ Hz), 71.2 ppm (d, $J_{P,C} = 20.7$ Hz)) located *trans* to the phosphorus atom and H-3′ and H-4′ at this carbon atom. The assignments are based on comparison with the analogous Pd complexes,[17b] in particular upon the line broadening and coalescence of the upfield proton signals (H-1′ and H-2′) upon addition of acetic acid. The hydrogen bridging bond to oxygen weakens the coordination at the palladium center (but not the chelate ring) and influences mainly the bond in the *trans* position. The downfield signals of H-3′ and H-4′ like the ^{31}P resonances remain rather unaffected. The greater upfield shift of C_a as compared to C_c in the Ni complexes, which is found closer to the C=C(Ni) resonance in [Ni(1,5-cod)$_2$] ($\delta(^{13}C) = 90$ ppm), indicates some σ-character of the Ni–C_a bond. The resonances to much higher field in related methylnickel phosphanylphenolates (i.e.$\delta(^{13}C^1H_3) = -19.9/-0.82$) in [Ni(Me)(2-$Ph_2P$-4,6-*t*$Bu_2C_6H_2O$)($PMe_3$)]),[16] however, provide evidence that the bonding mode corresponds rather to a η^3-allyl than a fictive bidentate η-alkyl-π-olefin complex. The greater upfield chemical shift of $^{13}C_a$ and the greater ^{31}P coordination chemical shift in $\mathbf{3_{CCHH}}$ as compared to $\mathbf{3_{PPHH}}$ indicates an increase of the basicity at the oxygen and phosphorus centers which in turn diminishes the acceptor strength of the dicyclohexylphosphanyl versus the diphenylphosphanyl group. This electronic and steric impact of the phosphanyl substituents on the Ni–P and the adjacent Ni–C bonds implies different properties of dialkyl- and diphenyl-substituted phosphanylphenolate nickel catalysts for the ethylene polymerization which, as shown below, causes considerable differences in the average molecular weights and, to a low degree, differences in the branching of the resulting polymers.

Comparison of various types of phosphanylphenolate nickel catalysts for the polymerization of ethylene: Heating a solution of catalytic amounts of $\mathbf{3_{PPHH}}$ and ethylene in toluene in an autoclave (batch mode, $p_{start} \approx 50$ bar) to 100 °C furnishes linear low molecular weight polyethylene $\mathbf{PE_{3PPHH}}$. The higher molecular weights as compared to the oligomers formed with the related methallylnickel diphenylphosphanylcarboxylate or 2-diphenylphosphanylbenzoate catalysts[27] show that the more O-basic phosphanylphenolate ligands diminish the chain transfer relative to the chain propagation rate. The turnover numbers, however, are comparable under equal conditions. Replacing $\mathbf{3_{PPHH}}$ by a solution of equimolar amounts of $\mathbf{2_{PPHH}}$ and [Ni(cod)$_2$] in toluene, mixed at 0 to 20 °C, affords almost the same results, equal conditions provided. The conversion of ethylene and the properties of the polyethylene $\mathbf{PE_{PPHH}}$ obtained with the in situ formed brown precatalyst $\mathbf{4_{PPHH}}$ are very similar (Table 1) and suggest nearly identical catalysts. A defined product allowing unambiguous identification could not be isolated, but some information on the nature of the complexes in this solution is furnished by NMR data. The ^{31}P NMR spectrum in [D$_8$]toluene reveals the disappearance of the signals for $\mathbf{2_{PPHH}}$ and the occurrence of two new signals, a strong resonance at $\delta = 16.3$ ppm and a weak one at $\delta = 29.2$ ppm. The former, close to $\delta(^{31}P) = 13.1$ of [Ni^0(2-Ph_2P-4,6-*t*Bu_2-C_6H_2OH)(PMe_3)$_3$],[26] suggests formation of a Ni^0 phosphanylphenol precursor complex, whereas the weak signal is very close to that of $\mathbf{3_{PPHH}}$ ($\delta = 29.7$ ppm) and is indicative of a η^3-allyl-type organonickel complex. This fits with the presence of 1,3-COD, formed quantitatively by isomerization of the 1,5-COD ligand and unambiguously identified by its typical ^{1}H and ^{13}C chemical shifts. Furthermore, the proton NMR spectrum displays two sets of broad signals for strongly acidic hydroxy and for agostic protons, respectively, the more intensive at $\delta = 12.55$ and -2.09 ppm, the less intensive at $\delta = 11.1$ and -5.53 ppm. Typical upfield NiH resonances like the one in [($Ph_2PCH_2C(CF_3)_2O$–*P*,*O*)NiH(PCy_3)] ($\delta = -24.1$[28]) are absent, while broad signals for side-on-coordinated olefinic groups are detected ($\delta = 3.1$ and 3.6 ppm). Based on the NMR spectra it is supposed that two forms of a primary Ni^0 complex **I** with acidic OH and with agostic protons (the nature of the COD ligand remains unclear) are formed rapidly and undergo slow formal oxidative addition of the OH group to give an organonickel complex **II**, which

Table 1. Polymerization of ethylene with single component and various in situ generated 2-phosphanylphenolate nickel catalysts.[a]

Product (conditions)[a]	Yield PE [%] (from C_2H_4 [g])	TON [mol mol^{-1}]	M.p. [°C]	ρ [g cm^{-3}]	M_w[h] [g mol^{-1}]	M_n[h] [g mol^{-1}]	M_w/M_n	^{1}H NMR:M [g mol^{-1}][i]	α/internal[i] olefins [%]	Me/C=C[i] (Me/1000 C)
$\mathbf{PE_{3PPHH}}$[b]	53 (12.6)	1190	118–122[g]	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.
$\mathbf{PE_{PPHH}}$ [b,c]	50–66 (12.6)	2250–2960	124–126	(0.96)	5510	4430	1.2	2000	93:7	1.5 (11)
$\mathbf{PE_{PPHH}}$ (80 °C)[c]	83 (11.5)	3400	122–124	(0.96)	3760	1230	3.1	1360	93:7	1.4 (14)
$\mathbf{PE_{5PPHH}}$[d]	72 (13.8)	3530	126–128	(0.95)	8900	3050	2.9	3370	96:4	1.3 (5.3)
$\mathbf{PE_{2PPHH}}$[e]	91 (11.4)	3710	128–130	(0.95)	5900	2100	2.8	2600	98:2	1.5 (8)
$\mathbf{PE_{2PPOH}}$[e]	64 (13.3)	3030	122–124	(0.96)	4370	1800	2.4	1860	81:19	1.6 (13)
$\mathbf{PE_{2BPHH}}$[e]	51 (14.5)	2640	124–126	(0.96)	2180	1560	1.4	1420	92:8	1.3 (13)
$\mathbf{PE_{3CCHH}}$ (100 °C)[c]	7–16 (13.0)	320–740	131–133	(0.95)	n.d.	n.d.	n.d.	29400	96:4	2.1 (1)
$\mathbf{PE_{3CCHH}}$ (120 °C)[f]	95 (6.1)	2070	131–133	(0.94)	40300	16300	2.5	35000	90:10	≈3 (1.2)

[a] Catalyst subscript without number means formed in situ with [Ni(cod)$_2$]; conditions: $p_{start} = 50$ bar C_2H_4, catalyst in toluene (20 mL), 15 h, 100 °C unless indicated otherwise; n.d. not determined. [b] 0.2 mmol $\mathbf{3_{PPHH}}$ or **2**/[Ni(cod)$_2$]. [c] 0.1 mmol **2**/[Ni(cod)$_2$] or $\mathbf{3_{CCHH}}$. [d] 0.1 mmol **2**, 0.2 mmol $NiBr_2\cdot$DME, 0.3 mmol NaH. [e] 0.1 mmol **2**, 0.3 mmol $NiBr_2\cdot$DME, 0.3 mmol NaH. [f] $p_{start} = 30$ bar C_2H_4, else like [c]. [g] Without extraction of oligomers by CH_2Cl_2. [h] M_w and M_n by SEC. [i] Average molecular weight/olefin and Me/olefin ratio based on ^{1}H NMR analysis.



Scheme 3. Proposed formation of 2-phosphanylphenolatonickel hydride catalysts.

is similar to **3** and may eliminate 1,3-COD with formation of the proposed Ni–H polymerization catalyst **III** (Scheme 3). The isomerization of COD is probably caused by the intermediate phosphanylphenol nickel complexes. Neutral 2-diphenylphosphanylphenolate complexes of the type $\mathbf{3_{PPHH}}$ do not catalyze the isomerization of olefins.

To establish the role of NiH species, attempts were made to generate nickel hydride complex catalysts directly. For this purpose ethylene was heated under pressure with a stirred mixture of $\mathbf{2_{PPHH}}$ (0.1 mmol), excess $NiBr_2$·DME, and sodium hydride (each 0.3 mmol) and, in a further experiment, with the nickel bis(P∩O- chelate) complex $\mathbf{5_{PPHH}}$, excess $NiBr_2$·DME, and sodium hydride (0.1, 0.2, and 0.3 mmol), each in toluene. In both procedures, linear α-polyethylenes ($\mathbf{PE_{2PPHH}}$ and $\mathbf{PE_{5PPHH}}$, respectively) were formed efficiently (Table 1). It is assumed that an intermediate nickel phosphanylphenolate bromide is formed and activated by NaH. The slow polymerization rate as compared to that with $\mathbf{4_{PPHH}}$, illustrated by the pressure–time plot (Figure 1), suggests that the concentration of the catalyst is low, while the higher total conversion of ethylene accounts for a continuous generation of the catalyst, for example at the NaH surface. The higher weight-average molecular weight of $\mathbf{PE_{5PPHH}}$ as compared to that of $\mathbf{PE_{4PPHH}}$ and the higher polydispersity may be attributed to the higher initial ratio of the ethylene to catalyst concentration and its final decrease, respectively. The selectivity for linear α-olefins, however, is preserved and supports a close similarity of the catalytically active species.

Considerable changes are observed if substituents are introduced that increase the basicity of the phenolate oxygen atom or the phosphanyl group. The polymerization of ethylene with $\mathbf{2_{PPOH}}$-$NiBr_2$·DME/NaH proceeds much slower and less selectively than with the analogous $\mathbf{2_{PPHH}}$ catalyst and gives lower conversion, whereas the catalyst $\mathbf{4_{PPOH}}$ obtained with $[Ni(cod)_2]$ is highly active. Similarly, polymerization of ethylene with the catalyst formed from the more P-basic $\mathbf{2_{BPHH}}$ and $NiBr_2$·DME/NaH (Table 1) led to lower conversion and molecular weights than with the diphenylphosphanyl analogue, whereas the opposite is observed when $[Ni(cod)_2]$ was used as nickel source (Table 2). The divergent properties of the two catalyst systems become even more evident for the strongly P-basic 2-dialkylphosphanylphenols. Mixtures of $\mathbf{2_{EEHH}}$, $\mathbf{2_{IIHH}}$, or $\mathbf{2_{CCHH}}$ with $NiBr_2$·DME and NaH in toluene are completely inactive. The yellow solutions of $\mathbf{4_{EEHH}}$, $\mathbf{4_{IIHH}}$, and $\mathbf{4_{CCHH}}$ formed with $[Ni(cod)_2]$ in toluene, however, proved to be highly active polymerization catalysts and give much higher molecular weights than $\mathbf{4_{PPHH}}$ (Table 2). Even the bulky $\mathbf{2_{BBHH}}$, which does not display a color change on combining with the $[Ni(cod)_2]$ solution at 0–20 °C, forms an active catalyst $\mathbf{4_{BBHH}}$. It is assumed that nickel hydride complexes, if generated at all with $NiBr_2$·DME/NaH, are more rapidly deactivated, whereas the olefins eliminated from the organonickel precursors in **4** provide sufficiently stable resting states, for example of the type **II(4)**. Thus, the conversion of ethylene and TON with $\mathbf{4_{CCHH}}$ are similar to those with the analogous diphenylphosphanyl catalyst (Figure 1). The η^3-methallyl complex $\mathbf{3_{CCHH}}$, as mentioned above, is more stable than $\mathbf{3_{PPHH}}$ and exhibits remarkable catalytic activity only above 100 °C (Table 1). Even at 120 °C the reaction rate is lower, the conversion of ethylene, however, is nearly quantitative (Figure 1). This may be due to a slower degradation of $\mathbf{3_{CCHH}}$ and formation of catalyst species over a longer period but also gives evidence of sufficient stable resting states.

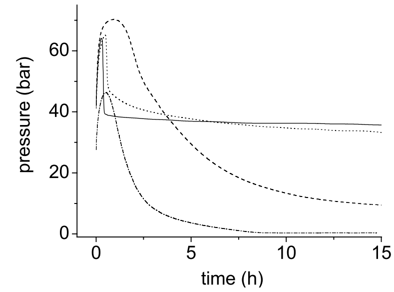


Figure 1. Pressure–time plots for batch polymerization of ethylene with catalysts formed in situ from $\mathbf{2_{PPHH}}$ and $[Ni(1,5\text{-}cod)_2]$ (solid), $\mathbf{2_{PPHH}}$ and $NiBr_2$·DME and NaH (dash), $\mathbf{2_{CCHH}}$ and $[Ni(1,5\text{-}cod)_2]$ (dot) (p_{start} 50 bar, 100 °C each) and with $\mathbf{3_{CCHH}}$ (p_{start} 30 bar, 120 °C, dash dot).

Table 2. Polymerization of ethylene with in situ prepared 2-dialkylphosphanylphenolate nickel catalysts **4** (without substitutents in 4- or 6-position).

Product (conditions)[a]	Yield PE [%] (from C_2H_4 [g])	TON [mol mol^{-1}]	M.p. [°C]	ρ [g cm^{-3}]	M_w[d] [g mol^{-1}]	M_n[d] [g mol^{-1}]	M_w/M_n	^{1}H NMR:M [g mol^{-1}][h]	α/internal[h] olefins [%]	Me/C=C[h] (Me/1000 C)
$\mathbf{PE_{EEHH}}$ (70 °C, 30 bar)	98 (5.6)	1960	129–131 [c] 133–136	0.96	31350	9300	3.4	11000	94:6	1.3 (1.7)
$\mathbf{PE_{EEHH}}$[b]	64 (12.8)	2923	134–136	0.935	n.d.	n.d.	n.d.	12000	> 97:3	1.1 (1.2)
$\mathbf{PE_{EEHH}}$	84 (12.3)	3673	132–134	0.955	21800	7940	2.7	9930	> 97:3	2.0 (2.8)
$\mathbf{PE_{IIHH}}$ [b]	40 (12.7)	1818	133–135	0.93	38400	13100	2.9	19460	> 97:3	2.6 (2.0)
$\mathbf{PE_{IIHH}}$	60 (13.5)	2887	128–130	0.955	25800	6230	4.2 [e]	6490	88:12	2.3 (4.9)
$\mathbf{PE_{BBHH}}$[b]	25 (12.8)	1140	129–131	0.94	30000	7300	4.1 [f]	15000 [f]	90:10	2.2 (2.0)
$\mathbf{PE_{BBHH}}$	94 (12.6)	4207	128–130	0.96	14000	2330	6.0 [g]	4230 [g]	77:23	1.8 (6.0)
$\mathbf{PE_{CCHH}}$[b]	51 (12.0)	2176	135–137	0.935	97500	32100	3.0	uncertain	> 97:3	(≈0.7)
$\mathbf{PE_{CCHH}}$	72 (15.3)	3920	134–136	0.95	59000	26500	2.2	uncertain	87:13	1.4–2 (2–3)

[a] 0.1 mmol catalyst in toluene (20 mL), 15 h, 50 bar, 100 °C, else given. [b] Like [a] but 80 °C. [c] Before extraction of soluble oligomers with CH_2Cl_2. [d] M_w and M_n by SEC. [e] Bimodal, maximum 2.5×10^4, sh 6×10^3. [f] Bimodal, maximum 2×10^4, sh 6×10^3. [g] Bimodal, maximum 1.2×10^4, sh 600 g mol^{-1}. [h] Results from ^{1}H NMR analysis.

Ligand screening and investigation of substituent and solvent effects with catalysts of type 4: The easy preparation of the polymerization catalysts **4** from **2** and [Ni(cod)$_2$] prompted us to screen several ligand types and to study the effects of reaction conditions, substituents, solvents, and additives on polymerization and some properties of the polymers.

Ligand screening: In the screening tests all tertiary 2-phosphanylphenols **2**, 2-phosphanyl-1-naphthols, and even the secondary and some primary 2-phosphanylphenols were found to react with [Ni(cod)$_2$] to give catalysts for the polymerization of ethylene. *O*-Trimethylsilyl ethers of **2** behave similarly except that their reactivity is lowered by steric hindrance and low basicity of phosphorus as in the trimethylsilyl ether of $\mathbf{2_{PPBB}}$. The MOM ethers **1**, so far tested, have all been unable to form catalysts with [Ni(cod)$_2$]. This indicates that hydroxy or similar functional groups are required that allow the generation of a phosphanylphenolate ligand under neutral or slightly basic conditions. 2-Hydroxy-2′-diphenylphosphanyl-1,1′-diphenyl and -dinaphthyl were also found to be inactive. Since the electronic situation at the OH group and the phosphorus atom is similar to that in $\mathbf{2_{PPHH}}$, the failure in this case hints at the necessity of a sufficiently stable P∩O chelate backbone which seems not to be the case for more flexible seven-membered P∩O chelates. Finally it should be mentioned that also 2-phosphanylanilines did not form polymerization catalysts with [Ni(cod)$_2$].

Influence and selection of reaction conditions: The catalyst system $\mathbf{4_{PPHH}}$ formed in situ from $\mathbf{2_{PPHH}}$ and [Ni(cod)$_2$] in toluene was chosen as a reference to determine suitable reaction conditions for comparison with related catalysts. Initially the temperature, pressure, and ethylene-to-catalyst ratio were varied. The conversion of ethylene was found to be slow at 40 °C and to increase strongly on raising the temperature to 70 °C. The effect of higher temperatures up to 120 °C depends on the ethylene-to-catalyst ratio (TON$_{\text{lim}}$). A small molar ratio of roughly 600–800 causes a further increase, a higher ratio (4600–4800) a decrease of the conversion (Figure 2). This indicates growing thermal deactivation of the catalyst and decreasing TON at high temperature which at low ethylene loading is overcompensated by an excessive amount of the precatalyst. Furthermore Figure 2 shows that for a given temperature the TON increases with the ethylene-to-catalyst ratio and pressure, suggesting that the stability of the catalyst increases with the ethylene concentration and should allow much higher TON in flow systems with constant high pressure of ethylene. Figure 3 illustrates the growing rates of the polymerization with increasing temperature and the rapid catalyst deactivation at high temperature.

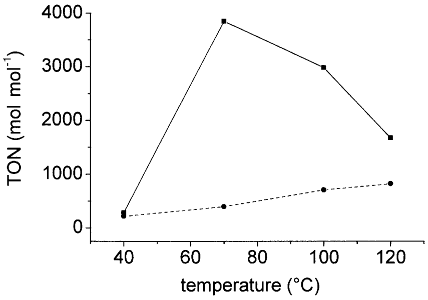


Figure 2. Temperature dependence of the TON for the polymerization of ethylene with $\mathbf{4_{PPHH}}$ in toluene, a) $p_{\text{start}} = 30$ bar, C_2H_4 150–200 mmol, $\mathbf{4_{PPHH}}$ 0.24 mmol (dash), b) $p_{\text{start}} = 50$ bar, C_2H_4 460–480 mmol, $\mathbf{4_{PPHH}}$ 0.1 mmol (solid).

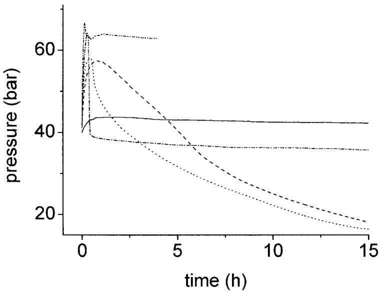


Figure 3. Pressure–time plots for batch polymerization of ethylene with $\mathbf{4_{PPHH}}$ at bath temperatures of 40 °C (solid), 70 °C (dash), 80 °C (dot), 100 °C (dash dot), 120 °C (dash dot dot); yields of isolated HDPE 7, 84, 83, 63, 35 %.

Catalysts prepared from 2-alkylphenylphosphanyl- and 2-dialkylphosphanylphenols and [Ni(cod)$_2$] in toluene usually become active around 70 °C and cause a slightly slower reaction rate. The maximum pressure decrease within 10 min was −26 and −18.5 bar for catalysis with **4**$_{\mathbf{PPHH}}$ and **4**$_{\mathbf{CCHH}}$ (each 12 g C_2H_4, 0.1 mmol **4** in 20 mL toluene), respectively, corresponding activities of roughly 360 and 270 g(PE) mmol^{-1}h^{-1}. In the case of moderate steric hindrance the 2-dialkylphosphanylphenolate catalysts display a stronger increase of the TON and ethylene conversion on raising the temperature from 80 to 100 °C. Steric congestion by two *tert*-butyl groups at the phosphorus center demands higher temperature for the catalyst formation so that **4**$_{\mathbf{BBHH}}$ needs 120 °C for high activity (Table 2). In contrast to the effect at phosphorus, *tert*-butyl groups in *ortho* and *para* position to the oxygen atom lower the formation temperature. In the case of **4**$_{\mathbf{BPBB}}$ the exothermic reaction begins during the addition of ethylene at room temperature. Similarly, **4**$_{\mathbf{IIBB}}$ induces a rapid start but then reacts much slower. The pressure–time plot with this catalyst (Figure 4) displays an atypical "starting needle" which was observed also for other 4,6-di-*tert*-butyl-substituted catalysts and suggests a different initial mechanism, for example by formation of di-*tert*-butylphenoxy radicals, but then returns to the usual reaction mode. *p*-Methoxy groups, which like 4,6-*tert*-butyl groups increase the basicity at the oxygen center, also cause slow reactions and high conversions. To compare phosphanylphenolate nickel catalysts with different substituents, most experiments were run at 100 °C and at an ethylene pressure of about 50 bar (p_{start}) using toluene as solvent.

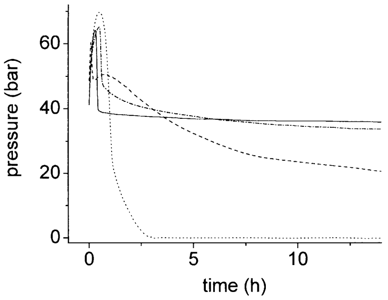


Figure 4. Pressure–time plots for the polymerization of ethylene with **4**$_{\mathbf{PPHH}}$ (solid), **4**$_{\mathbf{CCHH}}$ (dash dot), **4**$_{\mathbf{IIBB}}$ (dash) and **4**$_{\mathbf{PPOH}}$ (dot); bath temperature 100 °C.

Effects on catalyst stability: The pressure–time plot for the ethylene polymerization with **4**$_{\mathbf{PPHH}}$ in toluene at 100 °C reveals the maximum pressure roughly after the time necessary to heat up the reaction mixture to ≈70 °C (inside). Then, the reaction proceeds with rapid consumption of ethylene. **4**$_{\mathbf{CCHH}}$ behaves similarly with a slightly slower reaction rate (Figure 1). Addition of **4**$_{\mathbf{CCHH}}$ to a solution of ethylene in toluene (50 bar) preheated to 80 °C led to immediate polymerization, but strongly reduced the lifetime of the catalyst and gave low TON. The effect is even stronger with the solution formed from the secondary phosphanylphenol **2**$_{\mathbf{HIOH}}$ and [Ni(cod)$_2$]. In the usual batch procedure this catalyst[17a] causes high productivity and molecular weights of HDPE (Table 3), whereas the addition to a preheated solution of ethylene in toluene leads to deposition of inactive black nickel. These observations provide evidence that the use of high temperature in the initial phase favors the production of nickel at the expense of catalyst formation. Catalysts formed by slower heating in the presence of ethylene are more stable and display higher productivity. Since additives of α-olefins and also internal olefins increase the catalyst lifetime and conversion of ethylene considerably (see below), this effect may be attributed to resting states in which the catalyst is attached to the C=C bond of oligomers or polymers. The deactivation is then slow and depends also on the substitution pattern. Thus, using a larger amount of **4**$_{\mathbf{EEHH}}$, the inactive bis(chelate) **5**$_{\mathbf{EEHH}}$, for comparison syn-

Table 3. Polymerization of ethylene with 2-phosphanylphenolate nickel catalysts **4**, substituted in 4- or 4,6-position.

Product (conditions)[a]	Yield PE [%] (from C_2H_4 [g])	TON [mol mol^{-1}]	M.p. [°C]	ρ [g cm^{-3}]	M_w[f] [g mol^{-1}]	M_n[f] [g mol^{-1}]	M_w/M_n	^{1}H NMR:M [g mol^{-1}][j]	α/internal[j] olefins [%]	Me/C=C[j] (Me/1000 C)
PE$_{\mathbf{PPMH}}$	68 (13.0)	3140	125–127	0.96	n.d.	n.d.	n.d.	1560	94:6	1.4 (12.2)
PE$_{\mathbf{PPOH}}$[b]	53 (13.6)	2567	125–127	0.95	3600	1400	2.5	1850	95:5	1.5 (11.4)
PE$_{\mathbf{PPOH}}$	99 (13.2)	4670	124–126	0.95	n. d.	n. d.	n. d.	2340	89:10:1[k]	1.6 (9.7)
PE$_{\mathbf{PPFH}}$	83 (10.0)	2960	127–129	0.95	6600	2700	2.5	2840	92:8	1.4 (6.8)
PE$_{\mathbf{PPBB}}$	54 (11.8)	2285	124–126	0.95	n.d.	n.d.	n.d.	2200	88:12	1.6 (12)
PE$_{\mathbf{PPNA}}$[c]	74 (11.9)	3125	117–119 [e]	0.93	n.d.	n.d.	n.d.	1200	88:12	1.5 (20)
PE$_{\mathbf{MPMH}}$	68 (14.2)	3430	127–129	0.96	n.d.	n.d.	n.d.	3500	97:3	1.4 (5.8)
PE$_{\mathbf{IPMH}}$[d][15a]	48 (8.7)	700	121–124 [e]	n.d.	9300	6100	1.5	n.d.	n.d.	n.d.
PE$_{\mathbf{BPMH}}$	97 (15.2)	5250	120–122	0.95	n.d.	n.d.	n.d.	1700	94:6	1.6 (13)
PE$_{\mathbf{BPBB}}$	98 (14.9)	5200	126–128	0.945	5700	2800	2.0	2240	87:13	1.6 (13.7)
PE$_{\mathbf{IIFH}}$[b]	41 (12.4)	1818	130–132	0.95	17380	4000	4.3	5330	93:7	1.6 (4.2)
PE$_{\mathbf{IIFH}}$	79 (15.9)	4493	129–131	0.96	25690	4340	5.9 [g]	9000	92:8	1.4 (2.2)
PE$_{\mathbf{IIBB}}$[b]	54 (11.5)	2216	122–124 [e]	0.95	23200	1810	12.8 [h]	n.d.	n.d.	n.d.
PE$_{\mathbf{IIBB}}$	80 (17.6)	5030	130–132	0.95	30200	3630	8.3	5300	73:27	2.6 (6.9)
PE$_{\mathbf{CCOH}}$	97 (15.2)	5250	125–127	0.955	6710	2200	3.1	1900	92:8	1.4 (10.4)
PE$_{\mathbf{CCBB}}$	93 (9.0)	2994	116–118	0.955	2800	1800	1.6	1300	93:7	1.3 (14)
PE$_{\mathbf{HIOH}}$[b][17a]	94 (12.3)	4123	129–131	0.97	8.13×10^5	9.5×10^3	86 [i]	n.d.	n.d.	n.d.

[a] Conditions: 0.1 mmol catalyst in toluene (20 mL), $p_{\mathrm{start}} = 50$ bar C_2H_4, 100 °C, 15 h, else indicated. [b] as [a] but 80 °C. [c] **PPNA** means 1-diphenylphosphanylnaphth-2-ol[20b]. [d] 0.22 mmol **4**$_{\mathbf{IPMH}}$, C_2H_4 $p_{\mathrm{start}} = 40$ bar, $T = 140$ °C. [e] Without extraction of soluble oligomers with CH_2Cl_2. [f] M_w and M_n by SEC. [g] Bimodal, maximum 1.2×10^4, sh 1000. [h] Bimodal, maxima 4×10^3 and 5×10^4. [i] Maxima 3×10^3 and 1.6×10^5 g mol^{-1}. [j] Results from ^{1}H NMR analysis. [k] $CH_2{=}CRR'$ end groups.

thesized independently,[17b] could be detected in the solution ($\delta(^{31}P) = 39.0$ ppm). Catalysts with bulky substituents at the phosphorus atom or in position 6, form less favored *trans*- or distorted *cis*-bis(P∩O-chelates),[17,26] the majority of which display increased lifetimes and cause high conversion of ethylene (e.g. $\mathbf{4_{BBHH}}$ 94 %, $\mathbf{4_{BPBB}}$ 99 %, $\mathbf{4_{CCBB}}$ 93 %, $\mathbf{4_{IIBB}}$ 80 % HDPE) with turnover numbers limited by the molar ratio of C_2H_4 to **4** in the batch procedure. Thus, further addition of ethylene to the polymer catalyst ($\mathbf{4_{PPOH}}$) mixture at 100 °C led to continued polymerization.

Influence of the substituents at phosphorus: Substituents at P-phenyl groups have been considered only marginally. Introduction of one *o*-methoxy group on each phenyl ring causes similar conversion (56 %) and TON (2300) as $\mathbf{4_{PPHH}}$ under analogous conditions but lower molecular weights (M_w 2000, M_n 1120).[29] Replacement of the phenyl group by alkyl substituents at the phosphanyl group of **4** usually leads to increased TON and conversion of ethylene and in particular to higher molecular weights. The latter effect is strong for dialkylphosphanyl catalysts if there are no interfering substituents in the 4- or 6-positions (Table 2). The weight average molecular weights of the polyethylenes obtained with catalysts **4** of the type $2\text{-}R_2P\text{–}C_6H_4O^-$ increase roughly in the order R = Ph < Et ≈ *t*Bu < *i*Pr < *c*Hex. This indicates a superposition of two opposing effects, an increase of M_w with growing basicity of the phosphanyl group but decrease with increasing steric demand of the P-alkyl groups. The polydispersity M_w/M_n rises in the order R = Et ≈ *c*Hex < *i*Pr < *t*Bu and in case of $\mathbf{PE_{IIHH}}$ and $\mathbf{PE_{BBHH}}$ also with the temperature. With the exception of the *c*Hex_2P catalyst this corresponds to increasing Tolman angles (Et_2PPh, *i*Pr_2PPh, *c*Hex_2PPh, *t*Bu_2PPh $\vartheta = 136, 155, 162, 170°$[30]). The drop of the molecular weights with increasing polymerization temperature (80 versus 100 °C) agrees with the usual behavior of polymerization catalysts. The effect of one alkyl besides a phenyl group at phosphorus is quite low but shows the same trend as illustrated by the molecular weights observed for $\mathbf{PE_{MPMH}}$, $\mathbf{PE_{IPMH}}$, and $\mathbf{PE_{BPMH}}$ (Table 3) as compared to $\mathbf{PE_{PPHH}}$ and $\mathbf{PE_{PPMH}}$.

Influence of the substituents at the aryloxy group: The influence of a 4-methyl group in phosphanylphenolate nickel catalysts on the conversion of ethylene and the molecular weights of PE is low. *tert*-Butyl (+*I* effect), 4-methoxy and 4-flourine substituents (−*I*, +*M* effects) cause usually increased conversion of ethylene (temperature each 100 °C). The influence on the molecular weight distribution, however, is distinct and depends on the nature of the PR_2 group. 4,6-Di-*tert*-butyl, 4-methoxy and 4-fluorine combined with a 2-diphenylphosphanyl group cause slightly increased molecular weights of $\mathbf{PE_{PPFH}}$, $\mathbf{PE_{PPOH}}$ and $\mathbf{PE_{PPBB}}$ as compared to $\mathbf{PE_{PPHH}}$ (each prepared at 100 °C) while the combination with a 2-diisopropyl or dicyclohexylphosphanyl group leads to considerably lower molecular weights ($\mathbf{PE_{IIFH}}$ and $\mathbf{PE_{IIBB}}$ versus $\mathbf{PE_{IIHH}}$, each prepared at 80 °C). The effect is most pronounced for $\mathbf{PE_{CCBB}}$ and $\mathbf{PE_{CCOH}}$ versus $\mathbf{PE_{CCHH}}$ (100 °C, Table 2 and Table 3). Interestingly, 4-methoxy groups in secondary phosphanylphenolate ligands behave completely different and cause a strong increase of the weight average molecular weights. The high polydispersity and bimodal molecular weight distribution in this case might be due to insufficient mixing.[17a]

Influence of solvents and additives: The above investigations were all conducted in toluene. To explore the influence of the medium other solvents and additives have been tested, mainly with $\mathbf{4_{PPHH}}$ and $\mathbf{4_{CCHH}}$ as representatives of diphenyl- and dialkylphosphanylphenolate precatalysts. It was found that toluene, hexene, THF, DME, acetone, or DMF allow the ethylene polymerization (Figure 5, Table 4), while chlorobenzene leads to decomposition of $[Ni(cod)_2]$. Nonpolar solvents like *n*-hexane and strongly polar solvents like ethanol or ethyl acetate prevent a catalytic reaction by insufficient solubility or by favoring the formation of inactive bis(P∩O-chelate) nickel complexes,[14a] respectively. The suitability of the solvents depends also on the formation of sufficiently stable resting states to prevent deactivation, while coordination and subsequent insertion of ethylene into the Ni–H or Ni–C bond should not be seriously hindered in any of the solvents. The pressure–time plots for ethylene polymerization with $\mathbf{4_{PPHH}}$ or $\mathbf{4_{PPMH}}$ (Figure 6) and $\mathbf{4_{CCHH}}$ (Figure 7) in various solvents give an impression of the relative rates of ethylene consumption. They are lower for O-donor solvents like DME, THF, acetone (similar as

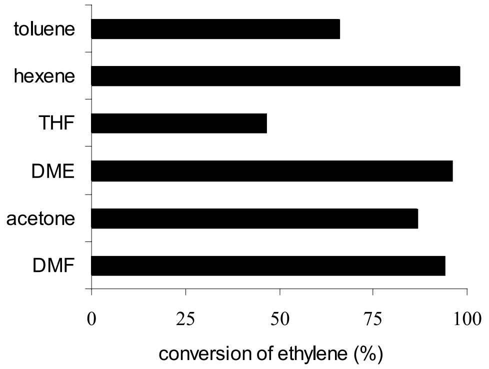


Figure 5. Polymerization of ethylene with $\mathbf{4_{PPHH}}$ in various solvents (conditions: C_2H_4 0.4–0.6 mol, p_{start} 50 bar, $\mathbf{4_{PPHH}}$ 0.1 mmol, 100 °C).

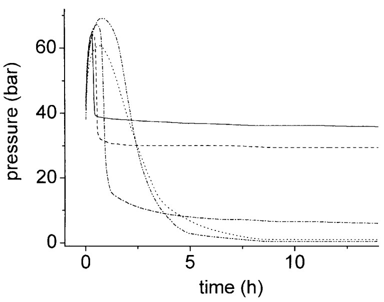


Figure 6. Pressure–time plots for batch polymerization of ethylene with $\mathbf{4_{PPHH}}$ in toluene (solid), THF (dash), DME (dash dot), hexene-1 (dash dot dot) and with $\mathbf{4_{PPMH}}$ in DMF (dot); bath temperature 100 °C.

Table 4. Polymerization of ethylene with $\mathbf{2_{PPHH}}$ or $\mathbf{2_{CCHH}}$ and [Ni(cod)$_2$] in various solvents systems

Product (conditions)[a]	Ligand	Solvents [mL]	Yield PE [%] (from C_2H_4 [g])	TON [mol mol^{-1}]	M.p. [°C]	ρ [g cm^{-3}]	M_w/M_n [g mol^{-1}][f]	^{1}H NMR:M [g mol^{-1}][h]	α/internal[h] olefins [%]	Me/C=C[h] (Me/1000 C)
95% HDPE 5% oil, wax	$\mathbf{2_{PPHH}}$	DME (20)	96 (11.3)	3850	125–127	0.955	3400 1600	1600	91:9	1.4 (12)
HDPE	$\mathbf{2_{PPHH}}$	acetone (20)	87 (13.7)	4230	125–127	0.955	n.d.	2140	88:12	2.0 (13)
HDPE	$\mathbf{2_{PPMH}}$	DMF (20)	94 (9.0)	3020	123–125	0.95	n.d.	2000	86:14	1.8 (12)
HDPE	$\mathbf{2_{PPHH}}$	THF (20)	66 (14.5)	3420	122–124	0.95	n.d.	1700	95:5	1.3 (11)
HDPE	$\mathbf{2_{CCHH}}$	THF (20)	57 (13.2)	2680	120–122[e]	0.96	3160 1630	2180	95:5	1.1 (7)
copolymer [b]	$\mathbf{2_{PPHH}}$	toluene (10) hexene-1 (10)	99 (15.9)	5700	112–114[e]	0.94	8700 6400[g]	[i]	65:35[i]	3.3 (7)[i]
sticky PE	$\mathbf{2_{PPHH}}$	toluene (20) isoprene (2)	57 (10.0)	2040	n.d.	n.d.	4940 2470	[i]	90:10[i]	1.4 (8)[i] 0.7 (4)[j]
PE, contamin. by oleate	$\mathbf{2_{PPHH}}$	toluene (15) ethyl oleate (5 g)	87 (12.7)	3960	117–119	n.d.	3840 1900	n.d.	[k]	≈3
PE	$\mathbf{2_{PPHH}}$	toluene (19) H_2O (1)	30 (13.1)	1400	123–125	0.945	2260 1340	1320	96:4	1.5 (17)
PE	$\mathbf{2_{CCHH}}$	toluene (19) H_2O (1)	28 (13.7)	1360	128–129	0.94	n.d.	n.d.		
PE	$\mathbf{2_{CCHH}}$	toluene (2) H_2O (18) [c]	20 (7.4)	540	n.d.	n.d.	n.d.	n.d.		
HDPE	$\mathbf{2_{CCHH}}$	THF (19) H_2O (1)	69 (6.1)	1500	129–131	0.955	34000 12600	uncertain	>97:3	≈1.6 (2.5)
HDPE	$\mathbf{2_{CCHH}}$	THF (10) H_2O (10)	40 (10.7)	1530	131–133	0.96	39000 14500	uncertain	97:3	≈1.3 (1.9)
HDPE	$\mathbf{2_{PPHH}}$	toluene (15) $nC_5H_{11}Br$ (5)	88 (11.2)	3490	123–125	0.96	n. d.	2000	73:27	1.5 (11)
HDPE	$\mathbf{2_{PPHH}}$	toluene (18) CH_3CN (2)	60 (14.5)	3100	117–119[e]	0.95	n. d.	1850	97:3	2.1 (23)
80% wax 20% oil	$\mathbf{2_{PPHH}}$	toluene (18) pyridine (2)	84 (12.3)	3670	wax 75–77[e]	n.d.	n.d.	325	95:5	1.2
hard wax	$\mathbf{2_{PPHH}}$	toluene (18) THT (2)[d]	63 (13.4)	3000	110–112[e]	0.94	n. d.	780	97:3	1.2

[a] Conditions: 0.1 mmol catalyst, $p_{start} = 50$ bar C_2H_4, 100 °C, 15 h. [b] *Co*-hexene content about 3% of C atoms. [c] In the presence of $C_{16}H_{33}SO_3Na$ (131 mg). [d] THT = tetrahydrothiophene. [e] Without extraction of soluble oligomers with CH_2Cl_2 [f] M_w and M_n by SEC. [g] Small maximum at 3.7×10^5 g mol^{-1}. [h] Results from ^{1}H NMR analysis, unless indicated otherwise measured at 100 °C after swelling. [i] Measured at 80 °C without swelling, integral ratio towards CH_2 not reliable. [j] Separate Me signal $\delta = 0.90$. [k] *E/Z*-CH=CH signal superimposed by oleate contamination.

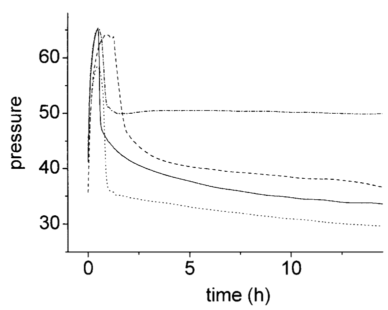


Figure 7. Pressure–time plots for batch polymerization of ethylene with $\mathbf{4_{CCHH}}$ in THF (dash) and in THF/water (19:1 mL, dot, and 10:10 mL, dash dot) versus $\mathbf{4_{CCHH}}$ in toluene (solid); bath temperature 100 °C.

THF) or DMF and for hexene-1 compared to toluene due to stronger solvent catalysts interactions. In the case of O-donor solvents this is accompanied by lower molecular weights indicating that the olefin elimination step is effected to a lesser extend by weak coordination of solvents in competition with ethylene than the chain growth step. Hexene causes higher molecular weights, but some hexene is taken up and the NMR spectra of the polymer show formation of copolymers and thus the solvent no longer acts as a mere accessory. Copolymerizations of ethylene with olefins in presence of $\mathbf{4_{PPHH}}$ and $\mathbf{4_{CCHH}}$ will be reported separately.[17c] Additions of ethyl oleate, which does not react with but stabilizes $\mathbf{4_{PPHH}}$, lead to increased conversion of ethylene with slightly decreased molecular weights of the polymer. Addition of the conjugated diene isoprene lowers the yield and gives a sticky polymer, whereas additions (2 mL each) of butadiene-1,3 and of conjugatedly unsaturated hard–soft chelate ligands such as ethyl methacrylate, ethyl vinylacetate, acrylonitrile or vinylpyridine deactivate the catalyst in toluene. Vinyltrimethoxysilane and vinylbromide also suppress the polymerization of ethylene by $\mathbf{4_{PPHH}}$. As shown by the activity in presence of O- or N-donor solvents or auxiliaries as well as in presence of bromopentane (5 mL) (Table 4), the deactivation is not due to simple Lewis base properties but to the neighborhood of the C=C bond and a Lewis base center.

It should be emphasized that 2-phosphanylphenolate nickel catalysts not only tolerate ethers or some carbonyl compounds but like the related P∩O-enolate SHOP-catalysts[12,13] also permit to work in presence of moisture or even higher amounts of water. The effects depend on the solvent. Additions of 5% water decrease the conversion of ethylene in toluene to about 30%, with $\mathbf{4}_{\mathbf{PPHH}}$ as well as with $\mathbf{4}_{\mathbf{CCHH}}$ as precatalyst, whereas the same amount of water in THF induces an increased conversion. The pressure–time plot of the latter shows that the reaction becomes faster than in dry THF (Figure 7). Increase of the water content to 50% has no further effect on the rate and lowers the conversion to 40% but the molecular weight of the polymer is higher than in the presence of only 10% of water. Further increase of the water content leads to precipitation of the ligand or catalyst and low activity. Attempts with the biphasic system water/toluene (18:2 mL) using sodium 1-hexadecanesulphonate (131 mg) as phase-transfer reagent gave only slightly higher conversions (20%) than reaction in water/THF (19:1 mL).

Finally, it should be mentioned that phosphanylphenolate nickel catalysts tolerate acetonitrile and even amine or thioether additives. The effect of acetonitrile (2 mL) is relatively low while tetrahydrothiophene (2 mL, 226 molar excess relative to $\mathbf{4}_{\mathbf{PPHH}}$) and pyridine (2 mL, 246 molar excess), which are softer and known to strongly coordinate to nickel(II), cause a significant drop of the reaction rate (Figure 8) and molecular weights but stabilize the catalysts and increase the conversion of ethylene. The presence of tetrahydrothiophene leads to linear low-molecular weight polyethylene (hard wax α-olefins), that of pyridine to liquid and waxy oligomers with an increased content of β- and internal olefins. The effects resemble that of phosphane additives which, depending on the basicity and Tolman angle, give hard or soft waxes, lower linear α-olefins or isoolefines (C4-20), or suppress the conversion.[17b,31]

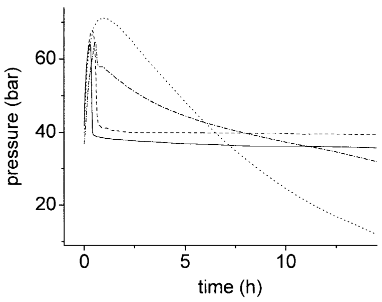
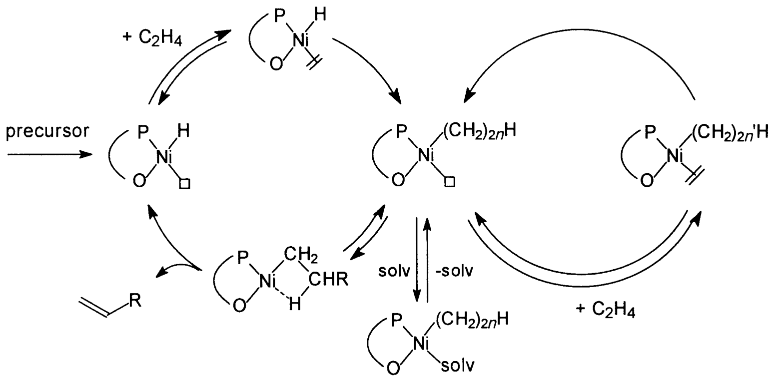


Figure 8. Pressure–time plots for batch polymerization of ethylene with $\mathbf{4}_{\mathbf{PPHH}}$ in toluene (18 mL) in the presence of an additive (2 mL): acetonitrile (dash), pyridine (dot), tetrahydrothiophene (dash dot); $\mathbf{4}_{\mathbf{PPHH}}$ in toluene (solid) as reference; bath temperature 100 °C.

Polymer structure: Density, NMR and IR spectra as well as X-ray powder diffraction measurements of representative samples give evidence that the polyethylenes obtained with 2-phosphanylphenolate catalysts are mainly linear α-olefins with a high degree of crystallinity. Smaller amounts of β- and further internal olefins and low methyl and long-chain branching were detected by NMR studies. The ratio of α to internal olefins and the average content of methyl group per olefin and per 1000 carbon atoms based on ^{1}H NMR integration are given in Table 1 Table 2 Table 3 Table 4. To get reliable data, the measurements were conducted in C_6D_5Br at 100 °C after swelling at 120 °C for one day. Under these conditions the average molecular weights calculated per olefin agree sufficiently with the M_n values determined by GPC except for high molecular weight polymers ($M_n >$ 20000 g mol^{-1}). The highest contents of internal olefins are observed for polyethylenes obtained with branched 2-dialkylphosphanylphenolate nickel catalysts at 100 °C ($\mathbf{PE}_{\mathbf{BBHH}}$ 23%, $\mathbf{PE}_{\mathbf{CCHH}}$ 13%, $\mathbf{PE}_{\mathbf{IIHH}}$ 12%) or with catalysts combining 4-methoxy or 4,6-di-*tert*-butyl with diphenyl- or diisopropylphosphanyl groups (up to 27%). The characteristic doublets for the *E/Z* methyl groups adjacent to the double bond in β-olefins ($\delta = 1.56$, 1.58) are usually superimposed by satellites of the intensive CH_2 signals allowing no closer separation of β- and internal olefins while both are easily distinguished from α-olefins (vinyl multiplets at $\delta = 5.77$, 5.00, 4.96 ppm) by the different chemical shifts of the CH=CH protons at $\delta = 5.40$ ppm. The degree of branching is low, ranging from 1.1 to 1.6 methyl groups per olefin in the polyethylenes obtained with diphenyl- and about 1.8 to 2.6 methyl per olefin in the polymers formed with dialkylphosphanylphenolate nickel catalysts. The higher values are observed with catalysts containing diisopropylphosphanyl, 4-methoxy or 4,6-di-*tert*-butyl substituents (except for $\mathbf{4}_{\mathbf{CCME}}$ or $\mathbf{4}_{\mathbf{CCBB}}$) while 4-fluorine gives rise to less branching. The catalyst type seems to have no significance, $\mathbf{PE}_{\mathbf{PPHH}}$, $\mathbf{PE}_{\mathbf{2PPHH}}$, and $\mathbf{PE}_{\mathbf{5PPHH}}$ as well as $\mathbf{PE}_{\mathbf{PPOH}}$ and $\mathbf{PE}_{\mathbf{2PPOH}}$ each display the same degree of branching. Also additions of pyridine or tetrahydrothiophene to $\mathbf{4}_{\mathbf{PPHH}}$ did not effect the branching despite its strong influence on the rate and molecular weights. ^{13}C NMR spectra of selected polymers, measured under similar conditions as the proton spectra but in the presence of chromium acetylacetonate, give evidence that the excess methyl groups derive from methyl and long-chain branching. Based on the relative intensities of the αB_1 to αB_n and βB_1 to βB_n signals (assignment as described in[32]), the ratio in most cases is about 2:1 to 3:1 ($\mathbf{PE}_{\mathbf{PPHH}}$, $\mathbf{PE}_{\mathbf{PPMH}}$, $\mathbf{PE}_{\mathbf{IIBB}}$; $\mathbf{PE}_{\mathbf{CCHH}}$, $\mathbf{PE}_{\mathbf{5PPHH}}$, $\mathbf{PE}_{\mathbf{2PPOH}}$) or higher ($\mathbf{PE}_{\mathbf{BBHH}}$, $\mathbf{PE}_{\mathbf{IIFH}}$). Preferred long-chain branching was observed only for $\mathbf{PE}_{\mathbf{2PPOH}}$ (ca. 1:2).

Discussion: Based on the experiments with different types of phosphanylphenolate catalysts, the structural requirements observed in the screening tests, and the effects of substituents and solvents, a mechanism is proposed for the polymerization of ethylene by the title catalysts (Scheme 4).

Nickel–hydride complexes formed from organonickel complexes by olefin elimination or by reaction with sodium hydride initiate the polymerization by coordination and insertion of ethylene. The polymerization is maintained by continuous insertion of ethylene into the C(alkyl)–Ni bond. Termination occurs through β-hydride elimination and regeneration of the nickel–hydride species. Chain transfer is possible, but its relative rate is low and causes only minor methyl and long-chain branching, slightly higher in the case of dialkylphosphanyl- than diphenylphosphanylphenolate catalysts.



Scheme 4. Proposed mechanism of the polymerization of ethylene by phosphanylphenolate nickel catalysts.

The strong increase in molecular weight of the polyethylenes by the use of dialkyl- instead of alkylphenyl- and diphenylphosphanylphenolate nickel catalysts is attributed to the weaker *trans* influence of dialkylphosphanyl as compared to alkylphenyl- and diphenylphosphanyl groups, that is the weaker back donation indicated by the larger ^{31}P coordination chemical shift. The weaker back donation diminishes the positive charge at the nickel center as compared to that in diphenylphosphanylphenolate catalysts and weakens the bonding of ligands in *trans* position to the phosphorus atom. This is illustrated by the lower coalescence temperature in the ^{31}P NMR spectra of the kinetically unstable square-planar diisopropyl- as compared to diphenylphosphanylphenolato-methylnickel(trimethylphosphane) complexes (−70 versus −25 °C)[16] and suggests less efficient interaction with hydrogen at the β-C atom of the growing polymer chain. This impedes olefin elimination and results in higher average molecular weights when dialkylphosphanylphenolate catalysts are used.

The influence of 4,6-*tert*-butyl, 4-fluorine, and 4-methoxy substituents is probably due to the enhanced electron density at C1 and the increase of the basicity of the phenolate oxygen atom. This may lead to a (kinetic) stabilization of the Ni–C bond and be the reason for the slower ethylene consumption in $\mathbf{4}_{\mathbf{PPMH}}$ and $\mathbf{4}_{\mathbf{PPBB}}$ than in $\mathbf{4}_{\mathbf{PPHH}}$ (Figure 4). Because of the large excess of ethylene and the rapid ligand exchange in *trans* position to the phosphorus atom (ref.[16] and below) the insertion of C_2H_4 into the Ni–C bond, that is the chain growth, is regarded as the rate-limiting step of ethylene consumption (Scheme 4). A plausible explanation of the different effects of 4-methoxy groups on dialkylphosphanyl- and secondary phosphanylphenolate catalysts is that an increased steric demand of the P-substituents favors conformations of the polymer chain with the β-CH closer to the *trans* position of the phosphanyl group. This facilitates β-hydride elimination and thus leads to termination of the chain growth reaction and to shorter polymers. It also accounts for the steric effects observed for diisopropyl- and di-*tert*-butylphosphanyl groups. The much smaller influence in diphenylphosphanylphenolate catalysts may be attributed to the general higher relative rates of β-hydride eliminations.

The solvents influence the catalytic process by competing with ethylene for interactions with or coordination at the catalyst. Suitable solvents provide resting states sufficiently stable to prevent deactivation and sufficiently reactive to allow rapid coordination of ethylene. The stronger the coordination of the solvent or an additive to nickel the slower the polymerization (ethylene consumption). Except in the case of copolymerization with α-olefins this leads to a decrease in molecular weights and thus indicates that the termination by β-hydrogen transfer is less strongly influenced by the solvents than chain growth.

Conclusion

Ethylene is polymerized by a variety of 2-phosphanylphenolate nickel catalysts. The molecular weights can be tuned from $M_w < 1000$ up to $10^5\,\mathrm{g\,mol^{-1}}$ by selection of suitable substituents at the phosphorus atom or the aroxy group, or by choice of solvent and additives. The catalyst lifetime and TON can be increased by suitable reaction conditions, substituents, and solvents or additives stabilizing the catalyst. As the turnover number in many examples with conversion above 90% was limited by the ethylene-to-catalyst ratio, flow reactors will allow much higher TON than reported here. The low sensitivity of the 2-dialkylphosphanylphenolate nickel catalysts towards water allows the expectation that water-soluble phosphanylphenolate nickel catalysts can be found for polymerization of ethylene in an aqueous catalyst solution or in biphasic systems.

Experimental Section

General remarks: The reactions were carried out under carefully dried, oxygen-free argon, using Schlenk techniques and freshly distilled dry solvents. For work in aqueous mixtures, degassed water was used. $PhOCH_2OMe$,[33] $c\mathrm{Hex}_2PCl$,[34] $t\mathrm{BuPhPCl}$,[35] $t\mathrm{Bu}_2PCl$,[36] known 2-phosphanylphenols,[18–21] and $[Ni(cod)_2]$[37] were synthesized as reported, other chemicals were purchased. Ethylene (99.5%, Air Liquide) was used without further treatment. NMR spectra were recorded on a multinuclear FT-NMR spectrometer ARX300 (Bruker) at 300.1 (^1H), 75.5 (^{13}C), and 121.5 (^{31}P) MHz. Shift references are tetramethylsilane for ^1H and ^{13}C and H_3PO_4 (85%) for ^{31}P. Assignment numbers are given in Scheme 2. Proton or carbon nuclei of phenyl or cyclohexyl groups are denoted *i*, *o*, *m*, *p* and α, β, γ, δ, respectively. Coupling constants refer to $J_{H,H}$ in ^1H and $J_{P,C}$ in ^{13}C NMR data unless stated otherwise. Assignments are supported by DEPT and in part by CH-COSY experiments. IR spectra were measured on a FTIR-spectrometer System 2000 (Perkin Elmer), mass spectra on a single-focussing mass spectrometer AMD40 (Intectra). Melting points were determined with a Sanyo Gallenkamp melting point apparatus. TG/DTA were carried out with SETARAM TGDTA 92–16 ($5\,\mathrm{K\,min^{-1}}$, **3** was heated under argon) and elemental analyses with a CHNS-932 analyzer from LECO using standard conditions.

Aryl methoxymethyl ethers:

General procedure A: The corresponding phenols, the 4–5-fold molar amount of dimethoxymethane (100 mL, 1.13 mol), and *p*-toluenesulfonic acid (300 mg) were dissolved in dry dichloromethane (500 mL) and refluxed for 8–12 h in a Soxhlett apparatus charged with freshly dried molecular sieves (4 Å, 200 g) to bind the methanol formed. If the reaction was incomplete (NMR control), the molecular sieves were replaced by a freshly dried charge and refluxing was continued. Then, the mixture was cooled to 0 °C and, after addition of triethylamine (4 mL), was washed twice with 1 N aqueous sodium hydroxide solution (200 mL) and with water. After drying over sodium sulfate and removal of the solvent, the product was distilled. Product data are given in Table 5.

General procedure B: The phenol (0.1 mol) was added to a suspension of NaH (2.4 g, 0.1 mol) in toluene (500 mL) and heated for 2 h to 80 °C. After the mixture had been cooled to 0 °C, a solution of chloromethylmethyl ether (7.6 mL, 0.1 mol) in toluene (10 mL) was added dropwise. The suspension was refluxed for 2 h, cooled to 0–5 °C, and stirred for 1 h with cold 1 N NaOH (200 mL). Then the organic layer was separated, washed with cold 1 N NaOH, dried on sodium sulfate, and distilled in vacuum. Product data are given in Table 5.

Table 5. Yields, boiling points, and ^{1}H NMR data ($CDCl_3$, δ, J in Hz) of substituted aryl methoxymethyl ethers.

substituents R	4-OMe	4-F	2,4-*t*Bu$_2$	2-OMe	3-OMe
method A					
arOH g (mmol)	30.8 (248)	12.2 (109)	51.6 (250)	27.2 (219)	24.4 (197)
yield in g (%)	21.8 (52)	9.2 (54)	6.9 (11)	10.7 (29)	10.6 (32)
method B					
yield in g (%)	13.4 (80)	10.1 (65)	13.5 (54)		
b.p. in °C/Torr	101/1	113/10	130/0.02	97/1	77–80/1
OCH_3	3.46 (s, 3 H)	3.47 (s, 3 H)	3.49 (s, 3 H)	3.52 (s, 3 H)	3.48 (s, 3 H)
OCH_2O	5.09 (s, 2 H)	5.12 (s, 2 H)	5.21 (s, 2 H)	5.23 (s, 2 H)	5.16 (s, 2 H)
R	3.74 (s, 3 H)		1.29/1.42 (2s, 18 H)	3.88 (s, 3 H)	3.79 (s, 3 H)
Aryl	6.81 (d, 2 H) 6.97 (d, 2 H) ($J_{H,H}=9.2$)	6.97 (ddd, 2 H)[a] 6.98 (ddd, 2 H)[b] ($^3J_{F,H}=7.4$, $^4J_{F,H}=5.3$, $J_{HH}=9.3, 0.6$)	7.03 (d, 1H-6) 7.16 (dd, 1H-5) 7.33 (d, 1H-3) ($J_{H,H}=8.5, 2.5$)	6.87 (m, 1 H) 6.91 (m, 1 H) 6.99 (m, 1 H) 7.16 (m, 1 H)	6.56 (m, 1 H) 6.61 (m, 1 H) 6.64 m, 1 H) 7.18 (m, 1 H)

[a] H-3, H-5. [b] H-2, H-6 (A_2B_2X type).

2-Phosphanylphenyl methoxymethyl ethers:

2-(Diphenylphosphanyl)-4-methoxyphenyl methoxymethyl ether (1$_{\mathbf{PPOH}}$): A solution of *n*BuLi (39.0 mL, 1.6 M in hexane, 62.4 mmol) and TMEDA (7.0 g, 60.2 mmol) in diethyl ether (30 ml) was added dropwise at 0 °C to a solution of $4\text{-}CH_3OC_6H_4OCH_2OCH_3$ (10.0 g, 59.5 mmol) in the same solvent and stirred overnight. Subsequently, a solution of Ph_2PCl (13.1 g, 59.4 mmol) in petroleum ether (15 mL) was added dropwise at 0 °C, stirring was continued for 15 h at ambient temperature and the solvent removed in vacuum. The orange residue was extracted with CH_2Cl_2 (20 mL), and the extract was washed with aqueous NaH_2PO_4 solution (1 M) followed by water. Drying with Na_2SO_4, addition of methanol (80 mL), and storage at 0 °C for one day furnished white crystals which were dried at 10^{-4} Torr to yield **1**$_{\mathbf{PPOH}}$ (12.8 g; 61 %), m.p. 86 °C. ^{1}H NMR (C_6D_6): $\delta=3.04$ (s, 3 H; OCH_3), 3.18 (s, 3 H; 4-OCH_3), 4.78 (s, 2 H; OCH_2O), 6.60 (dd, $^4J=3.1$, $^3J_{P,H}=4.5$ Hz, 1 H; H-3), 6.71 (ddd, $^3J=8.9$, $^4J=3.1$, $^5J_{P,H}=0.7$ Hz, 1 H; H-5), 7.01–7.07 (m, 6 H; ArH), 7.10 (dd, $^3J=8.9$, $^4J_{P,H}=4.8$ Hz, 1 H; H-6), 7.40–7.50 ppm (m, 4 H; ArH); ^{13}C NMR (C_6D_6): $\delta=55.6$ (OCH_3), 56.3 (OCH_3), 95.7 (OCO), 115.7 (C-5), 116.2 (d, $^3J=1.8$ Hz; C-6), 120.3 (C-3), 129.4 (d, $^3J=7.0$ Hz; C-*m*), 129.5 (C-*p*), 129.6 (d, $^1J=16.4$ Hz; C-2), 135.1 (d, $^2J=21.0$ Hz; C-*o*), 138.3 (d, $^1J=11.7$ Hz; C-*i*), 154.4 (d, $^2J=15.0$ Hz; C-1), 156.0 ppm (C-4); ^{31}P{^{1}H} NMR (C_6D_6): $\delta=-14.1$ ppm; MS (EI, 200 °C): *m/z* (%): 352 (75) [M^+], 338 (22), 337 (100), 321(11), 309 (72), 308 (17), 292 (27), 231 (30), 229 (25), 183 (61), 121 (44), 45 (85); elemental analysis calcd (%) for $C_{21}H_{21}O_3P$ (352.37): C 71.58, H 6.01; found: C 71.18, H 6.24.

2-(Diphenylphosphanyl)-4-fluorophenyl methoxymethyl ether (1$_{\mathbf{PPFH}}$): A solution of *n*BuLi in hexane (29.4 mL, 1.6 M, 47.0 mmol) was added dropwise with stirring to a solution of $4\text{-}FC_6H_4OCH_2OCH_3$ (7.0 g, 44.8 mmol) in diethyl ether (80 mL) at −50 °C and then allowed to warm to room temperature. After 3 h the solution was cooled again to −50 °C, a solution of chlorodiphenylphosphane (9.9 g, 44.8 mmol) in diethyl ether (10 mL) was added dropwise, and the suspension was stirred overnight at room temperature. The precipitate was removed, the solvent was replaced by dichloromethane (10 mL), and methanol (100 mL) was added. At 0 °C white crystals separated and were dried at 10^{-4} Torr, yield 7.1 g (47 %), m.p. 76 °C. ^{1}H NMR (C_6D_6): $\delta=2.94$ (s, 3 H; OCH_3), 4.65 (s, 2 H; OCH_2O), 6.70–6.78 (m, 2 H; H-3, H-5), 6.84–6.91 (m, 1 H; H-6), 7.00–7.05 (m, 6 H; ArH), 7.32–7.40 ppm (m, 4 H; ArH); ^{13}C NMR (C_6D_6): $\delta=55.7$ (OCH_3), 94.7 (OCO), 115.3 (d, $^3J_{F,C}=8.5$ Hz; C-6), 116.5 (d, $^2J_{F,C}=23.3$ Hz; C-5), 120.4 (d, $^2J_{F,C}=23.4$ Hz; C-3), 128.8 (d, $^3J=7.1$ Hz; C-*m*), 129.1 (C-*p*), 130.3 (dd, $^1J=5.0$, $^3J_{F,C}=17.6$ Hz; C-2), 134.4 (d, $^2J=21.1$ Hz; C-*o*), 136.8 (d, $^1J=11.8$ Hz; C-*i*), 155.4 (dd, $^2J=15.3$, $^4J_{F,C}=2.2$ Hz; C-1), 158.5 ppm (d, $^1J_{F,C}=241.7$ Hz; C-4); ^{31}P{^{1}H} NMR (C_6D_6): $\delta=-14.6$ ppm; MS (EI, 200 °C): *m/z* (%): 341 (2) [M^+], 322 (35), 308 (21), 307 (100), 279 (48), 262 (43), 201 (31), 199 (65), 183 (86), 152 (33), 121 (31), 77 (12), 45 (32); elemental analysis calcd (%) for $C_{20}H_{18}FO_2P$ (341.33): C 70.58, H 5.33; found: C 70.76, H 5.20.

2-(Diethylphosphanyl)phenyl methoxymethyl ether (1$_{\mathbf{EEHH}}$): A solution of $C_6H_5OCH_2OCH_3$ (5.6 g, 40.5 mmol) in diethyl ether (80 mL) was allowed to react with *n*BuLi in hexane (26.3 mL, 1.6 M, 42.1 mmol) and subsequently with chlorodiethylphosphane (5.0 g, 40.2 mmol) in diethyl ether (10 mL) under the conditions described for **1**$_{\mathbf{PPFH}}$. After filtration and removal of the solvent an oily yellow residue was obtained which was distilled at 55–57 °C/2.4 × 10^{-4} Torr, to yield **1**$_{\mathbf{EEHH}}$ as a colorless oil (7.3 g; 80 %). ^{1}H NMR (C_6D_6): $\delta=1.02$ (dt, $^3J_{P,H}=14.2$, $^3J=7.6$ Hz, 6 H; CH_3), 1.70, 1.72 (m, $^2J\approx15$, $^3J_{(A)}=7.5$, $^3J_{(B)}=7.7$, $^2J_{P,H(A)}=2.0$, $^2J_{P,H(B)}=1.6$ Hz, 2 H; PCH_AH_B), 3.18 (s, 3 H; OCH_3), 4.89 (s, 2 H; OCH_2O), 6.90 (m, $^3J=7.6, 7$, $^4J=1.7$ Hz, 1 H; H-4), 7.06 (m, $^3J=8.3$, $^4J_{P,H}=3.1$, $^4J=1.7$ Hz, 1 H; H-6), 7.11 (m, $^3J=8.2, 7$, $^4J=1.5$ Hz, 1 H; H-5), 7.30 ppm (m, $^3J=7.6$, $^3J_{P,H}=4.7$, $^4J=1.5$ Hz, 1 H; H-3); ^{13}C NMR ($CDCl_3$): $\delta=9.6$ (d, $^2J=12.9$ Hz; CH_3), 17.4 (d, $^1J=11.6$ Hz; CH_2), 56.0 (OCH_3), 94.3 (OCO), 113.5 (d, $^3J=1.6$ Hz; C-6), 121.7 (d, $^3J=2.1$ Hz; C-4), 126.9 (d, $^1J=18.8$ Hz; C-2), 129.4 (C-5), 131.4 (d, $^2J=5.4$ Hz; C-3), 159.2 ppm (d, $^2J=12.1$ Hz; C-1); ^{31}P{^{1}H} NMR: $\delta(C_6D_6)=-23.5$ ppm; $\delta(CDCl_3)=-24.5$ ppm; MS (EI, 150 °C): *m/z* (%): 226 (42) [M^+], 211 (100), 183 (93), 138 (90), 125(46), 121 (22), 110 (42), 109 (53),107 (36), 91 (35), 77 (40), 61 (32), 47 (69), 45 (99); elemental analysis calcd (%) for $C_{12}H_{19}O_2P$ (226.26): C 63.70, H 8.46; found: C 63.90, H 8.60.

2-(Diisopropylphosphanyl)phenyl methoxymethyl ether (1$_{\mathbf{IIHH}}$): By using the procedure reported for **1**$_{\mathbf{EEHH}}$, a solution of $C_6H_5OCH_2OCH_3$ (6.4 g, 46.3 mmol) in diethyl ether (80 mL) was allowed to react with *n*BuLi in hexane (29 mL, 1.6 M, 46.4 mmol) and with chlorodiisopropylphosphane (7.0 g, 45.9 mmol) in diethyl ether (10 mL) to give **1**$_{\mathbf{IIHH}}$ as a colorless liquid (5.1 g; 44 %), b.p. 62–63 °C/4 × 10^{-4} Torr. ^{1}H NMR (C_6D_6): $\delta=0.97$ (dd, $^3J_{P,H}=11.5$, $^3J=6.9$ Hz, 6 H; CH_3), 1.17 (dd, $^3J_{P,H}=14.8$, $^3J=7.0$ Hz, 6 H; CH_3), 2.20 (sept d, $^3J\approx7.0$, $^2J_{P,H}=1.8$ Hz, 2 H; PCH), 3.20 (s, 3 H; OCH_3), 4.90 (s, 2 H; OCH_2O), 6.88 (m, 1 H; H-4), 7.09–7.15 (m, 2 H; H-5, H-6), 7.42 (m, $^3J\approx7.4$, $^3J_{P,H}\approx5.8$, $^4J\approx1.1\text{–}1.3$, $^5J\approx0.7$ Hz, 1 H; H-3); ^{13}C NMR (C_6D_6): $\delta=20.6$ (d, $^2J=10.7$ Hz; CH_3), 21.4 (d, $^2J=20.6$ Hz; CH_3), 24.2 (d, $^1J=14.1$ Hz; PCH), 56.6 (OCH_3), 95.5 (OCH_2O), 115.4 (d, $^3J=2.0$ Hz; C-6), 122.4 (d, $^3J=4.7$ Hz; C-4), 125.9 (d, $^1J=24.9$ Hz, C-2), 131.1 (C-5), 136.3 (d, $^2J=13.1$ Hz, C-3), 161.9 ppm (d, $^2J=10.0$ Hz; C-1); ^{31}P{^{1}H} NMR (C_6D_6): $\delta=2.7$ ppm; MS (EI): *m/z* (%): 254 (19) [M^+], 240 (14), 239 (100), 211 (37), 169 (14), 152 (40), 110 (28), 45 (52), 43 (21); elemental analysis calcd (%) for $C_{14}H_{23}O_2P$ (254.31): C 66.12, H 9.12; found: C 66.02, H 9.22.

2-(Diisopropylphosphanyl)-4-fluorophenyl methoxymethyl ether (1$_{\mathbf{IIFH}}$): By using the procedure reported for **1**$_{\mathbf{EEHH}}$, a solution of $4\text{-}FC_6H_4O\text{-}CH_2OCH_3$ (7.0 g, 44.8 mmol) in diethyl ether (80 mL) was allowed to react with *n*BuLi in hexane (29.0 mL, 1.6 M, 46.4 mmol) and *i*Pr_2PCl (6.7 g, 43.9 mmol) in diethyl ether (10 mL) to give $\mathbf{1}_{\mathbf{IIFH}}$ as a colorless oil (10.3 g; 86 %), b.p. 68–70 °C/4 × 10^{-4} Torr. ^{1}H NMR (C_6D_6): $\delta = 0.89$ (dd, $^{3}J_{P,H} = 11.7$, $^{3}J = 6.9$ Hz, 6H; CH_3), 1.08 (dd, $^{3}J_{P,H} = 14.7$, $^{3}J = 7.0$ Hz, 6H; CH_3), 1.99 (sept d, $^{3}J = 7.0$, $^{2}J_{P,H} = 1.2$ Hz, 2H; PCH), 3.17 (s, 3H; OCH_3), 4.81 (s, 2H; OCH_2O), 6.76 (ddd, $^{3}J = 9.0$, $^{3}J_{F,H} = 7.7$, $^{4}J = 3.2$ Hz, 1H; H-5), 6.92 (ddd, $^{3}J = 9.0$, $^{4}J_{F,H} = 4.6$, $^{4}J_{P,H} = 3.3$ Hz, 1H; H-6), 7.18 ppm (ddd, $^{3}J_{F,H} = 8.6$, $^{3}J_{P,H} = 4.0$, $^{4}J_{H} = 3.1$ Hz, 1H; H-3); ^{13}C NMR ($CDCl_3$): $\delta = 19.2$ (d, $^{2}J = 10.1$ Hz; CH_3), 20.0 (d, $^{2}J = 19.0$ Hz; CH_3), 22.9 (d, $^{1}J = 12.7$ Hz; CH), 56.0 (OCH_3), 95.2 (OCO), 115.5 (d, $^{3}J_{F,C} = 6.2$, $^{3}J = 1.7$ Hz; C-6), 116.2 (d, $^{2}J_{F,C} = 23.1$ Hz; C-5), 120.1 (dd, $^{2}J_{F,C} = 21.8$, $^{4}J = 6.5$ Hz; C-3), 126.5 (dd, $^{3}J_{F,C} = 25.3$, $^{1}J \approx 4.4$ Hz; C-2), 156.8 (dd, $^{2}J = 10.4$, $^{4}J_{F,C} = 2.2$ Hz; C-1), 157.3 ppm (dd, $^{1}J_{F,C} = 241.8$, $^{3}J = 2.3$ Hz; C-4); $^{31}P\{^{1}H\}$ NMR (C_6D_6, 25 °C): $\delta = 0.5$ ppm.

2-(Dicyclohexylphosphanyl)phenyl methoxymethyl ether ($\mathbf{1}_{\mathbf{CCHH}}$): By using the procedure reported for $\mathbf{1}_{\mathbf{EEHH}}$, a solution of $C_6H_5OCH_2OCH_3$ (15.0 g, 108.6 mmol) in diethyl ether (80 mL) was allowed to react with *n*BuLi in hexane (68.0 mL, 1.6 M, 108.8 mmol) and with chlorodicyclohexylphosphane (25.2 g, 108.3 mmol) in diethyl ether (10 mL) to give $\mathbf{1}_{\mathbf{CCHH}}$ as a viscous colorless oil (21.0 g; 58 %), b.p. 140–150 °C/2 × 10^{-4} Torr. ^{1}H NMR ($CDCl_3$): $\delta = 0.85–0.95$ (m, 2H; Cy), 1.10–2.05 (m, 20H; Cy), 3.49 (s, 3H; OCH_3), 5.21 (s, 2H; OCH_2O), 6.98 (td, $^{3}J = 7.4$, $^{4}J = 1.1$ Hz, 1H; H-4), 7.12 (ddd, $^{3}J = 8.3$, $^{4}J_{P,H} = 3.2$, $^{4}J = 1.1$ Hz, 1H; H-6), 7.28 (ddd, $^{3}J = 8.3$, 7.4, $^{4}J = 1.7$ Hz, 1H; H-5), 7.38 ppm (ddd, $^{3}J = 7.4$, $^{3}J_{P,H} = 5.5$, $^{4}J = 1.7$ Hz, 1H; H-3); ^{13}C NMR ($CDCl_3$): $\delta = 26.3$ (C-δ), 27.0 (d, $^{3}J = 8.1$ Hz; C-γ), 27.2 (d, $^{3}J = 12.8$ Hz; C-γ'), 29.2 (d, $^{2}J = 8.2$ Hz; C-β), 30.5 (d, $^{2}J = 17.6$ Hz; C-β'), 32.9 (d, $^{1}J = 12.1$ Hz; C-α), 56.1 (OCH_3), 94.5 (OCH_2O), 114.0 (d, $^{3}J = 1.7$ Hz; C-6), 121.2 (d, $^{3}J = 3.8$ Hz; C-4), 123.5 (d, $^{1}J = 20.8$ Hz; C-2), 130.0 (C-5), 135.0 (d, $^{2}J = 10.5$ Hz; C-3), 160.8 ppm (d, $^{2}J = 10.7$ Hz; C-1); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): $\delta = -8.4$ ppm; MS (EI, 200 °C): *m/z* (%): 334 (14) [M^+], 320 (22), 319 (100), 291 (8), 192 (11), 83 (25), 81 (13), 55 (39), 45 (25); elemental analysis calcd (%) for $C_{20}H_{31}O_2P$ (334.44): C 71.83, H 9.34; found: C 71.77, H 9.42.

2-(Dicyclohexylphosphanyl)-4,6-di-*tert*-butylphenyl methoxymethyl ether ($\mathbf{1}_{\mathbf{CCBB}}$): By using the procedure reported for $\mathbf{1}_{\mathbf{PPFH}}$, a solution of 2,4-*t*$Bu_2$-$C_6H_3OCH_2OCH_3$ (8.3 g, 33.1 mmol) in ether (80 mL) was allowed to react with *n*BuLi in hexane (21.0 mL, 1.6 M, 33.6 mmol) and with chlorodicyclohexylphosphane (7.7 g, 33.1 mmol) in diethyl ether (10 mL) to give $\mathbf{1}_{\mathbf{CCBB}}$ as white crystals (6.0 g; 41 %), m.p. 96 °C. ^{1}H NMR (C_6D_6): $\delta = 1.34$ (s, 9H; *t*Bu), 1.61 (s, 9H; *t*Bu), 1.00–1.45 (m, 10H; Cy), 1.50–1.80 (m, 8H; Cy), 1.90–2.08 (m, 4H; Cy), 3.61 (s, 3H; OCH_3), 5.57 (d, $^{5}J_{P,H} = 2.1$ Hz, 2H; OCH_2O), 7.46 ("t", $^{3}J_{P,H} \approx {}^{4}J = 2.5$ Hz, 1H; H-3), 7.56 ppm (d, $^{4}J = 2.5$ Hz, 1H; H-5); ^{13}C NMR (C_6D_6, CH-COSY): $\delta = 27.5$ (C-δ), 28.2 (d, $^{3}J = 7.0$ Hz; C-γ), 28.3 (d, $^{3}J = 12.2$ Hz; C-γ'), 30.2 (d, $^{2}J = 8.1$ Hz; C-β), 31.6 (d, $^{2}J = 18.2$ Hz; C-β'), 31.7 (C*Me*$_3$), 32.4 (C*Me*$_3$), 35.1 (d, $^{1}J = 15.4$ Hz; C-α), 35.4 (*C*Me_3), 36.4 (d, $^{4}J = 1.0$ Hz; *C*Me_3), 58.0 (d, $^{6}J = 1.5$ Hz; OCH_3), 101.2 (d, $^{4}J = 23.5$ Hz; OCH_2O), 126.1 (C-5), 129.5 (d, $^{1}J = 23.2$ Hz; C-2), 129.5 (d, $^{2}J = 2.9$ Hz; C-3), 143.5 (d, $^{3}J = 3.5$ Hz; C-6), 145.7 (C-4), 159.9 ppm (d, $^{2}J_{P,C} = 20.3$ Hz; C-1); $^{31}P\{^{1}H\}$ NMR(C_6D_6): $\delta = -10.4$ ppm; MS (EI, 150 °C): *m/z* (%): 446 (7) [M^+], 432 (35), 431 (100), 404 (8), 304 (16), 57 (36), 55 (18), 41 (23); elemental analysis calcd (%) for $C_{28}H_{47}O_2P$ (446.65): C 75.29, H 10.61; found: C 75.22, H 11.07.

2-(Dicyclohexylphosphanyl)-4-methoxyphenyl methoxymethyl ether ($\mathbf{1}_{\mathbf{CCOH}}$): By using the procedure reported for $\mathbf{1}_{\mathbf{EEHH}}$, a solution of 4-MeO-$C_6H_4OCH_2OCH_3$ (7.2 g, 42.8 mmol) in diethyl ether (80 mL) was allowed to react with *n*BuLi in hexane (27.0 mL, 1.6 M, 43.2 mmol) and with chlorodicyclohexylphosphane (10.0 g, 43.0 mmol) in diethyl ether (10 mL) to give $\mathbf{1}_{\mathbf{CCOH}}$ as viscous colorless oil (5.1 g; 33 %), b.p. 165–170 °C/4 × 10^{-4} Torr. ^{1}H NMR (C_6D_6): $\delta = 1.00–1.47$ (m, 10H; Cy), 1.52–1.80 (m, 8H; Cy), 1.95–2.20 (m, 4H; Cy), 3.30, 3.36 (2s, 6H; OCH_3), 4.96 (s, 2H; OCH_2O), 6.69 (dd, $^{3}J = 8.9$, $^{4}J = 3.1$ Hz, 1H; 5-H), 7.10 (dd, $^{3}J = 8.9$, $^{4}J_{P,H} = 3.0$ Hz, 1H; 6-H), 7.29 ppm (dd, $^{3}J_{P,H} = 6.3$, $^{4}J = 3.1$ Hz, 1H; 3-H); ^{13}C NMR (C_6D_6, CH-COSY): $\delta = 27.5$ (C-δ), 28.2 (d, $^{3}J = 7.3$ Hz; C-γ), 28.2 (d, $^{3}J = 12.5$ Hz; C-γ'), 30.8 (d, $^{2}J = 9.3$ Hz; C-β), 32.0 (d, $^{2}J = 18.7$ Hz; C-ß′), 34.6 (d, $^{1}J = 14.3$ Hz; C-α), 55.8, 56.6 (2 OCH_3), 96.5 (OCH_2O), 115.3 (C-5), 117.1 (d, $^{3}J = 1.6$ Hz; C-6), 122.5 (d, $^{2}J = 16.4$ Hz; C-3), 127.4 (d, $^{1}J = 25.7$ Hz; C-2), 155.4 (d, $^{3}J = 5.8$ Hz; C-4), 156.2 ppm (d, $^{2}J = 9.9$ Hz; C-1); $^{31}P\{^{1}H\}$ NMR: $\delta(C_6D_6) = -4.3$ ppm; $\delta(CDCl_3) = -7.6$ ppm; MS (EI, 150 °C): *m/z* (%): 364 (12) [M^+], 334 (27), 320 (44), 252 (41), 238 (100), 197 (24), 170 (74), 156 (70), 55 (71); elemental analysis calcd (%) for $C_{21}H_{33}O_3P$ (364.47): C 69.21, H 9.13; found: C 69.01, H 8.91.

2-(*tert*-Butylphenylphosphanyl)phenyl methoxymethyl ether ($\mathbf{1}_{\mathbf{BPHH}}$): By using the procedure reported for$\mathbf{1}_{\mathbf{PPFH}}$, a solution of $C_6H_5OCH_2OCH_3$ (10.0 g, 72.4 mmol) in diethyl ether (100 mL) was reacted with *n*BuLi in hexane (45.5 mL, 1.6 M, 72.8 mmol) and *tert*-butylchlorophenylphosphane (14.5 g, 72.3 mmol) in diethyl ether (10 mL) to give $\mathbf{1}_{\mathbf{PPFH}}$ as white crystals (9.8 g; 45 %), m.p. 88 °C. ^{1}H NMR ($CDCl_3$): $\delta = 1.24$ (d, $^{3}J_{P,H} = 12.6$ Hz, 9H; *t*Bu), 3.18 (s, 3H; OCH_3), 4.96 (d, $^{2}J = 6.9$ Hz, 1H; O–CH_AO), 5.07 (d, $^{2}J = 6.9$ Hz, 1H; O–CH_BO), 6.99 ("t"d, $^{3}J \approx 7.5$, 7.3, $^{4}J = 0.9$ Hz, 1H; H-4), 7.11 (ddd, $^{3}J = 8.0$, $^{4}J_{P,H} = 4.1$, $^{4}J = 0.9$ Hz, 1H; H-6), 7.22–7.32 (m, 4H; ArH), 7.43–7.53 ppm (m, 3H; ArH); ^{13}C NMR (C_6D_6): $\delta = 29.7$ (d, $^{2}J = 15.2$ Hz; C*Me*$_3$), 31.2 (d, $^{1}J = 16.9$ Hz; *C*Me_3), 56.4 (d, $^{6}J = 0.9$ Hz;OCH_3), 95.2 (d, $^{4}J = 1.0$ Hz; OCH_2O), 115.5 (d, $^{3}J = 1.3$ Hz; C-6), 122.4 (C-4), 128.1 (d, $^{1}J = 24.3$ Hz; C-2), 128.7 (d, $^{3}J = 6.4$ Hz; C-*m*), 128.8 (C-*p*), 130.7 (C-5), 135.3 (d, $^{1}J = 2.6$ Hz; C-3), 135.4 (d, $^{2}J = 20.0$ Hz; C-*o*), 139.6 (d, $^{2}J = 20.0$ Hz; C-*i*), 160.9 ppm (d, $^{2}J = 14.7$ Hz; C1); $^{31}P\{^{1}H\}$ NMR: $\delta(C_6D_6) = 5.0$ ppm, $\delta(CDCl_3) = 3.4$ ppm; MS (EI, 150 °C): *m/z* (%):302 (40) [M^+], 287 (100), 231 (40), 216 (22), 186 (22), 183 (27), 109 (31), 108 (33), 91 (59), 57 (69), 45 (93), 41 (36); elemental analysis calcd (%) for $C_{18}H_{23}O_2P$ (302.35): C 71.51, H 7.67; found: C 70.95, H 7.94.

2-Phosphanylphenols:

2-(Diphenylphosphanyl)-4-methoxyphenol ($\mathbf{2}_{\mathbf{PPOH}}$): A suspension of $\mathbf{1}_{\mathbf{PPOH}}$ (5.0 g, 14.2 mmol) in methanol (100 mL) was saturated with gaseous HCl at room temperature. After 15 h the mixture was refluxed for 1 h to complete the cleavage. Then the volatiles were evaporated in vacuum, the residue was dissolved in methanol (20 mL) and water was added until the solution became turbid. The product was allowed to crystallize at 0 °C, separated and dried at 10^{-4} Torr to give $\mathbf{2}_{\mathbf{PPOH}}$ as white crystals (2.5 g; 57 %), m.p. 86 °C. ^{1}H NMR ($CDCl_3$): $\delta = 3.61$ (s, 3H; OCH_3), 5.9 (s vbr, 1H; OH) 6.50 (dd, $^{3}J_{P,H} = 7.5$, $^{4}J = 3.0$ Hz, 1H; H-3), 6.88 (dd, $^{3}J = 8.9$, $^{4}J = 3.0$ Hz, 1H; H-5), 7.03 (dd, $^{3}J = 8.9$, $^{4}J_{P,H} = 5.8$ Hz, 1H; H-6), 7.40–7.72 ppm (m, 10H; ArH); ^{13}C NMR ($CDCl_3$): $\delta = 55.7$ (OCH_3), 116.9 (d, $^{3}J = 2.7$ Hz; C-6), 118.2 (C5), 118.8 (d, $^{2}J = 5.5$ Hz; C-3), 128.3 (d, $^{3}J = 13.0$ Hz; C-2), 128.9 (d, $^{1}J = 8.2$ Hz; C- *m*), 130.0 (C-*p*), 132.0 (d, $^{1}J = 10.5$ Hz; C-*i*), 133.5 (d, $^{2}J = 17.6$ Hz; C-*o*), 153.5 (d, $^{3}J = 4.7$ Hz; C-4), 153.7 ppm (d, $^{2}J = 14.4$ Hz; C-1); $^{31}P\{^{1}H\}$ NMR: $\delta(CDCl_3) = -21.0$ ppm (contaminated by hydrochloride); MS (EI, 150 °C): *m/z* (%): 308 (100) [M^+], 293 (26), 230 (22), 229 (31), 215 (37), 212 (13), 199 (13), 187 (29), 183 (15), 159 (17), 133 (25); IR (nujol): $\tilde{\nu} = 3293$ v br cm^{-1} (s); elemental analysis calcd (%) for $C_{19}H_{17}O_2P$ (308.32): C 74.02, H 5.56; found: C 73.71, H 5.60.

2-(Diphenylphosphanyl)-4-fluorophenol ($\mathbf{2}_{\mathbf{PPFH}}$): A suspension of $\mathbf{1}_{\mathbf{PPFH}}$ (5.1 g, 15.0 mmol) was allowed to react with gaseous HCl in methanol (100 mL) and worked up as reported for $\mathbf{2}_{\mathbf{PPOH}}$ to yield $\mathbf{2}_{\mathbf{PPFH}}$ as white crystals (2.9 g; 65 %), m.p. 92 °C. ^{1}H NMR (C_6D_6): $\delta = 6.1$ (s br, 1H; OH), 6.51 (ddd, $^{3}J = 8.9$, $^{4}J_{P,H,F,H} = 5.1$, 4.6 Hz, 1H; H-6), 6.66 (dd, $^{3}J = 8.9$, $^{3}J_{F,H} = 7.9$, $^{4}J = 3.1$ Hz, 1H; H-5), 6.83 (ddd, $^{3}J_{F,H} = 8.2$, $^{3}J_{P,H} = 4.4$, $^{4}J = 3.1$ Hz, 1H; H-3), 6.93–7.03 (m, 6H; ArH), 7.21–7.30 ppm (m, 4H; ArH); ^{13}C NMR (C_6D_6): $\delta = 116.9$ (dd, $^{3}J_{F,C} = 8.7$, $^{3}J = 1.7$ Hz; C-6), 118.1 (d, $^{2}J_{F,C} = 23.5$ Hz; C-5), 120.1 (dd, $^{2}J_{F,C} = 22.9$, $^{4}J = 3.4$ Hz; C-3), 124.3 (dd, $^{1}J = 11.3$, $^{3}J_{F,C} = 4.8$ Hz; C-2), 129.0 (d, $^{3}J = 7.3$ Hz; C-*m*), 129.3 (C-*p*), 133.9 (d, $^{2}J = 19.4$ Hz; C-*o*), 135.4 (d, $^{1}J = 7.5$ Hz; C-*i*), 155.7 (d, $^{2}J = 16.1$ Hz; C-1), 157.6 ppm (d, $^{1}J_{F,C} = 239$ Hz; C-4); $^{31}P\{^{1}H\}$ NMR (C_6D_6): $\delta = -24.8$ ppm; MS (EI, 150 °C): *m/z* (%): 296 (100) [M^+], 295 (44), 218 (23), 217 (87), 183 (16), 32 (30), 31 (45); IR (nujol): $\tilde{\nu} = 3165$ cm^{-1} (s br); elemental analysis calcd (%) for $C_{18}H_{14}FOP$ (296.28): C 72.97, H 4.76; found: C 73.09, H 5.07.

2-(Diethylphosphanyl)phenol ($\mathbf{2}_{\mathbf{EEHH}}$): A mixture of $\mathbf{1}_{\mathbf{EEHH}}$ (5.0 g, 22.1 mmol) and methanol (100 mL) was saturated with gaseous HCl, stirred for 15 h and refluxed for 1 h. Water (10 mL) was added followed by small portions of saturated aqueous sodium carbonate until the pH was 5–6. The product was extracted with diethyl ether, the solution was dried with anhydrous sodium sulfate, and the solvent was removed at 10^{-4} Torr to give $\mathbf{2}_{\mathbf{EEHH}}$ as an oil (2.8 g; 70 %) which becomes solid at 4 °C, m.p. 31–35 °C. (The compound is easily oxidized by air yielding the phosphane oxide, $\delta(^{31}P) = 59.8$ ppm.) ^{1}H NMR (C_6D_6): $\delta = 0.83$ (dt, $^{3}J_{P,H} = 16.7$, $^{3}J = 7.6$ Hz, 6H; CH_3), 1.40 (m, 4H; CH_2), 6.80 (td, $J = 7.3$, 1.5 Hz, 1H; H-6 or H-5), 6.97–7.13 ppm (m, 3H; ArH); ^{13}C NMR (C_6D_6): $\delta = 10.6$ (d, $^{2}J = 13.7$ Hz; CH_3), 20.3 (d, $^{1}J = 6.8$ Hz; PCH), 116.1 (d, $^{3}J = 2$ Hz; C-6), 121.5 (C-4), 122.1 (d, $^{1}J = 7$ Hz, C-2), 131.6/132.0 (2s, C-3, C-5), 162.0 ppm (d, $^{2}J = 20$ Hz; C-1); $^{31}P\{^{1}H\}$ NMR (C_6D_6): $\delta = -46.6$ ppm; MS (EI, 120 °C): *m/z* (%): 182 (71) [M^+], 154 (96), 126 (67), 125 (61), 124 (20), 94 (48), 77

(31), 47 (100); IR (nujol): $\tilde{\nu}\approx 3100\,cm^{-1}$ (s br); elemental analysis calcd (%) for $C_{10}H_{15}OP$ (182.20): C 65.92, H 8.30; found: C 65.71, H 8.33.

2-(Diisopropylphosphanyl)phenol ($\mathbf{2_{IIHH}}$): A mixture of $\mathbf{1_{IIHH}}$ (4.3 g, 16.9 mmol) and methanol (100 mL) was allowed to react with gaseous HCl and worked up as reported for $\mathbf{2_{EEHH}}$ to give $\mathbf{2_{IIHH}}$ as a colorless oil which was distilled at 100 °C/0.1 Torr, yield 2.1 g; 59 %. ^{1}H NMR (C_6D_6): $\delta=0.81$ (dd, $^3J_{P,H}=12.3$, $^3J=6.9$ Hz, 6H; CH_{3A}), 0.99 (dd, $^3J_{P,H}=16.4$, $^3J=7.0$ Hz, 6H; CH_{3B}), 1.90 (sept d, $^3J=7.0$, $^2J_{P,H}=3.5$ Hz, 2H; PCH), 6.77 (m, 1H; H-6 or H-5), 7.03–7.13 (m, 3H; ArH), 7.37 ppm (s br, 1H; OH); ^{13}C NMR (C_6D_6): $\delta=19.4$ (d, $^2J=7.3$ Hz; CH_{3A}), 20.8 (d, $^2J=18.1$ Hz; CH_{3B}), 23.8 (d, $^1J=7.0$ Hz; PCH), 116.3 (C-6), 119.2 (d, $^1J=9$ Hz, C-2), 120.8 (C-4), 132.1 (C-5), 133.7 (br, C-3), 162.7 ppm (d, $^2J=18.2$ Hz; C-1); ^{31}P{^{1}H} NMR (C_6D_6): $\delta=-23.1$ ppm; elemental analysis calcd (%) for $C_{12}H_{19}OP$ (210.26): C 68.55, H 9.11; found: C 68.44, H 9.26.

2-(Diisopropylphosphanyl)-4-fluorophenol ($\mathbf{2_{IIFH}}$): A mixture of $\mathbf{1_{IIFH}}$ (3.2 g, 11.7 mmol) and methanol (100 mL) was allowed to react with gaseous HCl (15 h, 20 °C, 1 h reflux) and worked up as reported for $\mathbf{2_{EEHH}}$ to give a solid which was sublimed at 60–70 °C/2 × 10^{-2} Torr to afford $\mathbf{2_{IIFH}}$ as white crystals (1.2 g; 45 %), m.p. 65 °C. ^{1}H NMR (C_6D_6): $\delta=0.70$ (dd, $^3J_{P,H}=12.5$, $^3J=6.9$ Hz, 6H; CH_3), 0.88 (dd, $^3J_{P,H}=16.5$, $^3J=7.0$ Hz, 6H; CH_3), 1.66 (sept d, $^3J=7.0$, $^2J_{P,H}=3.5$ Hz, 2H; CH), 6.72 (ddd, $^3J=8.9$, $^3J_{F,H}=8.0$, $^5J_{P,H}=3.1$ Hz, 1H; H-5), 6.82 (d"t", $^3J=8.9$, $^4J_{F,H}\approx{}^4J_{P,H}\approx 5.0$ Hz, 1H; H-6), 6.91 (d"t", $^3J_{F,H}=8.4$, $^4J\approx{}^3J_{P,H}\approx 2.7$–3.1 Hz, 1H; H-3), 6.96 ppm (d br, $^4J_{P,H}=10$ Hz, 1H; OH); ^{13}C NMR (C_6D_6): $\delta=19.2$ (d, $^2J=7.5$ Hz; CH_3), 20.5 (d, $^2J=18.0$ Hz; CH_3), 23.8 (d, $^1J=7.7$ Hz; CH), 117.2 (dd, $^3J_{F,C}=6.8$, $^3J=1.6$ Hz; C-6), 118.9 (dd, $^2J_{F,C}=21.1$, $^2J=1.7$ Hz; C-3), 119.1 (d, $^2J_{F,C}=23.1$ Hz; C-5), 120.8 (dd, $^3J_{F,C}=12.4$, $^1J=4.5$ Hz; C-2), 157.6 (d, $^1J_{F,C}=239.7$ Hz; C-4), 158.7 ppm (dd, $^2J=18.7$, $^4J_{F,C}=1.7$ Hz; C-1); ^{31}P{^{1}H} NMR (C_6D_6): $\delta=-22.2$ ppm; ^{19}F NMR ([D$_8$]THF, $CFCl_3$): $\delta=127.0$ ppm (m); MS (EI, 130 °C): *m/z* (%): 228 (78) [M^+], 186 (100), 144 (76), 143 (42), 77 (25), 43(23), 41 (18); IR (nujol): $\tilde{\nu}=3296\,cm^{-1}$ (vs br); elemental analysis calcd (%) for $C_{12}H_{18}FOP$ (228.24): C 63.15, H 7.95; found: C 62.99, H 8.12.

2-(Dicyclohexylphosphanyl)phenol ($\mathbf{2_{CCHH}}$): A mixture of $\mathbf{1_{CCHH}}$ (5.0 g, 15.0 mmol) and methanol (100 mL) was treated with gaseous HCl (20 °C for 15 h, 1 h reflux) and worked up as described for $\mathbf{2_{EEHH}}$ to give $\mathbf{2_{CCHH}}$ as a white solid (3.5 g; 81 %), which was recrystallized from diethyl ether/methanol, m.p. 86 °C. ^{1}H NMR ($CDCl_3$): $\delta=0.90$–1.25 (m, 10H; Cy), 1.45–1.65 (m, 8H; Cy), 1.70–1.90 (m, 4H; Cy), 6.76–6.84 (m, 1H; ArH), 7.05–7.12 (m, 2H; ArH), 7.15–7.20 (m, 1H; ArH), 7.41 ppm (d br, $^4J_{P,H}=10.5$ Hz, 1H; OH); ^{13}C NMR (C_6D_6): $\delta=27.2$ (C-δ), 27.7 (d, $^3J=8.2$ Hz; C-γ), 27.9 (d, $^3J=13.1$ Hz; C-γ'), 29.5 (d, $^2J=5.9$ Hz; C-β), 31.2 (d, $^2J=16.1$ Hz; C-ß'), 33.6 (d, $^1J=7.1$ Hz; C-α), 116.3 (C-6), 118.9 (d, $^1J=8.2$ Hz; C-2), 120.8 (C-4), 132.1 (C-5), 133.8 (C-3), 163.0 ppm (d, $^2J=19.8$ Hz; C-1); ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta=-33.7$ ppm; MS (EI, 150 °C): *m/z* (%): 290 (26) [M^+], 273 (9), 235 (7), 209 (12), 208 (63), 127 (39), 126 (100), 125 (26), 83 (28), 55 (55), 47 (39); IR (nujol): $\tilde{\nu}=3371\,cm^{-1}$ (s); elemental analysis calcd (%) for $C_{18}H_{27}OP$ (290.39): C 74.45, H 9.37; found: C 73.91, H 9.56.

2-(Dicyclohexylphosphanyl)-4,6-di-*tert*-butylphenol ($\mathbf{2_{CCBB}}$): A mixture of $\mathbf{1_{CCBB}}$ (4.8 g, 10.7 mmol) and methanol (100 mL) was treated with gaseous HCl (20 °C for 15 h, 1 h reflux) and worked up as described for $\mathbf{2_{EEHH}}$ to give $\mathbf{2_{CCBB}}$ as a white solid (2.1 g; 49 %), m.p. 110 °C. ^{1}H NMR (C_6D_6): $\delta=1.36$ (s, 9H; CH_3), 1.63 (s, 9H; CH_3), 0.90–1.30 (m, 10H; Cy), 1.40–1.70 (m, 8H; Cy), 1.80–2.05 (m, 4H; Cy), 7.34 ("t", $^3J_{P,H}=3.2$, $^4J=2.2$ Hz, 1H; H-3), 7.56 (d, $^4J=2.2$ Hz, 1H; 5-H), 7.88 ppm (d, $^4J_{P,H}=12.4$ Hz, 1H; OH); ^{13}C NMR (C_6D_6, CH-COSY): $\delta=27.2$ (C-δ), 27.8 (d, $^3J=7.8$ Hz; C-γ), 27.9 (d, $^3J=13.1$ Hz; C-γ'), 29.6 (d, $^2J=5.7$ Hz; C-β), 30.6 (*C*CH$_3$), 31.3 (d, $^2J=16.0$ Hz; C-β'), 32.6 (*C*CH$_3$), 33.8 (d, $^1J=6.9$ Hz; C-α), 35.2 (*C*CH$_3$), 36.1 (d, $^4J=1.6$ Hz; *C*CH$_3$), 118.5 (d, $^1J=4.6$ Hz; C-2), 126.3 (C-5), 128.1 (d, $^2J=1.7$ Hz; C-3), 135.9 (d, $^3J=1.8$ Hz; C-6), 141.9 (C-4), 159.0 ppm (d, $^2J=19.2$ Hz; C-1); ^{31}P{^{1}H} NMR: $\delta(C_6D_6)=-33.4$; $\delta(CDCl_3)=-32.5$ ppm; MS (EI, 150 °C): *m/z* (%): 403 (16), 402 (61) [M^+], 387 (22), 321 (25), 320 (100), 305 (14), 278 (14), 238 (25), 224 (13), 57 (53), 55 (31), 41 (18); IR (nujol): $\tilde{\nu}=3322\,cm^{-1}$ (s); elemental analysis calcd (%) for $C_{26}H_{43}OP$ (402.60): C 77.57, H 10.77; found: C 77.74, H 10.89.

2-(Dicyclohexylphosphanyl)-4-methoxyphenol ($\mathbf{2_{CCOH}}$): A mixture of $\mathbf{1_{CCOH}}$ (4.0 g, 11.0 mmol) and methanol (100 mL) was treated with gaseous HCl (20 °C for 15 h, 1 h reflux) and worked up as described for $\mathbf{2_{EEHH}}$ to give $\mathbf{2_{CCOH}}$ as a white solid (1.5 g; 43 %), m.p. 50 °C. ^{1}H NMR ($CDCl_3$): $\delta=1.00$–1.38 (m, 10H; Cy), 1.50–2.00 (m, 12H; Cy), 3.77 (s, 3H; OCH_3), 6.80–6.87 ppm (m, 3H; ArH); ^{13}C NMR ($CDCl_3$): $\delta=26.0$ (C-δ), 26.6 (d, $^3J=8.1$ Hz; C-γ), 26.8 (d, $^3J=13.6$ Hz; C-γ'), 28.4 (d, $^2J=6.1$ Hz; C-β), 30.0 (d, $^2J=15.8$ Hz; C-β'), 32.3 (d, $^1J=7.5$ Hz; C-α), 55.4 (OCH_3), 115.1 (C-5), 115.9 (C-6), 117.9 (C-3), 118.5 (d, $^1J=11.2$ Hz, C-2), 152.3 (C-4), 155.1 ppm (d, $^2J=18.3$ Hz; C-1); ^{31}P{^{1}H} NMR (C_6D_6): $\delta=-30.8$ ppm; IR (nujol): $\tilde{\nu}\approx 3200\,cm^{-1}$ (s sh); elemental analysis calcd (%) for $C_{19}H_{29}O_2P$ (320.40): C 71.23, H 9.12; found: C 71.36, H 8.98.

2-(*tert*-Butylphenylphosphanyl)phenol ($\mathbf{2_{BPHH}}$): A mixture of $\mathbf{1_{BPHH}}$ (5.0 g, 16.5 mmol) and methanol (100 mL) was treated with gaseous HCl (20 °C for 15 h, 1 h reflux) and worked up as described for $\mathbf{2_{EEHH}}$ to give $\mathbf{2_{BPHH}}$ as a white solid (2.6 g; 61 %), m.p. 86 °C. ^{13}C NMR ($CDCl_3$): $\delta=28.5$ (d, $^2J=13.4$ Hz; C*C*H$_3$), 31.4 (d, $^1J=8.1$ Hz, *C*CH$_3$), 115.3 (C-6), 119.1 (d, $^1J=6.0$ Hz; C-2), 120.0 (C-4), 128.2 (d, $^3J=7.0$ Hz; C-*m*), 128.4 (C-*p*), 131.7 (C-5), 133.6 (d, $^2J=17.1$ Hz; C-*o*), 134.5 (d, $^1J=9.5$ Hz; C-*i*), 134.8 (C-3), 160.9 ppm (d, $^2J=21.3$ Hz; C-1); ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta=-19.7$ ppm; MS (EI): *m/z* (%): 259 (4), 258 (21) [M^+], 202 (36), 183 (7), 124 (100), 108 (50), 107 (13), 77 (24), 57 (44), 41 (21); IR (nujol): $\tilde{\nu}=3296\,cm^{-1}$ (s). ^{1}H NMR data are as given in ref [23].

Methallyl complexes:

2-(Diphenylphosphanyl)phenolate(2-methylallyl)nickel(II) ($\mathbf{3_{PPHH}}$): a) Thallium ethylate (71 μL, 1.0 mmol) was added with stirring to a solution of $\mathbf{2_{PPHH}}$ (278 mg, 1.0 mmol) in THF (10 mL). White crystals, precipitated after some minutes and cooling, were separated, dried at 10^{-4} Torr (yield 450 mg, 93 %) and stored at −20 °C until use. b) The thallium phosphanylphenolate (450 mg, 0.934 mmol) was suspended in THF (20 mL), cooled to −10 °C, and a solution of (methallylNiBr)$_2$ (95 mg, 0.245 mmol) in THF (20 mL) was added. Then the suspension was allowed to warm to room temperature. The voluminous precipitation of TlBr formed after 5 min was filtered off (after stirring for 4 h) and washed carefully with small portions of THF. The solvent of the orange filtrate was removed in vacuum and replaced by pentane (5 mL). The insoluble part was separated and dried in vacuum to give air-sensitive orange $\mathbf{3_{PPHH}}$ (275 mg; 71 %). The product starts to decompose below 50 °C and was stored at −20 °C. ^{1}H NMR (C_6D_6): $\delta=1.34$ (s br, 1H; H-1'), 1.64 (s, 3H; CH_3), 2.16 (s br, 1H; H-2'), 2.98 (d, $^3J_{P,H}=5.4$ Hz, 1H; H-3'), 4.08 (s br, 1H; H-4'), 6.51 ("tt", $^3J=8.4$, 6.9, $^4J_{P,H}=1.3$, $^4J=1$ Hz, 1H; H-4), 6.90–7.08 (m, 6H; Ph), 7.15–7.22 (m, 2H; H-3, H-5), 7.32 (ddd, $^3J=8.8$, $^4J_{P,H}=5.9$, $^4J=1$ Hz, 1H; H-6), 7.40–7.60 ppm (m br, 4H; Ph); ^{13}C NMR (C_6D_6): $\delta=24.0$ (C-*d*), 43.9 (C-*a*), 70.6 (d, $J=22.6$ Hz; C-*c*), 115.7 (d, $^3J=6.4$ Hz; C-4), 117.8 (d, $^1J=50.6$ Hz; C-2), 120.9 (d, $^3J=8.0$ Hz; C-6), 125.7 (C-*b*), 128.9 (d, $^1J=51$ Hz, uncertain by superimposition; C-*i*), 129.5 (d, $^3J=9.3$ Hz; C-*m*), 129.7 (d, $^3J=8.6$ Hz; C-*m'*), 130.8 (C-*p*), 133.2 (C-3), 133.5 (d, $^2J=13.0$ Hz; C-*o*), 133.8 (d, $^2J=11.4$ Hz; C-*o'*), 134.9 (C-5), 180.4 ppm (d, $J=25.0$ Hz, C-1), ^{1}H and ^{13}C assignments except of Ph signals follow those in the Pd analogue of $\mathbf{3_{CCHH}}$ [17b], studied by CH-COSY; ^{31}P{^{1}H} NMR (C_6D_6): $\delta=29.7$ ppm; elemental analysis calcd (%) for $C_{22}H_{21}NiOP$ (391.07): C 67.57, H 5.41; found: C 67.12, H 5.39.

2-(Dicyclohexylphosphanyl)phenolate(2-methylallyl)nickel(II) ($\mathbf{3_{CCHH}}$): Thallium ethylate (77 μL, 1.0 mmol) was added to a stirred solution of $\mathbf{2_{CCHH}}$ (317 mg, 1.1 mmol) in THF (5 mL). White crystals, precipitated after cooling to −78 °C (one day), were separated, dried at 10^{-1} Torr, suspended in fresh THF (5 mL) and added to a cold (−20 °C) solution of methallyl nickel bromide (194 mg, 0.5 mmol) in THF (12 mL). The solution was stirred for 2 h at room temperature, the precipitate was filtered off and hexane was added cautiously to form a layer on the mother liquor slowly mixing in. Storage at −78 °C furnished orange crystals (with a second portion 280 mg, 70 %), m.p. 135–138 °C, in solid state air-stable. ^{1}H NMR ($CDCl_3$): $\delta=0.85$–2.05 (m, 23H; Cy, H-1'), 1.83 (s, 3H; CH_3), 2.09 (m, $J\approx 2$ Hz, 1H; H-2'), 3.90 (d, $J_{P,H}=5.1$ Hz, 1H; H-3'), 4.51 (m, $J\approx 3$ Hz, 1H; H-4'), 6.55–6.63 (m, 1H; ArH), 7.12 (t br, $^3J=7.4$ Hz, 1H; ArH), 7.18–7.23 ppm (m, 2H; ArH); ^{13}C NMR (C_6D_6): $\delta=24.3$ (C-*d*), 27.1 (C-δ), 27.68 (d, $^3J=10.5$ Hz; C-γ), 26.74, 27.9 (2 d, $^3J=11.5$, 12.0 Hz; 2 C-γ'), 29.3 (d, $^2J=7.8$ Hz; C-β), 30.17, 30.23 (2 d, $^2J=4.4$, 4.9 Hz; 2 C-β'), 34.3 (d, $^1J=24.6$ Hz; C-α), 34.6 (d, $^1J=24.2$ Hz; C-α'), 38.6 (d, $J=6.0$ Hz; C-*a*), 71.2 (d, $J=20.7$ Hz; C-*c*), 115.6 (d, $^1J=42.4$ Hz; C-2), 114.6 (d, $^3J=5.4$ Hz; C-4), 120.3 (d, $^3J=7.1$ Hz; C-6), 123.3 (C-*b*), 131.9, 134.0 (2s, C-3, C-5), 180.8 ppm (d, $^2J=21.3$ Hz; C-1); ^{31}P{^{1}H} NMR (C_6D_6): $\delta=44.4$ ppm; DTA/TG: endothermic mass loss at 60–140 °C (3.5 %, calc. for C_4H_7 13.7 %), maximum 120 °C, >160 °C stronger decay; elemental analysis calcd (%) for $C_{22}H_{33}OPNi$ (403.17): C 65.54, H 8.25; found: C 64.91, H 8.60.

Ethylene polymerization: *a) Equipment and general remarks*: The polymerization of ethylene was carried out as batch reaction in a stainless steel autoclave (75 mL), equipped with a manometer, two valves, a safety diaphragm, Teflon-coated magnetic stirrer, heating (temperature-controlled silicon bath). Reaction temperatures refer to the bath temperature. After placing the autoclave into the bath, mostly $100 \pm 5\,°C$, the inside temperature increased to 70 °C within 13–15 min (calibration without pressure).

Initial tests established that no reaction of ethylene occurs in absence of either 2-phosphanylphenols or $[Ni(cod)_2]$ and that products obtained in glass beakers and directly in the autoclave are almost identical. To limit wall effects, a relatively high amount of the catalyst, 0.1 mmol (initially 0.22 mmol), was used. The reproducibility within series with similar catalysts is sufficient.

b) Preparation of catalysts: The methallylnickel complexes **3** (0.1 mmol) were dissolved in toluene (20 mL) and used immediately. Catalysts **4** and **2**: Unless indicated otherwise, 0.1 mmol of the respective 2-phosphanylphenol **2** was dissolved in toluene or the given solvent (10 mL), cooled to 0 °C and added to a solution of $[Ni(cod)_2]$ (27.5 mg, 0.1 mmol) in toluene or the given solvent (10 mL) at 0 °C or, for catalysts **2**, to a suspension of $NiBr_2\cdot DME$ (0.2 or 0.3 mmol) in toluene (10 mL) to which finally NaH (7.2 mg, 0.3 mmol) was added. Catalysts **5** were prepared like catalysts **2** but using the bis(chelate) complex **5** instead of the protonated ligands **2**. The catalyst solution or suspension was stirred for 30 min at 20 °C, usually forming a brown (PhRP catalyst) or yellow-orange (Alk_2P-catalysts) solution or suspension (with $\mathbf{2}_{\mathbf{BBHH}}$ no color change). In experiments with additives, the amount of toluene or the given solvent was reduced (each 50% for **2** and for $[Ni(cod)_2]$) by the amount of the additive, and the latter was added to the preformed catalyst solution.

c) Polymerization: The autoclave was charged with argon and the catalyst solution (Teflon syringe). Then, ethylene was added (30 to 50 bar), the amount of ethylene determined by weight difference and the autoclave heated to the given temperature overnight (15 h). After cooling to room temperature and weight control, the autoclave was connected to a cooling trap (−78 °C, usually $\leq$ 0.1 g butenes condensed) and unreacted ethylene was allowed to escape. The content of the autoclave was separated by flash distillation at $80\,°C/10^{-2}$ Torr. The residual polymer was stirred for 1 d with methanol/hydrochloric acid (1:1), thoroughly washed with methanol and dried in vacuum. For melting point, density and NMR measurements soluble oligomers were removed (usually <10 mg/g) by extraction with CH_2Cl_2 (10 mL g^{-1} PE, 15 h). Conversion and characteristic polymer data are given in Tables 1–4.

d) Characterization of polyethylenes: The density of PE was determined by the sinking method using tablets obtained in an IR press and addition of ethanol to water in the presence of a detergent. The molecular weight distribution was determined by GPC, using WATERS 150C; eluent 1,2,4-trichlorobenzene (0.025% 2,6-di-*tert*-butyl-4-methylphenol) at 135 °C or 155 °C; flow rate 0.6–1.1 mL/min, injection 150 μL (sample conc. 4.9 g/L) or 500 μL (sample conc. 0.01–0.05 wt%); columns 3× htSDV10μ, 10^6, 10^5, 10^3 Å or 3× SHODEX AT 806 MS, 1× SHODEX UT 807, 1× SHODEX AT-G; detectors Waters 150C-RI, DP H5202B, IPH502B; calibration by defined mono- and polydispers polyethylenes for 10^2 to 10^7 $g\,mol^{-1}$; software WIN-GPC; ii) PSS-WIN-GPC v4.01. NMR spectra were measured at 100 °C using concentrated solutions of the polyethylene samples in C_6D_5Br, prepared by swelling for 1 d at 120 °C under argon. Further conditions: ^1H NMR, acquisition time 4.9–5.4 s, delay 1.0 s, reference *p*-C*H* of the solvent $\delta = 7.23$; ^{13}C NMR, addition of $[Cr(acac)_3]$, acquisition time 0.6–0.9 s, delay 0.1–0.4 s, reference *p*-C of the solvent $\delta = 126.70$ ppm. A table with ^{13}C NMR data is available as Supporting Information.

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