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O-Acylated 2-Phosphanylphenol Derivatives – Useful Ligands in the Nickel-Catalyzed Polymerization of Ethylene

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The title ligands were prepared by *O*-acylation of 2-diphenylphosphanyl-4-methylphenol (**1**) or directly by double lithiation of 2-bromo-4-methylphenol and stepwise coupling with $ClPPh_2$ and $ClP(O)Ph_2$ or RC(O)Cl (R = Me, *t*Bu, Ph, 4-$MeOC_6H_4$) to afford diphenylphosphinate **2** and carboxylic esters **3a**–**d**. X-ray crystal structure analyses of **3b**–**d** show conformations in which the *P*-phenyl substituents are rotated away from the ester group and the C(O)O π planes are nearly perpendicular to the phenol ring π plane. *O*-Acylated phosphanylphenols **2** and **3a**–**d** form highly active catalysts with Ni(1,5-cod)$_2$ (as does **1**) for polymerization of ethylene, whereas phosphanylphenyl ethers do not give catalysts under the same conditions. The reason is the cleavage of the *O*-acyl bond upon heating with nickel(0) precursor compounds in the presence of ethylene. The precursors are P-coordinated Ni^0 complexes, which are formed at room temperature, such as **4d** obtained from **3d** and Ni(cod)$_2$ (in a 2:1 molar ratio), and characterized by multinuclear NMR spectroscopy. Upon heating in the presence of ethylene, the precatalysts are activated. Catalysts $\mathbf{2}_{Ni}$ and **3a**–$\mathbf{d}_{Ni}$ convert ethylene nearly quantitatively, $\mathbf{2}_{Ni}$ slowly, and **3a**–$\mathbf{d}_{Ni}$ rapidly, into linear polyethylene with vinyl and methyl end groups, and in the latter case, C(O)R end groups are also detectable. This proves insertion of Ni^0 into the O–C(O)R bond of **3a**–**d** ligands for formation of the primary catalyst. Termination of the first chain growing cycle by β-hydride elimination changes the mechanism to the phosphanylphenolate–NiH initiated polymerization providing the main body of the polymer. A small retardation in the ethylene consumption rate with **3a**–$\mathbf{d}_{Ni}$ catalysts relative to that observed for $\mathbf{1}_{Ni}$ and stabilization of the catalyst, which gives rise to reproducibly high ethylene conversion, is observed.

Introduction

Organometallic nickel complexes bearing chelating phosphanyl–enolate ligands are of great importance in the large-scale production of linear α-olefins in the Shell Higher Olefin Process (SHOP),[1,2] but also allow the preparation of polyethylene and ethylene–olefin copolymers.[2,3] Organonickel 2-phosphanylphenolate catalysts[4,5] or related in situ prepared catalyst systems[5,6] likewise accomplish selective oligo- or polymerization of ethylene to linear α-olefin chains and allow tuning of the molecular weights over a wide range for polymers by variation of the substituents at phosphorus[4a] and for low-molecular-weight oligomers by phosphane additives.[4b,6c] P-Basic dicyclohexylphosphanylphenolate catalysts are somewhat less selective and allow limited incorporation of α-olefins yielding copolymers with various substituents at the main chain.[7] Cationic methallylnickel 2-phosphanylphenol complexes are more active but unselective and give rise to isomer mixtures, mainly of butenes and hexenes.[8] Neutral tertiary and secondary 2-phosphanylphenyl ethers were also screened in situ with Ni(cod)$_2$ (cod = 1,5-cyclooctadiene) but neither of these compounds formed catalysts.[4a,6b] This suggests that the selectivity mediated by neutral 2-phosphanylphenolate nickel catalysts requires a leaving group at oxygen. For use of phosphanylphenols a mechanism involving formation of NiH catalysts was postulated and experimentally supported by NMR spectroscopic data of precatalyst solutions generated at room temperature from 2-diphenylphosphanylphenol and Ni(cod)$_2$.[4a] Signals similar to those of [Ni^0(2-phosphanylphenol)(PMe_3)$_3$][9] and methallylnickel(II) 2-phosphanylphenolate complexes were detected.[4a] Additional support should be possible with 2-phosphanylphenol derivatives, which are less inert than 2-phosphanylphenyl ethers and, similarly to the O–H compounds, allow insertion of nickel(0) into an O–E bond (E = electrophile).

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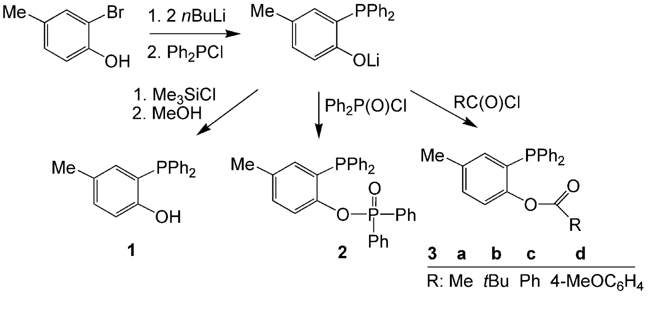
In this case, the O-substituent should be detectable in the oligomer or polymer fraction. Furthermore, the nature of the O-substituents might influence the catalyst and consequently the product properties. We report here on our endeavors to address these aspects by synthesis of 2-phosphanylphenyl esters, screening in the nickel-catalyzed ethylene polymerization and structural characterization of the ligands and oligomers.

Results and Discussion

Synthesis and Structure of the Ligands

First hints of the applicability of O-substituted 2-phosphanylphenol derivatives in the nickel-catalyzed ethylene polymerization were found in initial screening tests of 2-(isopropylphenylphosphanyl)phenyl silyl ether, which gave polymers similar to those afforded by the corresponding phosphanylphenol. Steric hindrance, for example, in 2-diphenylphosphanyl-4,6-di-*tert*-butylphenyl trimethylsilyl ether, prevented activation. Therefore, in this study we investigated derivatives without substituents at the 6-position. We focused on easily accessible 2-diphenylphosphanyl-4-methylphenol derivatives, synthesized by bromination of *p*-cresol, dilithiation, coupling with chlorodiphenylphosphane, and final O-substitution with chlorotrimethylsilane, $ClP(O)Ph_2$, or carboxylic acid chlorides RC(O)Cl (R = Me, *t*Bu, Ph, $4\text{-}MeOC_6H_4$) (Scheme 1). The trimethylsilyl ether was cleaved by methanol to provide 2-diphenylphosphanyl-4-methylphenol (**1**) as the reference ligand. Diphenylphosphinate **2** and various carboxylic esters **3a**–**d** were selected to determine the influence of O-substituents on the formation of catalysts and their activity and to detect, by characteristic ^{31}P, ^{1}H, or ^{13}C NMR signals, the transfer of the O-substituent to lower oligomer byproducts or to the polymer.



Scheme 1. Synthesis of 2-phosphanylphenol **1** and esters **2** and **3**.

New esters **2** and **3a**–**d** were structurally characterized by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy and in some cases by single-crystal X-ray diffraction (Figures 1, 2, and 3; Tables 1 and 3). The crystal structure analyses of **3b**–**d** show that in all three compounds the same conformation is preferred. The *P*-phenyl groups are turned away from the ester group to form a clockwise-turning propeller with one P–C axis nearly in the phenol ring plane (torsion angles ca. –165 to –178°) and the other nearly perpendicular (ca. 89–75°). The aryl and COO π planes of the benzoyl group of **3c** and **3d** are almost coplanar and form a delocalized π system, whereas the π planes of COO and the phenol ring are strongly rotated to positions slightly more than perpendicular with the double-bonded oxygen atom towards C6 for **3b** (ca. 100°) and even further for **3c** and **3d** (C2–C1–O–C ca. 121 and 129°, respectively) to minimize electron–electron repulsion to the *P* lone electron pair.

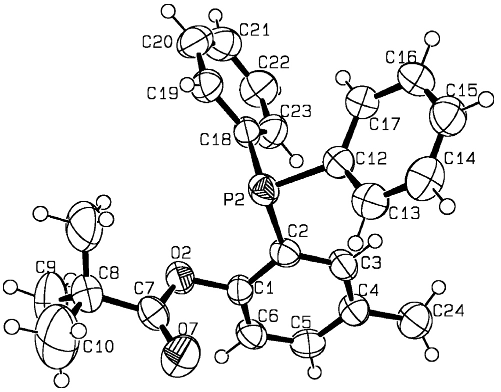


Figure 1. Molecular structure of **3b** in the crystal (*T* = 293 K, ellipsoids with 50% probability).

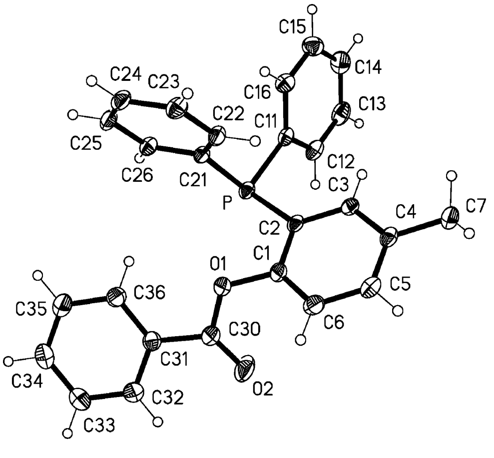


Figure 2. Molecular structure of **3c** in the crystal (*T* = 100 K, ellipsoids with 50% probability).

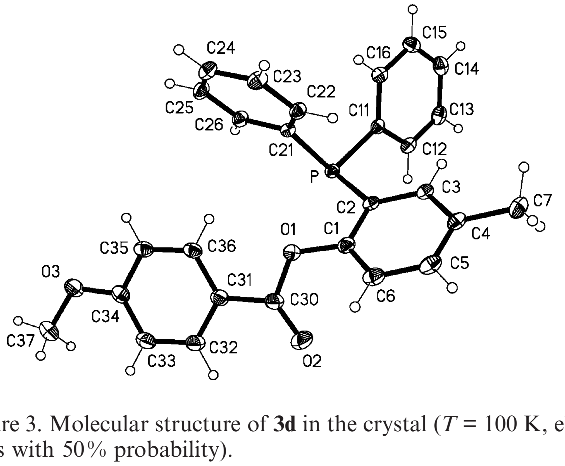


Figure 3. Molecular structure of **3d** in the crystal (*T* = 100 K, ellipsoids with 50% probability).

Table 1. Selected bond lengths [Å], angles [°], and torsion angles [°] of **3b**–**d**.

Assignment	**3b**	**3c**	**3d**
P–C2	1.829(4)	1.8406(12)	1.8412(11)
P–C_{Ph}	1.833(4), 1.819(4)	1.8303(12), 1.8329(13)	1.8311(11), 1.8316(11)
C1–O	1.412(4)	1.4065(15)	1.4014(13)
(Me)O–C	–	–	1.3654(14)
O–C	1.369(4)	1.3641(16)	1.3668(14)
C=O	1.190(5)	1.1953(17)	1.1979(15)
C–P–C	101.26(17)–103.92(17)	100.99(5)–103.44(5)	100.80(5)–103.84(5)
P–C2–C1	117.8(3)	117.34(9)	117.10(8)
P–C2–C3	125.5(3)	125.44(9)	125.47(8)
O–C1–C2	118.0(3)	116.24(11)	115.48(10)
O–C1–C6	119.5(3)	121.06(11)	122.06(10)
C1–C2–P–C	–88.4(3), 165.7(3)	76.36(10), –177.18(9)	75.26(9), –177.91(8)
C2–P2–C12–C13/17	–71.9(3), 119.5(3)	86.25(10), –98.06(11)	85.59(9), –99.71(9)
C2–P2–C18–C23/19	–25.9(4), 154.9(3)	26.04(12), –151.66(10)	23.80(10), –152.07(8)
C2–C1–O–C	–100.6(4)	120.77(13)	128.89(11)
C6–C1–O–C	82.5(4)	–63.08(16)	–56.02(15)
C1–O–C=O	–4.0(5)	5.1(2)	5.14(19)
O=C–C–C	–	13.0(2), –166.38(16)	4.2(2), –176.09(14)

Ethylene Polymerization

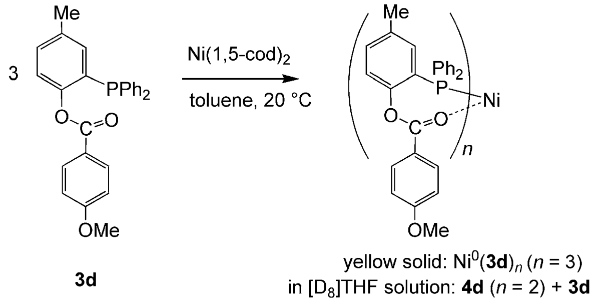
Screening of 2-phosphanylphenyl esters **2** and **3a**–**d** as ligands in the nickel-catalyzed polymerization of ethylene was performed as a batch procedure with an ethylene starting pressure of 40–50 bar, for studying the fate of the acyl groups at 20 bar, both at a bath temperature of 100 °C (Table 2). These conditions were optimized for comparison of variously substituted 2-phosphanylphenols[4a] and allow an extension of the comparison to the new *O*-acyl derivatives. As mentioned above, **1** served as a reference ligand. The precatalysts were generated in situ by mixing toluene solutions of Ni(1,5-cod)$_2$ and **1**, **2**, or **3a**–**d** at 0 °C (10 min) and stirring for 5 min at room temperature before pressurizing and heating with ethylene. Whereas the yellow color turned rapidly to brown for the precatalyst solution of $\mathbf{1}_{Ni}$, precatalyst solutions of $\mathbf{2}_{Ni}$ or $\mathbf{3a}$–$\mathbf{d}_{Ni}$ became only slightly deeper yellow. This hints at differences in the formation of the precatalysts. For Ni(cod)$_2$ and 2-diphenylphosphanylphenol, closely related to **1**, at room temperature, the formation of phosphanylphenol–nickel(0) and phosphanylphenolate–nickel(II) complexes as major and minor precatalysts was indicated by ^{1}H, ^{13}C, and ^{31}P NMR spectra [$\Delta\delta(^{31}P)$ = 44.8 and 57.7 ppm].[4a] Reaction of Ni(cod)$_2$ with **3d**, representing the behavior of ligands of type **3**, leads at room temperature only to a nickel(0) complex (Scheme 2). When the components were mixed in a 1:2 molar ratio in

Table 2. Polymerization of ethylene with catalysts generated from **1**–**3** and Ni(cod)$_2$.[a]

No.	Catalyst (μmol),[a] P_{start} (bar), amount of C_2H_4 (g)	Conversion (%), TON, TOF_{max}[b]	PE (g),[c] m.p. (°C), *d* (g cm^{-3})	η (dL g^{-1}), M_{vis},[d] (g mol^{-1}), M_{NMR}[e] (g mol^{-1})	Vin/olefin, Me/C=C, Me/1000C[e]
1	**1**/Ni (100), 50, 14.6	74, 3875, n.d.	10.9, 118–121, 0.958	0.15, 3600, –	0.92, 1.6, 7.6
2	**1**[f]/Ni (100), 50, 13.2	99, 4670, 7100	13.0, 124.5–125.5, 0.950	–, –, 2450	0.82, 1.6, 9.0
3	**2**/Ni (100), 50, 14.2	77, 3900, 250	11.1, 116–120, 0.955	–, –, 2620	0.95, 1.7, 9.3[g]
4	**2**/Ni (100), 50, 13.3	99, 4700, n.d.	13.1, 95–125 (127.5–129.5),[h] 0.950	0.16, 3940, 2440	0.88, 1.5, 8.6[g]
5	**3a**/Ni (100), 50, 13.0	98, 4552, n.d.	12.8, 107–120 (127–129),[h] 0.960	–, –, 2400	0.83, 1.8, 10.5 [i]
6	**3a**/Ni (100), 50, 14.2	98, 4955, 5600	13.9, 110–119, 0.958	0.18, 4620, 2200	0.91, 1.4, 9; 1/25[i]
7	**3b**/Ni (120), 50, 12.3	98, 3600, 15500	12.0, 122.9–124.5, 0.946	–, –, 2100	0.84, 2.0, 13.5[j]
8	**3c**/Ni (100), 40, 9.2	97, 3180, n.d.	8.2, 124.5–125.4, 0.950	–, –, 3400	0.93, 2.8, 11.6
9	**3c**/Ni (100), 50, 14.6	96, 4880, 30700	13.7, 125–126, 0.955	–, –, 2150	0.91, 1.9, 12.4[i]
10	**3d**/Ni (100), 40, 9.0	100, 3200, n.d.	8.6, 124.5–125.5, 0.945	–, –, 2150	0.87, 1.6, 10.5; 1/40[k]
11	**3d**/Ni (100), 50, 12.9	100, 4600, 12500	12.6, 124.5–125.5, 0.965	–, –, 2650	0.84, 1.7, 9.0; 1/30[k]
12	**3c**/Ni (500), 20, 3.6	97, 220, n.d.	3.1, 120.5–123.5, 0.956	–, –, 2050	0.75, 1.8, 11.8; 1/40[l]
13	**3d**/Ni (500), 20, 3.5	100, 240, n.d.	3.3, 120.5–124.8, 0.950	–, –, 1530	0.88, 1.3, 11.9; 1/16[k]
14	**2**/Ni (200), 40, 10.2	30, 550, n.d.	2.8, 120–122, 0.949	–, –, 2050	0.96, 1.4, 9.3; 1/10[g]
15	**2**/Ni (500), 20, 3.5	0	–	–	–

[a] Equimolar amounts of **1**, **2**, or **3a**–**d** and Ni(cod)$_2$ were each dissolved in toluene (10 mL), united, and transferred to the autoclave. Then the autoclave was pressurized and heated. [b] Conversion of C_2H_4 to oligomers and polymers, TON in mol/mol, TOF_{max} in mol/mol h. [c] Isolated and purified polymer. [d] M_{vis} calculated from intrinsic viscosity (in decalin at 135 °C) $[\eta] = 3.8 \times 10^{-4} M_{vis}^{0.73}$.[17] [e] Determined by ^{1}H NMR integration. [f] Trace impurity by P-oxide **6**. [g] Additional trace ^{1}H signals at δ = 2.45 (t), 3.8 (br) ppm; relative intensity 0.1/C=C groups. [h] Polymer purified with aqueous methanolic hydrochloric acid; m.p. in parenthesis after additional extraction with MeOH. [i] Additional trace ^{1}H signals at δ = 2.03 (s, Me), 2.45 (t, CH$_2$) ppm. [j] Additional trace ^{1}H signal at δ = 2.53 (t, CH$_2$) ppm. [k] Additional trace ^{1}H signals at δ = 2.98 (t, CH$_2$), 3.76 (OMe) ppm; relative intensity ≈2:3; δ = 6.97, 8.06 (d, ^3J = 8.8 Hz, *m*-, *o*-H) ppm; 1/*x* = ratio CH$_2$C(O)R to olefin groups estimated by ^{1}H integration. [l] Additional trace ^{1}H signal at δ = 2.98 (t, CH$_2$) ppm.

THF, yellow crystals could be obtained after several days by overlaying the concentrated solution with *n*-hexane. Prolonged storage led to an additional colorless precipitate and a few orange-brownish crystals of a Ni^{II} P,O-chelate complex. The yellow crystals were not suitable for X-ray diffraction, but allowed characterization by multinuclear NMR spectroscopy. $[D_8]$THF solution NMR spectroscopic data of crystals, washed with *n*-hexane and dried in vacuo, are assignable to a $Ni^0(\mathbf{3d})_2$ complex (**4d**), accompanied by **3d**, probably by ligand dissociation in solution. According to ^1H NMR integration, the ratio of 4-Me and 4-MeO groups is each 2:1, corresponding to a 1:1 molar ratio of **4d** and **3d**. Cleavage of the *O*-acyl or *O*-C(phenyl) bond by nickel(0) can be excluded at this stage, as most of the signals of **3d** were found to be only slightly shifted in **4d** as well. Exceptions are nuclei involved in the coordination to nickel and adjacent carbon nuclei. Phosphorus displays a coordination chemical shift of $\Delta\delta(^{31}P) = 45.1$ ppm, which is close to $\Delta\delta = 42.8$ ppm for $[Ni^0(2\text{-}Ph_2P\text{-}4,6\text{-}t\mathrm{Bu}_2C_6H_4OH\text{-}\eta^1 P)(PMe_3)_3]$,[9] whereas the $\Delta\delta(^{31}P)$ values for 2-phosphanylphenol or 2-phosphanylphenolate nickel(II) P,O-chelate complexes are slightly ($\Delta\delta = 48.2$ ppm)[10] or significantly larger ($\Delta\delta = 58\text{–}70$ ppm).[4,9] Phosphanylphenolate coordination is additionally excluded for **4d** by downfield shifts of the ^{13}C-2 and ^{13}C-*i*(Ph) nuclei compared to **3d** ($\Delta\delta = 7.4$, 3.1 ppm) and relatively small one-bond P–C coupling constants ($^1J_{P,C\text{-}2} = 11.9$ Hz, $^1J_{P,C\text{-}i} = 31.9$ Hz). For nickel(II) phosphanylphenolates, ^{13}C-2 and ^{13}C-*i*(Ph) signals are upfield shifted, and the one-bond P–C couplings are considerably larger ($^1J_{P,C} = 45\text{–}51$ Hz).[4,9] The coordination of a second ligand at nickel is indicated by a doublet of doublet for ^{13}C-*i*(Ph). Additional interactions of the carbonyl oxygen atom to Ni^0 are suggested by strong downfield shift of the ester $^{13}C(O)$ resonance ($\delta = 199.7$ ppm, $\Delta\delta = 36.1$ ppm). Coordinated carbon monoxide is improbable, as no other degradation products of **3d** were observed, likewise a benzoyl group at nickel, which in addition should display a much stronger downfield shift.[11] A closer investigation of compounds of type **4** will be subject of a separate study. It is assumed that they are formed stepwise and that during the short time of catalyst formation only one cod ligand is replaced.



Scheme 2. Reaction of $Ni(cod)_2$ with **3d** at room temperature.

Apart from the different nature of the precatalyst solutions of $\mathbf{1}_{Ni}$ and $\mathbf{2}_{Ni}$ or $\mathbf{3a\text{–}d}_{Ni}$, heating with ethylene under pressure led in almost all experiments to active catalysts and nearly quantitative conversion of ethylene (Table 2). The rate of the reaction is, however, different for $\mathbf{1}_{Ni}$, $\mathbf{2}_{Ni}$, and $\mathbf{3a\text{–}d}_{Ni}$, as visualized by pressure–time plots (Figures 4 and 5). The polymerization with $\mathbf{1}_{Ni}$ gives higher ethylene conversion (Table 2, Entries 1 and 2) than with the 2-diphenylphosphanylphenol/$Ni(cod)_2$ catalysts studied earlier.[4a] As in the latter, the variation in the conversions is larger than that for catalysts $\mathbf{3a\text{–}d}_{Ni}$ and depends sensitively on deviations from a 1:1 molar ratio of ligand and Ni.[6c] The polymerization with catalyst $\mathbf{2}_{Ni}$ (Table 2, Entries 3 and 4) differs from those with $\mathbf{1}_{Ni}$ and $\mathbf{3a\text{–}d}_{Ni}$ (Table 2, Entries 5–13) by a very long induction period and slow conversion. The formation of the active catalyst from **2** is the critical step and also led in some experiments with $\mathbf{2}_{Ni}$ to low conversion or inactivity, in particular for lower ethylene/catalyst ratios (Table 2, Entries 14 and 15), intended to trace the fate of the $Ph_2P(O)$ group. The selectivity for linear vinyl- and methyl-terminated polyethylene and for α-olefins in the small amount of volatile oligomers, separated along with 1,5-cod and solvent from the polymer by flash distillation, is however the same as with catalysts $\mathbf{1}_{Ni}$. This hints at a closely related mechanism apart from the initial step. The phosphorus signals of unconsumed **2** in the methanol extract of polyethylene obtained with $\mathbf{2}_{Ni}$ (Table 2, Entry 3) suggest slow cleavage of **2**, and two small, equally intensive phosphorus singlets at $\delta = 27.7$ ppm and $\delta = 32.2$ ppm in the same region as ^{31}P resonances of $Ph_2P(O)OR$ com-

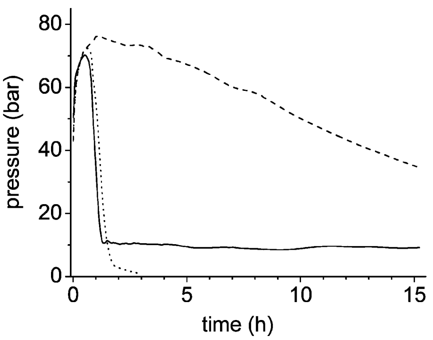


Figure 4. Pressure–time plots for batch polymerization of ethylene with catalysts prepared in situ from $Ni(cod)_2$ and **1** (solid), **2** (dashed), or **3a** (dotted) in toluene; bath temperature 100 °C.

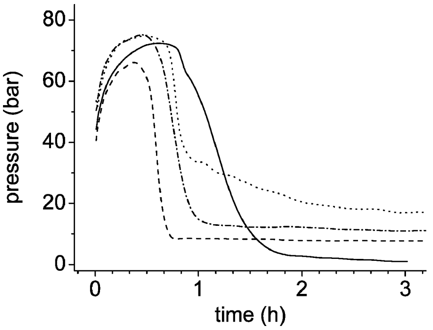
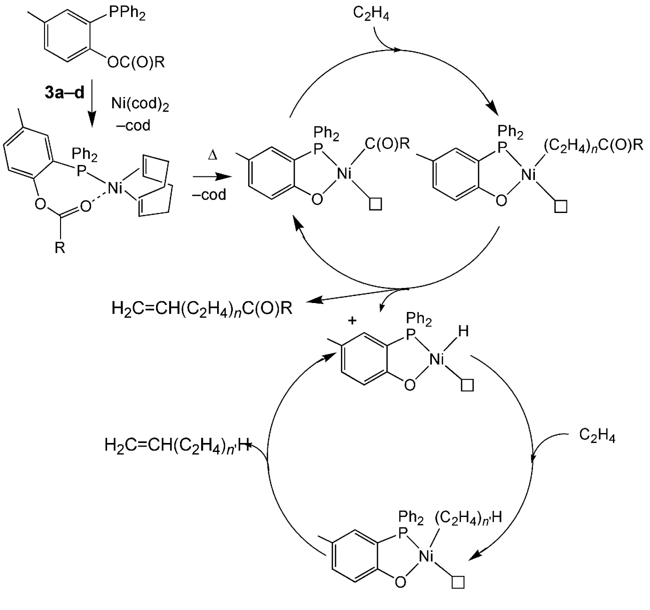


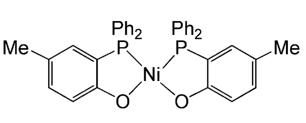
Figure 5. Pressure–time plots for batch polymerization of ethylene with catalysts prepared in situ from $Ni(cod)_2$ and **3a** (solid), **3b** (dashed), **3c** (dotted), or **3d** (dashed/dotted) in toluene; bath temperature 100 °C.

pounds (δ = 25–29 ppm)[12] and phosphanylphenolate nickel complexes indicate cleavage of the O–P bond and formation of a phosphanylphenolate catalyst. In the polymers, ^{31}P signals could not be detected. Nickel complexes with $Ph_2P(CH_2)_nP(O)Ph_2$ or $Ph_2PC_6H_4P(O)Ph_2$ ligands, which like **2** possess a phosphanyl and (P=)O donor group but are unable to degrade to P–C=C–O⁻ moieties, form cationic nickel catalysts that behave differently towards ethylene and provide isomeric mixtures of lower oligomers (mainly C_4–C_8).[13]

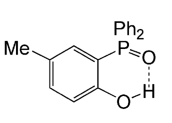
The short induction period for catalysts **3a**–$\mathbf{d}_{Ni}$ is attributed to rapid formation and low thermal stability of complexes of type **4**. It is known that $Ni(cod)_2$ reacts with benzoic acid esters in the presence of triphenylphosphane under mild heating (55–70 °C) mainly with scission of the acyl–OR bond, although for some R groups, acylO–R cleavage is also observed.[14] Complexes of type **4** prefer the first route, acyl–OR cleavage (Scheme 3). Evidence is given by detection of acyl end groups in the ethylene polymers and the presence of **5** and **6** in the methanol extracts of the crude polyethylenes. Compounds **5** and **6** were found also in the extracts of polyethylene obtained with $\mathbf{1}_{Ni}$ and characterize the ligand of the active catalyst by trapping in a stable complex or by air oxidation. The NMR spectroscopic data of **5** and **6** are identical to those of independently synthesized samples.



Scheme 3. Proposed mechanism of ethylene polymerization by **3a**–$\mathbf{d}_{Ni}$.



5 $\delta(^{31}P)$ = 34.4 ppm



6 $\delta(^{31}P)$ = 39.7 ppm

The polymerization of ethylene with catalyst systems **3a**–$\mathbf{d}_{Ni}$ generally proceeds rapidly, almost quantitatively within 1–1.5 h (including initiation period) and with good reproducibility. The turnover numbers were limited by the ethylene/catalyst ratio in the batch procedure. The products are mainly low molecular weight (M_{NMR} 2100–4000) linear polyethylenes with CH_3 and vinyl end groups, but a small amount of the polymers possess acyl end groups, as mentioned above, derived from ligand **3** employed in the catalyst. The ethylene consumption rate is not greatly different for catalysts **3a**–$\mathbf{d}_{Ni}$, but a clear dependence on the size of the substituent R can be seen in the pressure–time plots (Figure 5). The system with the bulky pivaloyl group reacted fastest, followed by the benzoyl- and 4-methoxybenzoyl systems, whereas the small acetyl group led to the slowest reaction. It is assumed that these findings are due to intermolecular interactions of polymer R–C(O) end groups with catalytically active nickel centers. They are facilitated for small acyl groups and cause slight retardation of the ethylene consumption, but stabilize the catalyst against deactivation routes and thus give higher conversions than most 2-phosphanylphenol-derived catalysts. In this light, the slow reaction with $\mathbf{2}_{Ni}$ may be attributable not only to slow catalyst formation, as supported by detection of unconsumed **2**, but also to stronger interactions of the $Ph_2P(O)OR$ species with the catalyst center.

The acyl end groups in the polymers obtained with catalysts $\mathbf{3a}_{Ni}$–$\mathbf{d}_{Ni}$ are detected in the ^1H NMR spectra by characteristic trace signals in addition to the usual signals for the linear vinyl-terminated polyethylene. The signals for $Me_3CC(O)$ end groups are superimposed by strong polymer methyl signals, but a tiny triplet for α-CH_2 attached to the terminal acyl group was detected at δ = 2.45 (at acetyl) and 2.53 (at pivaloyl) ppm, respectively (Table 2). For linear alkyl aryl ketones the α-CH_2 group is more strongly deshielded and appears at δ = 2.95 ppm.[15] The polymers obtained with $\mathbf{3c}_{Ni}$ and $\mathbf{3d}_{Ni}$ display this group clearly, in particular for a low ethylene/catalyst ratio, and allow a rough estimation of the ratio of primarily formed polymer chains with terminal acyl groups to Ni–H initiated chains with a methyl end group formed in later polymerization cycles (estimations see Table 2). In the polymers obtained with $\mathbf{3d}_{Ni}$, small signals for the 4-OMe group (δ = 3.76 ppm) and the doublets for *o*- and *m*-aryl protons were also detected (δ = 6.68, 8.06 ppm, d, ^3J = 8.8 Hz, *m*-, *o*-H) (Figure 6).

Mechanistic Aspects

Polyethylene obtained with catalyst $\mathbf{2}_{Ni}$ is formed more slowly but displays the same microstructure, linear chains with methyl and vinyl end groups, as in polyethylene prepared by means of catalyst $\mathbf{1}_{Ni}$. Apart from the above-mentioned different initiation step, the mechanisms will thus be the same. For catalysis with **3a**–$\mathbf{d}_{Ni}$, the occurrence of two types of linear polyethylenes hints at two different chain-growing cycles. The formation of small amounts of polymers with R–C(O) end groups suggests that, on heating, Ni^0 of the primary complexes of type **4** inserts into the *O*-acyl bond and generates 2-phosphanylphenolate Ni–C(O)R species that allow addition and insertion of ethylene. The growth of this chain is terminated by β-hydride elimination,

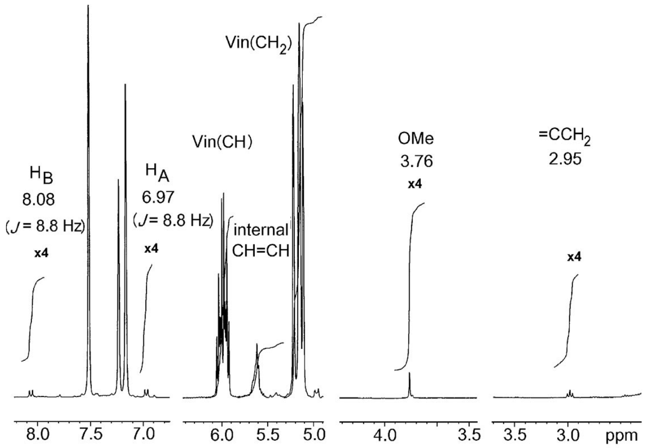


Figure 6. Characteristic ^1H NMR signals (in C_6D_5Br, 104 °C) of 4-$MeOC_6H_4COCH_2$ in addition to signals from vinyl end groups in polyethylene obtained with $\mathbf{3d}_{Ni}$.

which generates vinyl end groups and NiH starting catalysts for the subsequent chain growing cycles yielding CH_3 and vinyl-terminated linear polyethylenes as the main body of the polymer product.

Conclusions

2-Phosphanylphenyl carboxylic acid esters (**3**) and Ni(1,5-cod)$_2$ form highly active catalysts for the polymerization of ethylene to linear polymers with vinyl and methyl end groups. Detection of a small amount of the acyl end group instead of the methyl end group shows that the catalyst for the first chain growth cycle is formed by insertion of nickel(0) into the *O*-acyl bond of the ligands. Termination by β-hydride elimination then starts NiH-initiated polymerization cycles yielding methyl- and vinyl-terminated chains. The acyl groups in the polymer interact weakly with the catalyst metal, which leads to a small retardation of the ethylene consumption rate *t*Bu < Ph, 4-$MeOC_6H_4$ < Me, but also to stabilization of the catalyst and very high conversion of ethylene. 2-Phosphanylphenyl phosphinate **2** also forms ethylene polymerization catalysts with Ni(1,5-cod)$_2$, but the reaction rate is low. Slow O–P(O)Ph$_2$ cleavage to form the active phosphanylphenolate catalyst is assumed to be the main reason, as the microstructure of the polyethylene is the same as with $\mathbf{1}_{Ni}$ catalysts.

Experimental Section

General Methods: All manipulations and reactions were carried out under an atmosphere of dry argon by using Schlenk techniques and freshly distilled dry solvents. The acyl chlorides and KOH-dried triethylamine were recondensed or distilled before use. 2-Diphenylphosphanyl-4-methylphenol (**1**)[16] was prepared as reported earlier. Other chemicals were purchased. Ethylene (99.5%, Air Liquide) was used without further treatment. NMR spectra were recorded at 25 °C with a multinuclear FT-NMR spectrometer ARX300 (Bruker) at 300.1 (^1H), 75.5 (^{13}C), and 121.5 (^{31}P) MHz in $CDCl_3$ unless indicated otherwise. Chemical shift references are tetramethylsilane for ^1H and ^{13}C and H_3PO_4 (85%) for ^{31}P. Coupling constants refer to $J_{H,H}$ in ^1H and $J_{P,C}$ in ^{13}C NMR spectroscopic data unless indicated otherwise. Assignment numbers of the phenol ring follow the nomenclature, *P*-phenyl nuclei are indicated by *o*, *m*, *p*, *i*, benzoic acid nuclei by *o′*, *m′*, *p′*, *i′*. IR spectra were recorded with an FTIR spectrometer System 2000 (Perkin–Elmer), and mass spectra on a single-focusing mass spectrometer AMD40 (Intectra). Melting points were determined in a capillary and are uncorrected. Elemental analyses were carried out with a CHNS-932 analyzer from LECO by using standard conditions. ^1H NMR measurements of polyethylenes were carried out as described in ref.[4a] [η] was determined in tetralin at 120 °C (Dr. D. Lilge, BASELL).[17]

2-Diphenylphosphanyl-4-methylphenyl Diphenylphosphinate (2). A solution of BuLi (1.6 M in hexane, 62.5 mL, 0.1 mol) was added dropwise to 2-bromo-4-methylphenol (6.0 mL, 49.7 mmol) dissolved in diethyl ether (100 mL), followed by dropwise addition of a solution of Ph_2PCl (9.0 mL, 50.1 mmol) in diethyl ether (10 mL). After stirring overnight, $Ph_2P(O)Cl$ (9.7 mL, 50.9 mmol) in diethyl ether (10 mL) was added to the suspension without cooling. A large amount of insoluble material precipitated. Stirring was continued for 4 h, the solvent was evaporated in vacuo, and the residue was extracted with toluene (150 mL). After evaporation of toluene in vacuo, the residue was crystallized from ethanol to give 9.6 g (39%) of colorless **2**. M.p. 148–150 °C. $C_{31}H_{26}O_2P_2$ (492.49): calcd. C 75.60, H 5.32; found C 75.46, H 5.57. ^1H NMR: δ = 2.07 (s, 3 H, CH_3), 6.46 (m, 1 H, 3-H), 6.97 (dd, ^3J = 8.3 Hz, ^4J = 2.2 Hz, 1 H, 5-H), 7.27–7.35 (m, 14 H), 7.42 ("tq", ^3J = 7.5, 7.3 Hz, J = 2.8, 1.4 Hz, 2 H, *p′*-H), 7.49 (ddd, ^3J = 8.2 Hz, $^4J_{PH}$ = 4.6 Hz, J = 0.9 Hz, 1 H, 6-H), 7.76 (br. dd, $^3J_{P,H}$ = 12.6 Hz, ^3J = 7 Hz, $^4J \approx$ 1.4 Hz, 4 H, *o′*-H) ppm. $^{13}C\{^1H$, CH COSY$\}$ NMR: δ = 20.7 (s, CH_3), 119.0 (d, ^3J = 3.0 Hz, CH-6), 127.8 (dd, ^1J = 14.1 Hz, ^3J = 7.1 Hz, C_q-2), 128.2 (d, ^3J = 13.5 Hz, 4 CH-*m′*), 128.5 (d, ^3J = 7.1 Hz, 4 CH-*m*), 128.8 (s, 2 CH-*p*), 129.9 (s, C_q-4), 130.8 (s, CH-5), 131.8 (dd, ^2J = 10.6 Hz, ^6J = 2.1 Hz, 4 CH-*o′*), 132.1 (d, ^4J = 2.9 Hz, 2 CH-*p′*), 132.7 (d, ^1J = 144.5 Hz, 2 C_q-*i′*), 134.0 (d, ^2J = 21.1 Hz, 4 CH-*o*), 134.1 (s, CH-3), 135.7 (d, ^1J = 9.7 Hz, 2 C_q-*i*), 151.5 (dd, ^2J = 17, 8 Hz, C_q-1) ppm. $^{31}P\{^1H\}$ NMR: δ = –15.7, 30.4 (2 d, $^4J_{P,P}$ = 4.2 Hz, P^{III}, P^V) ppm. IR (KBr): $\tilde{\nu}_{P=O}$ region = 1232 (vs), 1204 (vs) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 492 (100) [M^+], 415 (64) [M^+ – Ph], 308 (36) [M^+ – PPh_2], 274 (46) [M^+ – $OP(O)Ph_2$], 214 (18), 202 (47) [$P(O)Ph_2^+$], 186 (13) [PPh_2^+], 78 (28) [Ph^+].

2-Diphenylphosphanyl-4-methylphenyl Acetate (3a): A solution of BuLi (1.6 M in hexane, 125 mL, 0.2 mol) was added at –50 °C to 2-bromo-4-methylphenol (12.0 mL, 99.3 mmol) dissolved in diethyl ether (200 mL), the first half dropwise, the second part rapidly without cooling. After stirring for 4 h at 20 °C, the reagent was cooled to –50 °C and a solution of Ph_2PCl (17.9 mL, 99.7 mmol) in diethyl ether (20 mL) was added dropwise. Stirring was continued overnight, followed by dropwise addition of a solution of acetyl chloride (8.6 mL, 120.9 mmol.) in diethyl ether (10 mL) at room temperature. The precipitate was filtered off and washed with diethyl ether. The solvent was evaporated from the filtrate. The residual oil was distilled under high vacuum (b.p. 155–160 °C/ 3.8×10^{-4} Torr) to give 18.4 g (55%) of **3a**. The compound solidified slowly at 20 °C, faster at 40–50 °C. M.p. 86–90 °C. $C_{21}H_{19}O_2P$ (334.35): calcd. C 75.44, H 5.73; found C 75.96, H 5.46. ^1H NMR: δ = 1.95 (s, 3 H, CH_3), 2.20 (s, 3 H, 4-CH_3), 6.64 (dd, $^3J_{P,H}$ = 4.7 Hz, ^4J = 2.1 Hz, 1 H, 3-H), 7.01 (dd, ^3J = 8.2 Hz, $^4J_{P,H}$ = 4.3 Hz, 1 H, 6-H), 7.17 (dd, ^3J = 8.2 Hz, ^4J = 2.1 Hz, 1 H, 5-H), 7.28–7.36 (m, 10 H, phenyl) ppm. $^{13}C\{^1H\}$ NMR: δ = 20.4, 20.90 (2 s, CH_3), 122.2 (s, C-6), 128.45 (d, ^3J = 7.5 Hz, 4 C-*m*), 128.9 (s, 2 C-*p*), 129.7 (d, ^1J = 15.1 Hz, C-2), 130.54 (s, C-5), 130.7 (d, ^3J =

3.8 Hz, C-4), 133.8 (d, ^{2}J = 20.4 Hz, 4 C-*o*), 135.57 (d, ^{1}J = 7.5 Hz, 2 C-*i*), 135.63 (d, ^{2}J = 2.3 Hz, C-3), 150.5 (d, ^{2}J = 17.4 Hz, C-1), 169.0 (CO) ppm. ^{31}P{^{1}H} NMR: δ = –15.3 ppm. IR (KBr): $\tilde{\nu}_{C=O}$ = 1765 (s) cm^{-1}. MS (EI, 70 eV, 90 °C): *m*/*z* (%) = 335 (16), 334 (65) [M^{+}], 320 (21), 319 (100) [M^{+} – CH$_3$], 292 (61), 291 (96) [M^{+} – COCH$_3$], 214 (76) [M^{+} – COCH$_3$ – Ph], 202 (59), 184 (50) [PPh$_2^{+}$], 108 (37) [M^{+} – COCH$_3$ – PPh$_2$], 44 (79).

2-Diphenylphosphanyl-4-methylphenyl 2,2-Dimethylpropanoate (3b): A solution of pivaloyl chloride (0.46 mL, 3.8 mmol) was added dropwise at 0 °C to a solution of **1** (0.73 g, 2.5 mmol) and Et$_3$N (0.52 mL, 3.8 mmol) in diethyl ether (20 mL). Stirring was continued overnight, and the precipitate was filtered off and washed with diethyl ether (3×). Ether was removed in vacuo leaving 0.87 g (92%) of crude NMR spectroscopic pure **3b**, which was crystallized from hexane. M.p. 109–110 °C. C$_{24}$H$_{25}$O$_2$P (376.44): calcd. C 76.58, H 6.69; found C 76.37, H 6.90. ^{1}H NMR: δ = 1.12 (s, 9 H, CMe$_3$), 2.17 (s, 3 H, 4-CH$_3$), 6.51 (ddd, $^{3}J_{P,H}$ = 4.2 Hz, *J* = 2.2, 0.5 Hz, 1 H, 3-H), 6.99 (dd, ^{3}J = 8.2 Hz, $^{4}J_{P,H}$ = 4.4 Hz, 1 H, 6-H), 7.16 (dd“t”, ^{3}J = 8.2 Hz, ^{4}J = 2.2 Hz, *J* ≈ 0.5 Hz, 1 H, 5-H), 7.25–7.35 (m, 10 H, phenyl) ppm. ^{13}C{^{1}H} NMR: δ = 21.0 (s, 4-Me), 26.9 (s, C*Me*$_3$), 39.1 (s, *C*Me$_3$), 121.9 (s, C-6), 128.5 (d, ^{3}J = 7.1 Hz, 4C-*m*), 128.8 (s, 2 C-*p*), 129.5 (d, ^{1}J = 14.5 Hz, C-2), 130.5 (s, C-5), 131.8 (d, ^{3}J = 3.6 Hz, C-4), 133.8 (d, ^{2}J = 21.2 Hz, 4 C-*o*), 134.0 (d, ^{1}J = 7.5 Hz, 2 C-*i*), 135.4 (s, C-3), 151.0 (d, ^{2}J = 17.5 Hz, C-1), 176.4 (CO) ppm. ^{31}P{^{1}H} NMR: δ = –15.7 ppm. IR (KBr): $\tilde{\nu}_{C=O}$ = 1747 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 376 (24) [M^{+}], 375 (78), 361 (18), 322 (64), 321 (99), 295 (73), 294 (100), 273 (48), 213 (78), 57 (81).

2-Diphenylphosphanyl-4-methylphenyl Benzoate (3c): As described for **3a**, a solution of 2-bromo-4-methylphenol (3.23 mL, 26.7 mmol) in diethyl ether (50 mL) was dilithiated with BuLi (2.5 M in hexane, 21.6 mL, 54.0 mmol) at –50 and 20 °C, stirred for 4 h at 20 °C, followed by dropwise addition of Ph$_2$PCl (4.8 mL, 26.8 mmol) dissolved in diethyl ether (5 mL) at –50 °C. After stirring overnight at room temperature, a solution of benzoyl chloride (3.70 mL, 32.0 mmol) in diethyl ether (5 mL) was added dropwise at 20 °C. The mixture was stirred at this temperature for 1 d. Then the precipitate was filtered off and washed with diethyl ether (3 × 30 mL). The filtrate was washed with air-free distilled water (3×) and then dried with Na$_2$SO$_4$. After evaporation of 60% of the solvent and cooling to +4 °C, 3.0 g of **3c** crystallized. M.p. 125.1–125.6 °C. A further 3.8 g portion of product was isolated by extraction of the precipitate with dichloromethane (50 mL). Total yield: 6.8 g (64%). C$_{26}$H$_{21}$O$_2$P (396.42): calcd. C 78.78, H 5.34; found C 78.53, H 5.26. ^{1}H NMR: δ = 2.23 (s, 3 H, 4-CH$_3$), 6.65 (dd, $^{3}J_{P,H}$ = 4.8 Hz, ^{4}J = 1.8 Hz, 1 H, 3-H), 7.17 (dd, ^{3}J = 8.4 Hz, $^{4}J_{P,H}$ = 3.8 Hz, 1 H, 6-H), 7.22 (dd, ^{3}J = 8.4 Hz, ^{4}J = 1.8 Hz, 1 H, 5-H), 7.28–7.37 (m, 12 H, phenyl), 7.52 (tt, ^{3}J ≈ 7.4 Hz, ^{4}J = 1.3 Hz, 1 H, *p*′-H), 7.52 (dm, ^{3}J = 8.3 Hz, 2 H, *o*′-H) ppm. ^{13}C{^{1}H} (DEPT) NMR: δ = 21.0 (4-CH$_3$), 122.2 (d, ^{4}J = 1.8 Hz, CH-6), 128.2 (2 CH-m′), 128.5 (d, ^{3}J = 7.2 Hz, 4 C-*m*), 128.9 (s, 2 CH-*p*), 129.2 (C$_q$-4), 130.1 (d, ^{1}J = 14.8 Hz, C$_q$-2), 130.1 (s, 2 CH-o′), 130.5 (CH-5), 133.2 (CH-p′), 133.8 (d, ^{2}J = 2.1 Hz, C-3), 134.0 (d, ^{2}J = 20.6 Hz, 4 C-*o*), 135.6 (d, ^{1}J = 14.4 Hz, 2 C-*i*), 135.6 (C$_q$, C-*i*′), 150.6 (d, ^{2}J = 16.7 Hz, C-1), 164.4 (CO) ppm. ^{31}P{^{1}H} NMR: δ = –15.2 ppm. IR (KBr): $\tilde{\nu}_{C=O}$ = 1739 (s) cm^{-1}. MS (EI, 70 eV, 160 °C): *m*/*z* (%) = 398 (6), 397 (23), 396 (12) [M^{+}], 368 (9), 320 (50) [M^{+} + 1 – Ph], 292 (20) [M^{+} + 1 – COPh], 213 (33), 183 (16) [PPh$_2^{+}$], 105 (100).

2-Diphenylphosphanyl-4-methylphenyl 4-Methoxybenzoate (3d): As described for **3a**, a solution of 2-bromo-4-methylphenol (3.23 mL, 26.7 mmol) in diethyl ether (50 mL) was dilithiated with BuLi (2.5 M in hexane, 21.6 mL, 54.0 mmol) at –70 and 20 °C, stirred for 4 h at 20 °C, followed by dropwise addition of Ph$_2$PCl (4.8 mL, 26.8 mmol) dissolved in diethyl ether (10 mL) at –70 °C. After stirring overnight at room temperature, a solution of 4-methoxybenzoyl chloride (4.33 mL, 32.0 mmol) in diethyl ether (10 mL) was added dropwise at 20 °C. The mixture was stirred at this temperature for 3 d. Then the precipitate was filtered off and washed with diethyl ether (3 × 30 mL) and dried in vacuo. The filtrate contained mainly impurities, only a small portion of product. Pure product (7.38 g, 65%) was extracted from the precipitate with dichloromethane (50 mL). M.p. 133.8–134.7 °C. C$_{27}$H$_{23}$O$_3$P (426.44): calcd. C 76.04, H 5.44; found C 75.68, H 5.35. ^{1}H NMR: δ = 2.23 (s, 3 H, 4-CH$_3$), 3.85 (s, 3 H, 4-OCH$_3$), 6.63 (dd, $^{3}J_{P,H}$ = 4.6 Hz, ^{4}J = 2.0 Hz, 1 H, 3-H), 6.81 (m$_{AA'BB'}$, ^{3}J = 8.9 Hz, 2 H, *m*′-H), 7.16 (dd, ^{3}J = 8.1 Hz, $^{4}J_{P,H}$ = 3.8 Hz, 1 H, 6-H), 7.21 (dd, ^{3}J = 8.1 Hz, ^{4}J = 1.8 Hz, 1 H, 5-H), 7.29–7.36 (m, 10 H, phenyl), 7.76 (m$_{AA'BB'}$, ^{3}J = 8.9 Hz, 2 H, *o*′-H) ppm. ^{13}C{^{1}H} NMR: δ = 20.98 (4-CH$_3$), 55.34 (*p*-OMe), 113.40 (2 CH-*m*′), 121.56 (C$_q$-*i*′), 122.29 (CH-6), 128.41 (d, ^{3}J = 6.8 Hz, 4 CH-*m*), 128.84 (s, 2 CH-*p*), 130.0 (d, ^{1}J = 13.0 Hz, C$_q$-2), 130.49 (s, CH-5), 132.16 (2 CH-*o*′), 133.69 (2 C$_q$-*i*), 134.00 (d, ^{2}J = 21.0 Hz, 4 C-*o*), 135.48 (CH-3), 135.64 (C$_q$-4), 150.65 (d, ^{2}J = 16.1 Hz, C$_q$-1), 163.56 (CO), 164.05 (C$_q$-*p*′) ppm. ^{31}P{^{1}H} NMR: δ = –15.2 ppm. IR (KBr): $\tilde{\nu}_{C=O}$ = 1732 (s) cm^{-1}. MS (EI, 70 eV, 120 °C): *m*/*z* (%) = 428 (7), 427 (23) [M^{+} + H], 351 (13), 350 (45), 334 (17), 213 (6), 183 (4), 136 (10), 135 (100), 197 (12), 77 (16).

Reaction of 3d with Ni(cod)$_2$ to form 4d: Solid **3d** (0.45 g, 1.06 mmol) was added to a solution of Ni(cod)$_2$ (0.14 g, 0.51 mmol) in THF (20 mL). After stirring for 12–15 h the solution was concentrated in vacuo and overlaid with *n*-hexane. After several days small orange-yellow column-shaped crystals and small white crystals deposited. The orange-yellow crystals displayed very weak X-ray diffraction and multiply split reflections that, despite repeated attempts, did not allow a crystal structure analysis. NMR spectra of the orange-yellow crystals separated from the mixture, washed with *n*-hexane and dried in vacuo, hint at a Ni^{0}(**3d**)$_3$ complex, which in solution dissociates into Ni^{0}(**3d**)$_2$ (**4d**) and **3d** (ratio of 4-Me and 4-MeO signals each 2:1 by ^{1}H NMR integration). A trace amount of noncoordinated 1,5-cod was detected as an impurity. Data for the yellow crystals: C$_{72}$H$_{75}$NiO$_6$P$_3$ (1187.98): calcd. C 72.79, H 6.36; found C 73.04, H 6.77. Complex **4d**: ^{1}H NMR ([D$_8$]THF): δ = 2.07 (s, 4-CH$_3$), 3.77 (s, 4-OCH$_3$), 6.69 (m$_{AA'BB'}$, ^{3}J = 8.9 Hz, *m*′-H), 7.0–7.2 (m, 5 H, aryl), 7.27–7.31 (m, 2 H, aryl), 7.35–7.41 (m, 3 H, aryl), 7.34 (m$_{AA'BB'}$, ^{3}J = 8.8 Hz, *o*′-H) ppm. ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 20.81 (4-Me), 55.50 (*p*-OMe), 113.67 (2 CH-*m*′), 122.53 (C$_q$-*i*′), 124.42 (CH-6), 128.55 (d, ^{3}J = 11.1 Hz, 4 CH-*m*), 129.22 (s, 2 CH-*p*), 131.53 (CH-5), 132.73 (2 CH-*o*′), 133.57 (d, ^{2}J = 15.2 Hz, 4 CH-*o*), 135.85 (s, Cq-4), 136.37 (d, ^{2}J = 17.7 Hz, CH-3), 137.39 (d, ^{1}J = 11.9 Hz, C$_q$-2), 137.65 (dd, ^{1}J = 31.9 Hz, ^{3}J = 4.0 Hz, 2 C$_q$-*i*), 150.79 (s, C$_q$-1), 163.90 (C$_q$-*p*′), 199.70 (br. t-shape, CO) ppm. ^{31}P{^{1}H} NMR ([D$_8$]THF): δ = 29.88 ppm.

Complex 5: A solution of **1** (1.6 g, 5.48 mmol) in methanol (5 mL) was added to a solution of NiCl$_2$(H$_2$O)$_6$ (650 mg, 2.74 mmol). An excess amount of triethylamine (1.1 g) was added until the green color disappeared and all material was orange. Volatiles were removed in vacuo, triethylamine hydrochloride was extracted with water, and the residue crystallized from dichloromethane/methanol (1:1) to give 1.1 g (80%) of **4**. C$_{38}$H$_{32}$NiO$_2$P$_2$ (641.30): calcd. C 71.17, H 5.03; found C 70.45 (incomplete combustion), H 5.15. ^{1}H NMR: δ = 2.05 (s, 3 H, 4-Me), 6.47 [br. t (A of AMXX′, X = X′ = P), |*J*+*J*′| = 10–11 Hz, 2 H, 6-H], 6.89 (dt, ^{3}J = 8.5 Hz, ^{4}J +$^{5}J_{P,H}$ = 5.6 Hz, 2 H, 5-H), 6.97 (br. d, $^{3}J_{P,H}$ = 8.7 Hz, 2 H, 3-H), 7.10

(br. t, ^{3}J = 7.4–7.6 Hz, 4 H, *m*-H), 7.32 (br. t, ^{3}J = 7.3–7.5 Hz, 2 H, *p*-H), 7.42 (td, $^{3}J_{PH}$ ≈ 5.3 Hz, 4 H, *o*-H) ppm. $^{31}P\{^{1}H\}$ NMR: δ = 34.3 ppm.

2-(Diphenylphosphoryl)-4-methylphenol (6): As described for **3a**, a solution of 2-bromo-4-methylphenol (6.0 mL, 49.7 mmol) in diethyl ether (100 mL) was dilithiated with BuLi (1.6 M in hexane, 62.5 mL, 0.1 mol) at –70 and 20 °C, stirred for 4 h at 20 °C. Then a solution of $Ph_2P(O)Cl$ (9.0 mL, 47.2 mmol) in diethyl ether (10 mL) was added dropwise at –50 °C. The suspension was stirred overnight at 20 °C and then acidified with a solution of glacial acetic acid (3.3 g, 0.6 mol) in diethyl ether (10 mL). The white precipitate was filtered off and washed with diethyl ether, and the residue was extracted with warm absolute ethanol. The crystals formed overnight were separated, washed with cold EtOH, and dried in vacuo to give 5.1 g (35%) of **5**. M.p. 188 °C. The yield is not optimized. The filtrate contains more product along with another phosphorus compound with $\delta(^{31}P)$ = 32.0 ppm. $C_{19}H_{17}O_2P$ (308.32): calcd. C 74.02, H 5.56; found C 74.15, H 5.99. ^{1}H NMR: δ = 2.18 (s, 3 H, 5-Me), 6.73 (ddd, $^{3}J_{P,H}$ = 13.4 Hz, J = 1.6, 0.5 Hz, 1 H, 6-H), 6.90 (dd, ^{3}J = 8.5 Hz, $^{4}J_{PH}$ = 4.9 Hz, 1 H, 3-H), 7.21 (dm, ^{3}J = 8.6, 1.6 Hz, 1 H, 4-H), 7.44–7.53 (m, 4 H, *m*-H), 7.55–7.62 (m, 2 H, *p*-H); 7.69 (m, $^{3}J_{P,H}$ = 12.3 Hz, ^{4}J = 1.5 Hz, 2 H, *o*-H), 10.9 (v br, 1 H, OH) ppm. $^{13}C\{^{1}H\}$ NMR: δ = 20.5 (4-Me), 110.5 (d, ^{1}J = 103.6 Hz, C-*i*), 118.5 (d, ^{3}J = 8.5 Hz, C-3), 128.1 (d, ^{3}J = 12.4 Hz, C_q-5), 128.7 (d, ^{3}J = 12.8 Hz, 4 C-*m*), 131.5 (d, ^{2}J = 10.0 Hz, C-6), 131.9 (d, ^{1}J = 104.8 Hz, 2 C-*i*), 132.0 (d, ^{3}J = 10.5 Hz, 4 C-*o*), 132.5 (d, ^{4}J = 2.6 Hz, C-*p*), 135.3 (d, ^{4}J = 2.4 Hz, C-4), 161.81 (d, ^{2}J = 2.7 Hz, C_q-2) ppm. ^{31}P NMR: δ = 39.7 ppm. MS (EI, 70 eV, 180 °C): *m*/*z* (%) = 309 (35), 308 (85) [M^{+}], 307 (100), 229 (20), 213 (16), 201 (14), 199 (16), 183 (14), 152 (11), 77 (21).

Ethylene Polymerization: The corresponding phosphanylphenol derivative (Table 2) and $Ni(cod)_2$ were dissolved in toluene (each in 10 mL, unless indicated otherwise), cooled to 0 °C (10 min), and mixed. The resulting slightly deeper yellow (with **2** and **3**) or brown (with **1**) solution was stirred at room temperature for 5 min. If indicated in Table 2 an additive was added. The mixture was transferred to an argon-filled stainless steel autoclave (75 mL) (details see in ref.[4a]). The autoclave was pressurized with ethylene (see Table 2) and placed into a heating bath at 100 °C. After heating for ca. 15 h, cooling to room temperature and weight control, unconverted ethylene was allowed to escape through a cooling trap (–78 °C). The polymer with solvent and oligomers was transferred to a flask, and all volatiles were flash-distilled at 3–4 mbar/70–80 °C to a cooling trap (–196 °C) for GC analysis. The polymer residue was extracted in most samples (except Entries 4–6) first with methanol (50 mL) and then methanol (36.5 mL)/concentrated aqueous HCl (13.5 mL) by stirring overnight at room temperature. The polymer was thoroughly washed with methanol and dried in vacuo. Conversion and characteristic polymer data are given in Table 2. GC analysis of the flash distillate apart from toluene indicated small amounts of 1,5-cod and linear α-olefins C_4–C_{12} (mostly $C_6 \le C_8$

Table 3. Crystallographic data of compounds **3b**–**d**.

Compound	**3b**	**3c**	**3d**
Empirical formula	$C_{24}H_{25}O_2P$	$C_{26}H_{21}O_2P$	$C_{27}H_{23}O_3P$
Formula weight	376.41	396.40	426.42
Temperature [K]	293	100	100
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a [Å]	7.792(2)	9.1570(6)	9.1385(7)
b [Å]	11.195(3)	24.1370(16)	9.8116(7)
c [Å]	13.483(4)	10.0608(6)	13.2947(9)
α [°]	70.74(3)	90	87.572(4)
β [°]	81.82(2)	110.021(3)	81.590(4)
γ [°]	73.80(2)	90	69.623(4)
Volume [Å^3]	1064.6(5)	2089.3(2)	1105.39(14)
Z	2	4	2
$D_{calcd.}$ [Mg m^{-3}]	1.174	1.260	1.281
Absorption coefficient [mm^{-1}]	0.144	0.151	0.151
F(000)	400	832	448
Crystal size [mm^3]	0.60 × 0.40 × 0.35	0.20 × 0.20 × 0.10	0.2 × 0.1 × 0.1
θ range for data collection	2.7 to 26.3	2.51 to 30.51	2.64 to 30.51°
Index ranges	$-9 \le h \le 0$ $-13 \le k \le 13$ $-16 \le l \le 16$	$-13 \le h \le 13$ $-34 \le k \le 34$ $-14 \le l \le 14$	$-13 \le h \le 13$ $-14 \le k \le 14$ $-18 \le l \le 18$
Reflections collected	4576	53765	27382
Independent reflections	4256 [R(int) = 0.049]	6379 [R(int) = 0.0482]	6725 [R(int) = 0.0310]
Completeness [%] to θ = 30.00°	98.6 to θ = 26.29	100 to θ = 30.50	99.8 to θ = 30.50
Absorption correction	None	None	None
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4256/0/248	6379/0/263	6725/0/282
Goodness-of-fit on F^2	0.991	1.044	1.019
Final R indices	R_1 = 0.0583 wR_2 = 0.1445 for $I > 2\sigma(I)$	R_1 = 0.0432 wR_2 = 0.1047 for $I > 2\sigma(I)$	R_1 = 0.0377 wR_2 = 0.0973 for $I > 2\sigma(I)$
R indices (all data)	R_1 = 0.2020 wR_2 = 0.1871	R_1 = 0.0560 wR_2 = 0.1126	R_1 = 0.0489 wR_2 = 0.1049
Largest diff. peak and hole [e Å^{-3}]	0.633 and –0.211	0.494 and –0.234	0.411 and –0.239

$\geq$ 1.5-cod $> C_{10}$) and trace amounts of isomers ($<5\%$). In the methanol extract small amounts of 1,5-cod and linear α-olefins from C_{10} to C_{22} ($C_{14} > C_{16} > C_{12} >$ others) were detected; the isoolefin content was very low.

Crystal Structure Analysis of 3b–d: A crystal of **3b** was measured with an Enraf Nonius CAD-4 diffractometer at 20 °C (Mo-K_α radiation, $\omega/2\theta$ scan technique, $2\theta < 52.6°$). The structure was solved by direct methods with the use of SIR[18] and refined by full-matrix least-squares by using SHELXL97.[20] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined by using a riding model. All calculations were performed with the use of WinGX.[21] Cell parameters, data collection, and data reduction were performed by using MolEN.[19]

Crystals of **3c** and of **3d** were measured with a Bruker APEX-2 diffractometer at low temperature (Mo-K_α radiation, ω-scans, $2\theta < 61°$). The structures were solved by direct methods and refined as above. H atom positions were refined by using a riding model or rigid methyl groups.[20]

Selected bond lengths, angles, and torsion angles of **3b**–**d** are presented in Table 1, and the crystal data is summarized in Table 3. CCDC-709792 (for **3b**), -709793 (for **3c**), and -709794 (for **3d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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