A Novel Access to Phenylnickel-phosphinophenolate Trimethylphosphine Complexes as Single Component Oligo- or Polymerization Catalysts

Joachim Heinicke*,^a, Normen Peulecke^a, Markus K. Kindermann^a, and Peter G. Jones^b

^a Greifswald, Institut für Chemie und Biochemie, Ernst-Moritz-Arndt-Universität

^b Braunschweig, Institut für Anorganische und Analytische Chemie der Technischen Universität

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Abstract. A novel access to phenylnickel-2-phosphinophenolate trimethylphosphine complexes, which unlike the "P-ylide method" is not limited to P-arylphosphino derivatives, consists of the reaction of 2-phosphinophenols and diphenylnickel-bis(trimethylphosphine), easily prepared from phenyllithium and NiCl₂(PMe₃)₂. [PhNi(2-Ph₂PC₆H₄O)(PMe₃)], [PhNi(2-*c*Hex₂PC₆H₄O)(PMe₃)] and [PhNi(2-Ph₂P-4-MeOC₆H₃O)(PMe₃)], the latter two with more basic dialkylphosphino or 4-methoxy substituents, were synthesized and tested in the oligomerization of ethylene. The molecular structure of $[PhNi(2-cHex_2PC_6H_4O)(PMe_3)]$ in the crystal is reported.

Keywords: Nickel complex; O,P chelate; Crystal structure; Homogeneous catalysis; Oligomerization

Ein neuer Zugang zu Phenylnickel (2-phosphinophenolat)(trimethylphosphin)-Komplexen als Einkomponentenkatalysatoren für Oligomerisierungs- oder Polymerisierungs-Reaktionen

Inhaltsübersicht. Ein neuer Zugang zu Phenylnickel(2-phosphinophenolat)(trimethylphosphin)-Komplexen, im Gegensatz zur "P-Ylid Methode" nicht auf P-Arylphosphinoderivative beschränkt, besteht in der Reaktion von 2-Phosphinophenolen und Diphenylnickel-bis(trimethylphosphin), das in einfacher Weise aus Phenyllithium und NiCl₂(PMe₃)₂ erhalten wird. Die Verbindungen

Introduction

Organonickel $P^{\cap}O^{-}$ monochelate complexes are highly active oligo- or polymerization catalysts and have found large scale industrial application in the Shell Higher Olefin Process [1]. They have also been the subject of considerable academic interest [2, 3], which was recently revitalized by the discovery of novel nickel chelate polymerization catalysts [4–7] and their tolerance of water and functional groups [8–10]. The standard synthesis of single component phenylnickel 2-diphenylphosphino-enolate phosphine catalysts is the reaction of acylidenetriphenylphosphoranes with one equivalent of nickelbis(1,5-cyclooctadiene) (Ni(COD)₂) and tertiary phosphines [11–15]. Phenylnickel 2-diphenylphosphinophenolate phosphine complexes have similarly

Inst. f. Chemie u. Biochemie der Universität Soldmannstr. 16 D-17487 Greifswald Tel.: +49 (0)3834/86-4318 fax: +49 (0)3834/86-4319 E-mail address: heinicke@uni-greifswald.de been obtained from o-benzochinone-2-ylidene-triphenylphosphorane, Ni(COD)₂ and PR₃ (Scheme 1) [12, 15]. The ylide route was also applicable to the synthesis of phenylnickel 2-alkylphenylphosphinoenolates from acylidenealkyldiphenylphosphoranes by migration of the phenyl group [16], but 2-dialkylphosphino derivatives have not been reported so far. Investigations on in situ generated organonickel 2-phosphinophenolate polymerization and oligomerization catalysts revealed that nickel 2-dialkylphosphinophenolates give rise to products with higher molecular weights than do related nickel diphenyphosphinophenolates [10, 17, 18]; we have therefore studied an alternative access to phenylnickel 2-phosphinophenolate complexes that does not depend on the migration of a P-substituent. We report here on a novel, convenient and generally applicable synthesis of the single component catalysts, represented by three derivatives with different basicity at phosphorus or oxygen. Some screening tests in the oligo/polymerization of ethylene allowing a comparison with the activity and selectivity of related *in situ* generated catalysts and an estimation of the influence of the basicity of the donor atoms are also described.

^{*} Prof. Dr. J. Heinicke



Scheme 1





Results and Discussion

Synthesis

For the conversion of 2-phosphinophenols 1 to phenylnickel 2-phosphinophenolate trimethylphosphine complexes 2, the direct replacement of a phenyl group of diphenylnickel complexes by the acidic hydroxyl group of phosphinophenols was found to be a superior method. Because of the general stabilization of organometallic compounds of transition metals by trimethylphosphine [19], Ph₂Ni(PMe₃)₂ was chosen as reagent. This compound, to the best of our knowledge not yet reported in the literature, is available easily and in good yield from two equivalents of phenyllithium and NiCl₂(PMe₃)₂. Heating with equimolar amounts of 2-phosphinophenols 1a-c in toluene / THF provides the complexes 2a-c in high yields and without byproducts (Scheme 2), showing the applicability of the method for diarylphosphino- and dialkylphosphinophenols as well as methoxy-substituted derivatives. Small amounts of unconverted starting compounds were removed by recrystallization or by extraction with hexane.

Structure elucidation

Structural evidence of the phenylnickel 2-phosphinophenolate trimethylphosphine complexes 2a-c was provided by multinuclear NMR studies, in particular by the characteristic ¹³C and ³¹P NMR data. The ¹³C chemical shifts are in accordance with the substitution pattern. The strong downfield shifts of the ¹³C-1 nuclei as compared to those of the corresponding phosphinophenols **1a-c** ($\Delta \delta = 17.2$ -19.9) are attributable to deprotonation and coordination, and confirm the formation of chelates. Small but indicative downfield coordination shifts (deshielding) are observed for the C-6 nuclei ($\Delta \delta = 2.9-4.3$) while C-2 and C-4 are shifted upfield (C-2: 2a,b $\Delta \delta \approx -2.7$, 2c $\Delta \delta = -11.8$; C-4: 2a,b $\Delta \delta \approx -6.6$, **2c** $\Delta \delta = -3.9$). The stronger shielding of C-2 at the expense of C-4 in 2c demonstrates the +M-effect of the 4-methoxy group and the increased basicity of the phenolate oxygen atom in this complex. The magnitude of the coupling constants with the ³¹P nuclei, large for C2 (${}^{1}J_{PC} =$

46-47 Hz for **2a,b**, 38.7 Hz for **2c**) and C1 (${}^{2}J_{PC} = 26-28$ Hz for **2a,b**, 22.2 Hz for **2c**) and moderate for C6 (${}^{3}J_{PC} = 8.0$ -10.2 Hz) and C4 (${}^{3}J_{PC} = 5.1-6.6$ Hz), indicates the P^OO⁻chelate coordination mode of nickel(II). ${}^{2}J_{PC-1}$ and ${}^{3}J_{PC-6}$ are markedly lower for n¹-P-coordination of phosphinophenols [20]. The phenvl ligand in **2a-c** is indicated by its downfield shifted C-i and upfield shifted C-p signals, the trimethylphosphine ligand by its characteristic doublet with ${}^{1}J_{PC} = 24.5-25.8$ Hz. The *trans*-position of the two phosphorus atoms follows from the large P-P coupling constants, at $-60 \degree C 303$ and 304.6 Hz for 2a and 2c and somewhat smaller (293.3 Hz) for **2b** with the more basic P^{O}^{-} ligand. 2a and 2c display two broad singlets at 25 °C and need low-temperature measurements to produce sharp ³¹P doublets. Similarly the ¹³C doublets of C-1 of the P^O-ligand and C-i of NiPh couple only at low temperature with the phosphorus nucleus of PMe₃. In contrast, 2b shows sharp ³¹P doublets and coupling of carbon nuclei C-2, C-i and C-a even at 25 °C. This indicates increased fluxionality of the trimethylphosphine ligand in the diphenylphosphinoas compared to dicvclohexvlphosphino-phenolate phenylnickel complexes and is surprising, as the opposite behavior was observed by us in related methylnickel trimethylphosphine complexes. Methylnickel trimethylphosphine diisopropylphosphinophenolates (sec-alkyl groups at phosphorus as in $cHex_2PC_6H_4O^-$) are more fluxional than methylnickel trimethylphosphine diphenylphosphinophenolates and need lower temperature (-60 versus -30 °C) to afford sharp doublets in the ³¹P NMR spectra (each in tolu $ene-d_8$) [18]. The reason for this unusual behavior is not yet clear; it may be associated with the different hybridization of the carbon atom bonded to nickel and with cis-effects. No signals from free PMe₃ were observed. Signal averaging is assumed, e.g. from 2, free PMe₃ and a pentacoordinate complex formed by trapping of PMe₃ by another molecule of 2. Thus, the pentacoordinate methylnickel-phosphinophenolate bis(trimethylphosphine) complex 3, characterized by crystal structure analysis, was accessible from the respective square-planar mono-PMe₃ complex and PMe₃ [18]. 3 is highly fluxional and displays the ³¹PMe₃ signal upfield from the corresponding square-planar PMe₃ complex ($\Delta\delta$ ca. 20). The phosphinophenolate nickel chelate unit in 2 (and 3) is quite rigid and not fluxional. The hemilabile character observed in complexes with phosphinophenolether ligands [21] or in cationic phosphinophenol complexes [22] is strongly reduced by the negative charge of the ligand and is limited to slow processes such as the E/Zisomerization of moderately bulky P-substituted nickel bis(2-phosphinophenolates) [20].

Closer structural information on complexes of type 2 is provided by the crystal structure analysis of 2b (Figure 1, Tables 1 and 2). To the best of our knowledge it is the first structure report of a four-coordinate σ -organonickel phosphinophenolate complex. Selected bond lengths and angles are compiled in Table 1, for comparison together with the corresponding data of 3 and the vinylogous phenylnickel phosphinoenolate phosphine complexes 4 [23] and 5 [11].



Table 1 Selected bond lengths/Å and angles/° of 2b and comparison with the corresponding data of 3-5.

	2b	3 [18]	4 [23]	5 [11]
Ni-C(1)	1.8929(4)	1.981(5)	1.867(6)	1.893
Ni-P(2)	2.1917(4)	2.224(2), 2.245(2)	2.184(2)	2.230
Ni-P(1)	2.1775(4)	2.191(2)	2.189(2)	2.168
Ni-O	1.9108(10)	1.984(3)	1.914(4)	1.914
P(1)-C(11)	1.8003(14)	1.797(5)	1.797(6)	1.769
P(1)-C(21)	1.8393(14)	1.818(5)	1.822(6)	1.813
P(1)-C(31)	1.8495(14)	1.831(5)	1.826(6)	1.829
C(11)-C(12)	1.4182(18)	1.411(6)	1.392(7)	1.385
O-C(12)	1.3241(17)	1.332(5)	1.308(7)	1.313
C(1)-Ni-P(1)	92.77(4)	92.6(2)	93.0(2)	90.6
C(1)-Ni-P(2)	88.56(4)	91.7(2), 88.9(2)	89.6(2)	91.7
O-Ni-P(2)	92.37(3)	93.43(11), 87.24(11)	93.6(1)	91.5
O-Ni-P(1)	87.12(3)	86.35(10)	85.2(1)	86.5
Ni-P(1)-C(11)	99.49(5)	99.2(2)	101.5(2)	99.3
P-C(11)-C(12)	111.58(10)	114.3(4)	108.7(5)	113.8
Ni-O-C(12)	119.75(8)	118.9(3)	119.9(4)	118.9
C(1)-Ni-O	176.32(5)	177.7(2)	173.1(2)	
P(1)-Ni-P(2)	166.990(16)	114.02(6), 120.71(7)	167.1(1)	

products depend on the substituents of the catalysts and increase in the order 2c < 2a < 2b (Table 3). Catalysis with 2a leads to roughly equal amounts of liquid and waxy oligomers along with a smaller fraction of volatiles (mainly 1butene, small amount of hexene). 2c, which differs from 2a in the 4-methoxy group (+M-effect) and a more basic phenolate oxygen (cf. $\Delta \delta_{C-1}$), gives rise to formation of significantly lower oligomers, mainly butenes and lower liquid oligomers. This is attributed to the increased basicity of the chelate-oxygen atom. Increased basicity at phosphorus, in **2b** accomplished by cyclohexyl instead of phenyl groups, causes the opposite effect, markedly longer chains and almost exclusive formation of low molecular weight polyethylene. As compared to the polyethylenes obtained with related methallylnickel phosphinophenolates or allyl-type catalysts formed in situ from 1a-c and Ni(COD)₂ [10], however, the molecular weights of the products from exp. 1-3 are very low, because of the effect of trimethylphosphine. Conversions of ethylene with catalysts of 2a or 2b and equimolar amounts of Ni(COD)₂, which trap a major part of the trimethylphosphine (see below), lead to significantly increased molecular weights but the values of polyethylenes formed with 1/Ni(COD)₂ are not even approached. Only the M_w value of the small high molecular weight fraction of the bimodal polyethylene obtained in exp. 5 resembles that of polyethylene formed in presence of $1/Ni(COD)_2$. Possibly the transfer of PMe₃ to the catalyst site is less easy than that of ethylene after a critical chain length is reached. Altogether, the oligomerization of ethylene by 2a-c can be explained by a competition of ethylene and PMe₃ for coordination at nickel and insertion of coordinated ethylene into the Ni-C bond (chain propagation) (Scheme 3).

For the chain termination, β -hydride eliminations are assumed, which yield α -olefins and Ni-H species, starting new chain growth cycles. This is suggested by the detection of trace amounts of styrene in the above ethylene oligomerization experiments and with [PhNi(Ph₂PC₆H₄O)(PPhMe₂)]

Figure 1 Molecular structure of 2b (ellipsoids with 50 % probability).

The Ni-phenyl ring is arranged perpendicular (interplanar angle 85.2°) to the chelate ring. The Ni-C σ -bond in **2b** is significantly shorter than in **3** but nearly identically with that in **4** and **5** and is typical for Ni-C bonds with an sp²-hybridized carbon atom, whereas Ni-C(sp³) bonds are usually found in the range 1.92-1.97 Å [24]. The Ni-P(2) bond is similar to that in **4** but shorter than in the triphenylphosphine complex **5**. The bonds C(11)-C(12) are longer in **2b** and **3** as compared to **4** and **5** but the other bond lengths and angles of the rigid planar five-membered chelate rings are similar and give evidence for close structural relations of phosphinophenolate and phosphinoenolate complexes.

Oligomerization of ethylene

The phenylnickel phosphinophenolate trimethylphosphine complexes **2a-c**, dissolved in toluene and heated with ethylene (110 °C) under pressure (batch procedure, p_{start} ca. 50 bar) catalyze the oligomerization of ethylene with high selectivity for linear α -olefins (Vin/ Σ (C=C) > 90-98 %). The content of branched products, based on the Me/olefin ratio, is low (Table 3). The oligomerization of ethylene with **2a**, however under constant ethylene pressure, has already been reported [15]. With respect to selectivity and molecular weights the results of both methods, batch and flow procedure, are similar and show that the results can be compared in this respect. The average molecular weights of the



Figure 2 Pressure time plots for batch polymerization of ethylene with a) 2a (129 µmol, exp.1; solid), b) 2b (90 µmol, exp.2; dash) or c) 2c (100 µmol, exp.3; dot) in toluene (20 mL), d) with 1a/Ni-(COD)₂/PMe₃ (each 100 µmol [17]; dash-dot) in toluene (20 mL) at 100 °C.

[15] and the generation of ethylene polymerization catalysts from **1a**, nickel bromide and sodium hydride [10], respectively, but other possibilities should not be excluded.

The coordination of PMe₃ in competition with ethylene has a strong influence on the reaction rates, as illustrated by the pressure-time plots (Figures 2 and 3). The conversion of ethylene by 2a is slow, by 2b and 2c with more basic phosphorus or oxygen even slower (Figure 2a-c, Table 3), but the oligomerization by the catalyst formed in situ from 1a / Ni(COD)₂ and PMe₃ [17] is much slower (Figure 2d). The latter might be caused by incomplete reaction of 1a and Ni(COD)₂ and thus excess PMe₃. The replacement of PMe₃ by ethylene occurs only to a small extent or is slow despite its flexibility, shown in the NMR-spectra of 2a and 2c at normal pressure. Thus, bubbling ethylene (10 min) through a solution of **2b** in D₈-toluene at 60 °C, 20 °C above the boiling point of PMe₃ (38-40 °C), did not lead to a detectable replacement of PMe₃. Only a small amount of uncoordinated ethylene ($\delta^{13}C = 123.1$) was observed in the subsequent NMR-measurement. After addition of Ni(COD)₂ (25 µmol) to the solution of **2b** (66 µmol) and subsequent reaction with ethylene in D₈-toluene under similar conditions, both coordinated ($\delta^{13}C = 49.7$ (br)) and uncoordinated ethylene were observed. The trapping of the major part of PMe₃ by Ni(COD)₂ leads not only to the above-mentioned increase of the molecular weights but also to a strong acceleration of the ethylene consumption rate ((Figure 2).

Experimental Section

General

All reactions were carried out under carefully dried, oxygen-free argon, using Schlenk techniques and freshly distilled ketyl-dried solvents. The phosphinophenols **1a** [25], **1b** and **1c** [10] and Ni(COD)₂ [26] were synthesized as reported, other chemicals were



Figure 3 Pressure time plots for batch polymerization of ethylene with a) **2a** and Ni(COD)₂ (exp. 4; solid), b) **2b** and Ni(COD)₂ (exp. 5; dash), c) **1a**/Ni(COD)₂ (dot [10]) each in toluene (20 mL).

purchased. Ethylene (99.5%, Air Liquide) was used without further treatment. NMR spectra were recorded on a multinuclear FT-NMR spectrometer ARX300 (Bruker) at 299.6/300.1 (1H), 75.3/75.5 (13C), and 121.3/121.5 (31P) MHz. Shift references are tetramethylsilane for ¹H and ¹³C and H₃PO₄ (85 %) for ³¹P. Assignment numbers are given partly in Scheme 2; to denote proton or carbon nuclei of P-phenyl or P-cyclohexyl groups *i*, *o*, *m*, *p* or α , β , γ , δ , for Ni-Ph *i'*, *o'*, *m'*, *p'* are used, respectively. Pseudotriplets (X of AA'X; A,A' = P) of ¹H or ¹³C nuclei formed by coupling with two ${}^{31}P$ nuclei are referred to as τ . Coupling constants refer to $J_{\rm HH}$ in ¹H and $J_{\rm PC}$ in ¹³C NMR data unless stated otherwise. Assignments are supported by DEPT and in part by CH-COSY experiments. Melting points were determined with a Sanyo Gallenkamp melting point apparatus, elemental analysis with a CHNS-932 analyzer from LECO using standard conditions. ¹H NMR spectra of polymers were measured on a multinuclear FT-NMR spectrometer ARX300 (Bruker) (300.1 MHz) at 100 °C, acquisition time 4.9-5.4 s, delay 1.0 s, using concentrated solutions of the polyethylene samples prepared by swelling for 1 d at 120 °C under argon in C₆D₅Br (*p*-CH, $\delta = 7.23$ as reference). Molecular weight determination by GPC was performed as reported in ref. [10]. GC analyses were carried out using a gas chromatograph Hewlett Packard 5890, column HP-5(30m) (crosslinked 5 %PhMe silicone), 40-150 °C, 10 min isotherm, 4 °C/min.

Nickel complexes

Diphenylnickel-bis(trimethylphosphine).

Phenyllithium (0.87 mL 2M in diethylether, 1.74 mmol) was added at -60 °C to a stirred solution of [NiCl₂(PMe₃)₂] (0.245 g, 0.87 mmol) in Et₂O/THF (15 mL). The mixture was allowed to warm to room temperature (color change to pale yellow), and the solvent was removed. Repeated extraction by warm hexane afforded 191 mg (61 %) of spectroscopically pure pale yellow crystals, mp. 138-139 °C. (The compound was used immediately after synthesis; it decomposes slowly at room temperature with color change to black.)

¹H NMR (C₆D₆, 25 °C): δ = 0.62 (s br, 18 H, PMe₃), 7.02 (m, 2 H, H-*p*), 7.19 (m, 4 H, H-*m*), 7.60 (d, ³*J* = 6.8 Hz, 4 H, H-*o*). ¹³C NMR (D₈-THF,



Scheme 3

Table 2 Crystal data and structure refinement of 2b.

Empirical formula Formula weight Temperature Wavelength Crystal system Space group Unit cell dimensions	$\begin{array}{l} C_{27}H_{40}\text{NiOP}_2\\ 501.24\\ 133(2) \text{ K}\\ 0.71073 \text{ Å}\\ \text{Monoclinic}\\ P2_1/c\\ a = 9.3475(6) \text{ Å}\\ b = 9.8384(6) \text{ Å}\\ c = 28 593(2) \text{ Å} \end{array}$	$\alpha = 90^{\circ}$ $\beta = 97.065(4)^{\circ}$ $\gamma = 90^{\circ}$	
Volume	$2609.6(3) Å^3$	1 , , ,	
Z	4		
Density (calculated)	1.276 Mg/m ³		
Absorption coefficient	0.883 mm^{-1}		
F(000)	1072		
Crystal size	0.4 x 0.3 x 0.1 mm ³		
Theta range for data collection	1.44 to 30.51°		
Index ranges	-13<=h<=13,		
	$-14 \le k \le 14$,		
	-40 <=1 <=40		
Reflections collected	50734		
Independent reflections	/964 [R(int) = 0.0391]		
Completeness to theta = 30.00°	99.9 %		
Absorption correction	Semi-empirical from eq	uivalents	
Refinement method	Evil matrix loost square	$r = E^2$	
Data / restraints / parameters	7964 / 0 / 283	S 011 1	
$Goodness-of-fit on F^2$	1 067		
Final R indices [I>2sigma(I)]	$R_1 = 0.0314 \text{ wR}_2 = 0$	0713	
R indices (all data)	R1 = 0.0463, WR2 = 0	.0778	
Largest diff. peak and hole	0.486 and -0.242 e Å-	3	

-60 °C: δ = 13.2 (τ, $|^{1}J^{+3}J|$ = 28.5 Hz, PMe₃), 121.1 (C-*p*), 126.3 (C-*m*), 137.8 (C-*o*), 151.4 (τ, $|^{2}J_{E}^{+2}J'_{Z}|$ = 63.4 Hz, C-*i*). ³¹P{¹H} NMR (C₆D₆): δ = -10.5.

Phenylnickel-2-(diphenylphosphino)phenolate(O,P) (trimethylphosphine) (2a).

A solution of **1a** (450 mg, 1.62 mmol) in THF (5 mL) was added to a stirred solution of Ph₂Ni(PMe₃)₂ (800 mg, 2.19 mmol) in 15 mL of a THF/toluene mixture. The orange solution was heated to 50 °C and stirred for 4h. After cooling to 20 °C, the solvent was removed in vacuum, and the residue was washed with *n*-hexane. The solution of the residue in a small amount of toluene was overlayered with *n*-hexane to give yellow-ochre crystals of **2a** (635 mg, 81 %), mp. 189-192 °C. $C_{27}H_{28}OP_2Ni$ (489.16); found C 66.18 (calc. 66.30); H, 6.01 (5.77) %.

¹H NMR (D₈-toluene, -60 °C): $\delta = 0.74$ (d, ${}^{2}J_{PH} = 9.3$ Hz, 9 H, PMe₃), 6.53 (dd, ${}^{3}J = 7.6$, $J_{PH} = 3.9$ Hz, 1 H, 3-H or 6-H), 6.79-7.47 (ArH). ¹H NMR (D₈-THF, 25 °C): $\delta = 1.10$ (d, ${}^{2}J_{PH} = 9.3$ Hz, 9 H, PMe₃), 6.28 ("t", ${}^{3}J = 7.2$ -7.3 Hz, 1 H, ArH), 6.50-6.64 (m, 4 H, ArH), 6.93-7.02 (m, 4 H, ArH), 7.23-7.37 (m, 10 H, ArH). ¹³C NMR (D₈-THF, 25 °C): $\delta = 11.5$ (d, ${}^{1}J = 25.7$ Hz; PMe₃), 114.3 (d, ${}^{3}J = 5.3$ Hz; C-4), 118.3 (d, ${}^{1}J = 46.8$ Hz; C-2), 119.8 (d, ${}^{3}J = 8.3$ Hz; C-6), 121.6 (C-*p*'), 126.2 (2 C-*m*'), 128.8 (d, ${}^{3}J = 9.8$ Hz; 4 C-*m*), 130.4 (2 C-*p*), 132.2 (d, ${}^{1}J = 45.3$ Hz; 2 C-*i*), 133.1, 133.2 (C-3, C-5), 133.8 (d, ${}^{2}J = 10.6$ Hz; 4 C-*o*), 138.0 (d, ${}^{3}J = 3.0$ Hz; 2 C-*o*'), 150.3 (d, ${}^{2}J = 29.4$ Hz; C-*i*'), 179.0 (d, ${}^{2}J = 26.4$ Hz; C-1). ³¹P{¹H} NMR (toluene-d₈, -60 °C): $\delta = 23.6$ (d), -13.4 (d), $J_{PP} = 303.0$ Hz; at 25 °C: $\delta = 22.7$ (br), -12.9 (br).

Phenylnickel-2-(dicyclohexylphosphino)phenolate(O,P) (trimethylphosphine) (2b).

A solution of **1b** (200 mg, 0.685 mmol) and Ph₂Ni(PMe₃)₂ (250mg, 0.685 mmol) in THF/toluene (20mL), prepared as described for **2a**, was heated for 3 d to 60 °C (slight color change to yellow). The solvent was removed in vacuum, and the residue was washed with hexane affording 320 mg (92 %) of **2b** as pale yellow powder, mp. 189-191 °C, contaminated by a trace of Ph₂Ni(PMe₃)₂. Pure single crystals were grown from *n*-hexane.

 $C_{27}H_{40}OP_2Ni$ (501.25), found: C 64.25 (calc. 64.70); H 7.90 (8.04) %.

¹H NMR (C₆D₆, 25 °C): δ = 0.83 (d, ²J_{PH} = 9.0 Hz, 9 H, PMe3), 0.91-2.29 (multiplets, 22 H, Cy), 6.59 ("t", ³J = 7.0, 7.3 Hz, 1 H, ArH), 6.87 ("t", J ≈ ³7.0 Hz, 1 H, ArH), 7.05 ("t", ³J = 7.4-7.5 Hz, 2 H, ArH), 7.08-7.22 (m, 2 H, ArH), 7.26 ("t", ³J = 7.8 Hz, 1 H, ArH), 7.56 (d, ³J = 7.4 Hz, 2 H, ArH), 7.26 ("t", ³J = 7.8 Hz, 1 H, ArH), 7.56 (d, ³J = 7.4 Hz, 2 H, ArH), 1³C NMR (C₆D₆, 25 °C): δ = 11.9 (d, ¹J = 24.5 Hz; PMe₃), 27.0 (C-δ), 27.8 (d, ³J = 10.4 Hz; C-β or γ), 28.14 (d, ³J = 13.3 Hz; C-β or γ), 28.06 (C-γ or β), 28.5 (d, ²J = 3.3 Hz; C-γ or β), 32.7 (d, ¹J = 24.2 Hz; C-α), 114.3 (d, ³J = 5.1 Hz; C-4), 116.2 (d, ¹J = 38.7 Hz; C-2), 120.0 (d, ³J = 8.0 Hz; C-6), 122.3 (C-γ'), 127.1 (2 C-m'), 132.0, 133.6 (C-3, C-5), 138.6 (br, 2 C-o'), 151.7 ("t", ²J ≈ 32, 33.5 Hz; C-i'), 180.2 (d, ²J = 22.2, ³J = 9.5 Hz; C-1). ³P{H} NMR (C₆D₆): 25 °C δ = 29.8 (d), -15.6 (d), ²J_{PP} = 295.7 Hz; -60 °C δ = 29.9 (d), -14.9 (d), ²J_{PP} = 293.3 Hz.

Phenylnickel-2-diphenylphosphino-4methoxyphenolate(O,P) (trimethylphosphine) (2c).

A solution of **1c** (244 mg, 0.79 mmol) and $Ph_2Ni(PMe_3)_2$ (288 mg, 0.789 mmol) in THF / toluene (20 mL), prepared as described for **2a**, was heated for 4 h at 50 °C. Then the solvent was removed in

Exp.	Catalyst (µmol)	Conversion of C ₂ H ₄ [g] (%)	$\begin{array}{c} \text{TON} \\ [\text{mol} \cdot \text{mol}^{-1}] \\ \text{TOF}_{\text{max}} \\ [\text{mol} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}] \end{array}$	Products ^{b)}	C ₆ , C ₈ , C ₁₀ , C ₁₂ (% of liquid oligomers) ^{b)}	Solid polymer data: mp. [°C], D [g cm ⁻³] mol. weights ^{c)} [g·mol ⁻¹] α-olefins (%), Me/Vin
1	2a (129)	9.2(72)	2540 1000	 1.6 g volatiles 4.0 g oligomers 3.6 g wax 	42, 38, 16, 2	83-85 M _{NMR} 420 >98, 1.6
2	2b (90)	9.7 (78)	3840 800	0.7 g oligomers 9.0 g polyethylene	28, 32, 21, 4	113-115, 0.934 M _{NMR} 800 >98, 1.5
3	2c (100)	8.6 (66)	3070 600	3.1 g volatiles (C₄)5.1 g oligomers0.4 g soft wax	69, 23, 3, <1	-
4	2a (120), Ni(COD) ₂ (120)	7.8(59)	2320 14000	0.5 g volatiles (C₄)1.3 g oligomers6.0 g polyethylene	64, 24, 9, 2	120-122, 0.943 M _{NMR} 1650 94, 1.3
5	2b (110), Ni(COD) ₂ (100)	10.3 (83)	3340 13000	< 0.1 g oligomers 10.3 g polyethylene	0	128-130, 0.952 M _w 8.900, M _n 4.600 ^d) M _w ' 90.000, M _n ' 82.000 >98, 1.3

Table 3 Oligomerization of ethylene with catalysts formed from 2a-c.^{a)}

^{a)} Catalysis in toluene (20 mL), $p(C_2H_4)_{start}$ ca. 50 bar, bath temperature 100 °C. ^{b)} Dissolved butenes in the flash distillate (>90 % 1-butene) added to volatiles (mainly C_4); percentages refer to 1-olefines; deviations from the Schultz-Flory distribution may be due to loss of hexene (to volatile fraction) and the solubility of C_{10} and C_{12} in the polymer. ^{c)} M_{NMR} based on ¹H NMR integration. ^{d)} Bimodal molecular weight distribution determined by GPC, M_w and M_n after band separation.

vacuum, and the yellow-orange residue was washed with *n*-hexane to yield 0.36 g (88 %) of **2c**, mp. 157-160 °C, slightly contaminated with $Ph_2Ni(PMe_3)_2$.

 $C_{28}H_{30}O_2P_2Ni$ (519.18); found: C 64.40 (calc. 64.78); H 5.75 (calc. 5.82) %.

¹H NMR (D₈-THF, -60 °C): δ = 1.05 (d, ²J_{PH} = 9.6 Hz, 9 H, PMe₃), 3.43 (s, 3 H, OMe), 6.40 (d, ³J = 9.0 Hz, 1 H, H-6), 6.42 (dd, ³J_{PH} = 8.8, ⁴J ≈ 3 Hz, 1 H, H-3), 6.48-6.00 (m, 4 H, ArH), 6.64 (dd, ³J = 9.0, ⁴J ≈ 3 Hz, 1 H, H-5), 6.83 (t, ³J = 7.3 Hz, 1 H, PhH), 6.96 (d, ³J = 7.1 Hz, 2 H, PhH), 7.25-7.40 (m, 8 H, PhH). ¹³C NMR (D₈-THF, -60 °C): δ = 11.1 (d, ¹J = 25.8 Hz; PMe₃), 55.1 (OMe), 113.8 (C-5 or C-3), 116.5 (d, ¹J = 45.7 Hz; C-2), 119.8 (d, ³J = 10.2 Hz; C-6), 121.35 (C-3 or C-5), 121.44 (C-p'), 126.1 (2 C-m'), 129.0 (d, ³J = 9.8 Hz; 4 C-m), 130.7 (2 C-p), 131.9 (d, ¹J = 45.9 Hz; 2 C-6), 131.9 (d, ²J = 10.9 Hz; 4 C-0), 138.1 (2 C-0'), 149.6 (d, ²J = 6.6 Hz; C-4), 151.4 (d, ²J = 34.4 Hz; C-i'), 172.7 (d, ²J = 28.1 Hz; C-1). ³¹P{¹H} NMR (D₈-THF): 25 °C: δ = 23.5 (br), -12.9 (br); -60 °C δ = 24.2 (d), -12.0 (d), J_{PP} = 304.6 Hz.

Crystal Structure Analysis.

Data collection: A crystal of **2b** was mounted on a glass fiber in inert oil and transferred to the cold gas stream of the diffractometer (Bruker SMART 1000 CCD). Data were collected with monochromated Mo- K_a radiation and corrected for absorption (program SA-DABS).

Structure refinement: The structure was refined anisotropically on F^2 using the program SHELXL-97 [27]. Hydrogen atoms were refined using a riding model or rigid methyl groups.

For selected bond lengths and angles of **2b** see Table 1. The crystallographic data are listed in Table 2. Complete crystallographic data for **2b** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-252210. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, Uk [Fax: (int. code) +44-(1223)/336-033, e-mail: deposit@ccdc.cam.ac.uk].

Ethylene oligomerization | polymerization

2a, 2b or 2c (quantities see Table 3) were dissolved in toluene. In experiments 4 and 5, additionally a solution of Ni(COD)₂ (quantities see Table 3) in toluene was added at 0 °C. In each experiment the total volume of the solvent(s) was 20 mL. The precatalyst solution was transferred to an argon-filled stainless steel autoclave (75 mL), equipped with Teflon-coated magnetic stirrer, gas and sample inlet valves, a safety diaphragm and an HEJU pressure sensor (1-100 bar, Juchheim) for automatic pressure registration. The autoclave was pressurized (ethylene ca. 50 bar), placed into a preheated bath (100 °C) and heated overnight (ca. 15 h). After cooling to 0-5 °C, unconverted ethylene was allowed to escape and butenes were condensed in a cooling trap (-78 °C). The remaining product was transferred to a flask, and volatiles were flash distilled (80-100 °C / 1 Torr) into a cooling trap (-196 °C). Residual waxes or polymers were stirred for 1 d with methanol / hydrochloric acid (1:1), washed with methanol and dried. Conversion, oligomer composition and characteristic data of polymers are given in Table 3. The maximum turnover frequency (TOF_{max}) was determined from the slope of the range with the steepest roughly linear pressure decrease.

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References

- W. Keim, in *Industrial Applications of Homogenous Catalysis* (Eds.: A. Mortreux, F. Petit), Dordrecht, **1988**, p. 335–347.
- [2] W. Keim, Angew. Chem. 1990, 102, 251–260; Angew. Chem. Int. Ed. Engl. 1990, 29, 235–244; W. Keim, New J. Chem. 1994, 18, 93–96.

- [3] K. A. Ostoja-Starzewski, J. Witte, K. H. Reichert, G. Vasiliou, in *Transition Metals and Organometallics as Catalysts for Olefin Polymerization [Proceedings of the International Symposium]*, (Eds.; W. Kaminsky, H. Sinn), Springer, Berlin, 1988, 349–360; K. A. Ostoja-Starzewski, J. Witte, in *Transition Metal Catalyzed Polymerizations [Proc. Int. Symp.]*, 2nd ed., (Ed.: R. P. Quirk), Cambridge University Press, Cambridge (UK), 1988, 472–496.
- [4] G. J. P. Britovsek, V. C. Gibson, D. F. Wass, Angew. Chem. 1999, 111, 448–468; Angew. Chem. Int. Ed. 1999, 38, 428–447.
- [5] S. D. Ittel, L. K. Johnson, M. Brookhardt, Chem. Rev. 2000, 100, 1169–1204.
- [6] T. R. Younkin, E. F. Connor, J. I. Henderson, S. K. Friedrich, R. H. Grubbs, D. A. Bansleben, *Science* **2000**, 287, 460–462.
- [7] Late Transition Metal Polymerization Catalysis, (Eds.: B. Rieger, L. Saunders, S. Kacker, S. Striegler), Wiley-VCH, Weinheim, 2003.
- [8] S. Mecking, Angew. Chem. 2001, 113, 550–557; Angew. Chem. Int. Ed. 2001, 40, 534–540; A. Held, F. M. Bauers, S. Mecking, Chem. Commun. 2000, 301–302; M. O. Kristen, L. Manders, S. Mecking, F. M. Bauers, (BASF A.G.), DE 199 61 340 (17. 12. 1999).
- [9] R. Soula, C. Novat, A. Tomov, R. Spitz, J. Claverie, X. Drujon, J. Malinge, T. Saudemont, *Macromolecules* 2001, 34, 2022–2026; A. Tomov, R. Spitz, T. Saudemont, X. Drujon, (Elf Atochem S.A.) FR 98 12 476 (06. 10. 1998).
- J. Heinicke, M. Köhler, N. Peulecke, M. He, M. K. Kindermann, W. Keim, G. Fink, *Chem. Eur. J.* 2003, *9*, 6093–6107;
 M. O. Kristen, J. Heinicke, W. Keim, M. Köhler, M. He, (BASF-A.G.), DE 199 47519 (01. 10. 1999).
- [11] W. Keim, F. H. Kowaldt, R. Goddard, C. Krüger, Angew. Chem. 1978, 90, 493; Angew. Chem. Int. Ed. Engl. 1978, 17, 466-467.
- [12] W. Keim, A. Behr, B. Gruber, B. Hoffmann, F. H. Kowaldt, U. Kürschner, B. Limbäcker, F. P. Sistig, *Organometallics* 1986, 5, 2356–2359.

- [13] U. Klabunde, R. Mühlhaupt, T. Herskovitz, A. H. Janowicz, J. Calabrese, S. D. Ittel, J. Polym. Sci. Part A: Polym. Chem. 1987, 25, 1989–2003.
- [14] P. Braunstein, Y. Chauvin, S. Mercier, L. Saussine, A. De Cian, J. Fischer, *Chem. Commun.* 1994, 2203–2204.
- [15] J. Pietsch, P. Braunstein, Y. Chauvin, New J. Chem. 1998, 467-472.
- [16] K. Hirose, W. Keim, J. Mol. Catal. 1992, 73, 271-276.
- [17] J. Heinicke, M. Köhler, N. Peulecke, W. Keim, J. Catal. 2004, 225, 16–23.
- [18] J. Heinicke, M. He, A. Dal, H.-F. Klein, O. Hetche, W. Keim, U. Flörke, H.-J. Haupt, *Eur. J. Inorg. Chem.* **2000**, 431–440.
- [19] H.-F. Klein, Angew. Chem. 1980, 92, 362–375; Angew. Chem. Int. Ed. Engl. 1980, 19, 362–375; H.-F. Klein, H. H. Karsch, Chem. Ber. 1972, 105, 2628–2636.
- [20] J. Heinicke, A. Dal, H.-F. Klein, O. Hetche, U. Flörke, H.-J. Haupt, Z. Naturforsch. 1999, 54b, 1235–1243; J. Heinicke, M. Köhler, N. Peulecke, W. Keim, P. G. Jones, Z. Anorg. Allg. Chem. 2004, 630, 1181–1190.
- [21] A. Bader, E. Lindner, Coord. Chem. Rev. 1991, 108, 27-110.
- [22] J. Heinicke, M. Köhler, N. Peulecke, M. K. Kindermann, W. Keim, M. Köckerling, *Organometallics*, submitted.
- [23] U. Klabunde, T. H. Tulip, D. C. Roe, S. D. Ittel, J. Organomet. Chem. 1987, 334, 141–156.
- [24] Nickel Hydride, Alkyl and Aryl Complexes, P. W. Jolly, in Comprehensive Organometallic Chemistry, Vol. 6 (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon Press, New York, 1982, pp. 37–100.
- [25] T. B. Rauchfuss, Inorg. Chem. 1977, 16, 2966-2967.
- [26] B. Bogdanovic, M. Kröger, G. Wilke, *Liebigs Ann. Chem.* 1966, 699, 1–23; W. A. Herrmann, C. Zybill, in *Synthetic Methods of Organometallic and Inorganic Chemistry, Vol. 1* (Eds.: W. A. Herrmann, A. Salzer), Thieme, Stuttgart, 1996, 157.
- [27] SHELXL-97, a program for refining crystal structures. G. M. Sheldrick, University of Göttingen, 1997.