2-Dialkyl- and 2-*tert*-Butylphenylphosphinophenol(ate) Nickel and Palladium Complexes: Control of E/Z-Configuration in Bis($P^{\frown}O^{-}$-chelates) and Activation of the Nickel Complexes for Polymerization of Ethylene

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Abstract. Nickel bis(2-dialkylphosphinophenolates), detected as the spent form of organonickel 2-dialkylphosphinophenolate catalysts for the polymerization of ethylene, were studied. In contrast to the impact of the P-basicity on the catalyst properties, the configuration of bis(2-dialkylphosphinophenolate) nickel is controlled only by steric effects. Small alkyl substituents favor, as do phenyl groups, square planar *cis*-bis($P^{\frown}O^{-}$-chelates) while more bulky alkyl groups lead to *trans*-isomers. Dicyclohexyl- and *tert*-butylphenylphosphino groups give rise to borderline cases. Analogous palladium complexes show a slightly smaller effect of the metal size on the *cis*/*trans*-control. Intermediates on the way to Pd^{II} bis($P^{\frown}O^{-}$-chelates), *trans*-dichloro-bis(phosphinophenol)- and chloro-phosphinophenol phosphinophenolate palladium(II) complexes could be isolated; the crystal structure of one of the latter was determined. The nickel bis(2-dialkylphosphinophenolates) can be activated as polymerization catalysts, to a limited extent by $NiBr_2$·DME and sodium hydride or triethylsilane in THF, more efficiently by *n*BuLi or *n*BuLi / $NiBr_2$·DME.

Keywords: O,P Ligands; Nickel; Chelate complexes; Coordination modes; Polymerization; Homogenous catalysis

2-Dialkyl- und 2-*tert*-Butylphenylphosphinophenol(ate) Nickel und Palladium Komplexe: Kontrolle der E/Z-Konfiguration in Bis($P^{\frown}O^{-}$-chelat)en und Aktivierung der Nickel Komplexe für die Polymerisation von Ethylen

Inhaltsübersicht. Nickel(II)-bis(2-dialkylphosphinophenolate), Desaktivierungsprodukte von Organonickel(II) bis(2-dialkylphosphinophenolat)-Polymerisationskatalysatoren, wurden untersucht. Im Gegensatz zum Einfluß der P-Basizität auf die Katalysatoreigenschaften ist für die Konfiguration der Nickel-bis(2-dialkylphosphinophenolate) nur der sterische Einfluß der P-Substituenten wesentlich. Kleine Alkylreste (Ethyl) begünstigen ähnlich Phenylgruppen quadratisch-planare *cis*-Bis($P^{\frown}O^{-}$-chelate) während sterische Hinderung durch Isopropyl- oder *tert*-Butylreste zu *trans*-Isomeren führt. Dicyclohexyl- und *tert*-Butylphenylphosphinogruppen stellen Grenzfälle dar. Analoge Palladium(II)-Komplexe zeigen bezüglich der *cis*/*trans*-Kontrolle nur marginale Unterschiede zum Nickel(II). Zwischenstufen der Bildung der Pd^{II} bis($P^{\frown}O^{-}$-chelate), *trans*-Dichloro-bis(phosphinophenol)- und Chloro(phosphinophenol)(phosphinophenolat)-palladium(II)-Komplexe, konnten isoliert und in einem Falle durch Kristall- und Molekülstruktur charakterisiert werden. Nickel(II)-bis(2-dialkylphosphinophenolat)e können zu Polymerisationskatalysatoren aktiviert werden, mit Einschränkungen durch $NiBr_2$·DME und Natriumhydrid oder durch Triethylsilan in THF, effizienter durch *n*BuLi oder *n*BuLi / $NiBr_2$·DME.

Introduction

Nickel chelate complexes, important industrial catalysts in the oligomerization of ethylene by the Shell Higher Olefin Process [1], have recently enjoyed a renaissance by the discovery of novel types of nickel and other late transition metal complex catalysts leading to branched polymers or improved tolerance towards functional groups and protic solvents [2–6]. In the course of continuous investigations on 2-phosphinophenols, O- and/or P-substituted derivatives and various nickel complexes thereof [7–12], we studied organonickel phosphinophenolate oligo- and polymerization catalysts [10–12] and observed by ^{31}P NMR the formation of nickel bis(phosphinophenolate) chelate complexes as the spent form of the catalysts when the ethylene / catalyst ratio was low [12]. The diphenylphosphino complex *cis*-[Ni(2-$Ph_2PC_6H_4O)_2$] [13] was found to be (re)activated by heating in toluene in the presence of ethylene,

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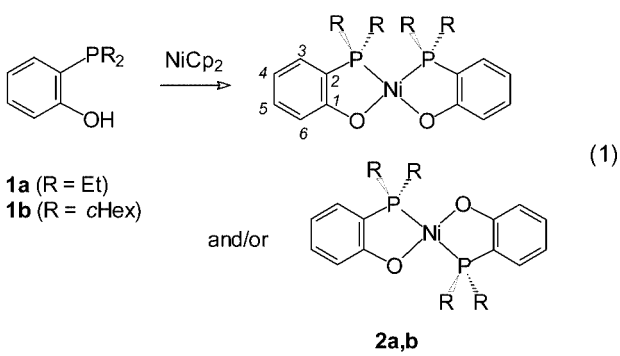
$NiCl_2$·DME and sodium hydride and to give higher turnover numbers and molecular weights than catalysts formed from methallylnickel diphenylphosphinophenolate or, in situ, from Ni(1,5-COD)$_2$ and diphenylphosphinophenol [12]. Analogous *cis*-bis(dialkylphosphinophenolate) nickel complexes had been unknown, and only after completion of the paper a first representative (alk = $C_2H_4OC_2H_5$) was reported [14]. The known isomers, *trans*-[Ni(2-*i*Pr$_2$P-4,6-*t*Bu$_2$C$_6$H$_2$O)$_2$] [11] and *trans*-[Ni(2-*t*Bu$_2$PC$_6$H$_4$O)$_2$] [15], could not be activated in the way found for *cis*-[Ni(2-Ph$_2$PC$_6$H$_4$O)$_2$]. Considering that dialkylphosphinophenolate nickel catalysts (2-R$_2$PC$_6$H$_4$ONiR′) give polyethylenes with much higher molecular weights than diphenylphosphinophenolate catalysts [12], a somewhat broader knowledge of nickel bis(dialkylphosphinophenolates) seemed desirable to us. Therefore, we prepared some nickel and, for more general conclusions, analogous palladium complexes of this type, studied the structure of the bis(chelates) and PdCl$_n$-phosphinophenol(ate) precursor complexes (n = 1,2) and the possibility of using the nickel bis(dialkylphosphinophenolates) for catalyst generation; here we report on the results.

Results and Discussion

Preparation of the complexes

The new bis(2-dialkylphosphinophenolate) nickel(II) and palladium(II) complexes were synthesized by known routes. 2-Dialkylphosphinophenols **1a** and **1b**, respectively, were heated with the semimolar amount of nickelocene in toluene at 80 to 110 °C to furnish the corresponding nickel bis(2-dialkylphosphinophenolates). The diethyl derivative **2a** forms orange, the dicyclohexyl derivative **2b** green microcrystals (eq. (1)). Intermediate cyclopentadienylnickel phosphinophenolates, known for 2-diphenyl-[13] and 2-alkylphenylphosphinophenolates [10], react readily with excess **1a** or **1b** and have not been observed.



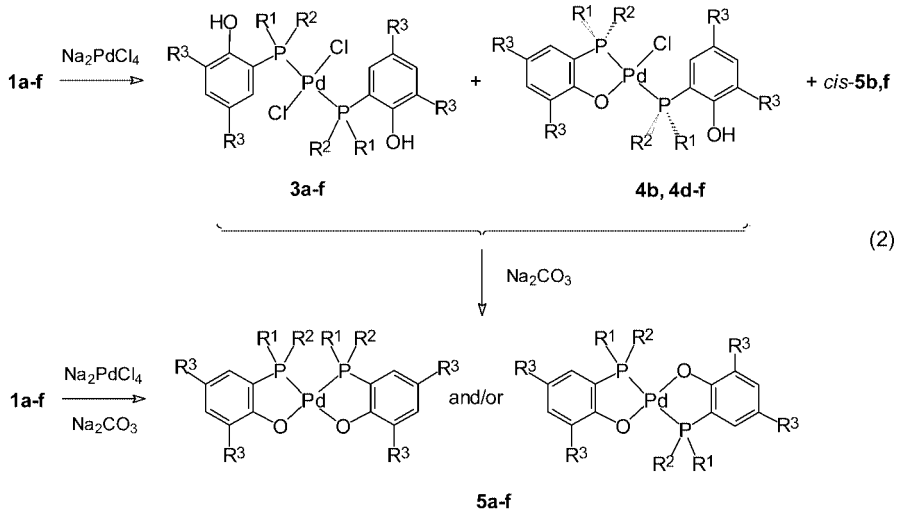
(1)

Compd.	*cis* : *trans*
2a in C_6D_6:	100 : 0 %
2b in C_6D_6:	0 : 100 %
2b in $CDCl_3$:	90 : 10 %

Reaction of **1a−f** with sodium tetrachloropalladate in methanol led to *trans*-[bis(phosphinophenol)PdCl$_2$] complexes **3**, pure in case of **3a** and **3c**, or mixtures with *trans*-[(phosphinophenol)(phosphinophenolate)PdCl] **4**. The isolated complexes **3a** and **3c** were converted to the palladium(II) bis(dialkylphosphinophenolates) **5a** and **5c** by treatment with sodium carbonate. The mixtures formed from **1b** or **1d−f** were heated under vacuum. This led to enrichment of the bis(chelates) **5b** or **5d−f**. *Cis*-**5b** was obtained in spectroscopically pure form by vacuum sublimation while addition of base was required to isolate pure **5d−f** (eq. (2)). It should be mentioned that **5b** as generated by vacuum sublimation is the *cis*-form, while **5b** synthesized at room temperature in presence of Na_2CO_3 is the *trans*-isomer (kinetic product) which at room temperature slowly converts to the *cis*-form (thermodynamic product). Apart from the palladium(II) bis(dialkylphosphinophenolates) **5a−e**, the *tert*-butylphenylphosphinophenolate **5f** was included in the investigation for comparison with related P-substituted nickel complexes (see discussion below).

Structure elucidation and discussion
Bis(2-phosphinophenol)- and mixed phosphinophenol-phosphinophenolate complexes.

Bis(2-phosphinophenol)- or mixed phosphinophenol-phosphinophenolate complexes of nickel(II) are unknown; to the best of our knowledge, only a 2-phosphinophenol Ni(0) complex has been reported [9]. The softer palladium(II), however, forms more stable bis(2-phosphinophenol) dihalides [15, 16] allowing isolation of the P-dialkyl derivatives **3a** and **3c** in pure form. The coordination at the phosphorus atom is established by the downfield phosphorus coordination shift ($\Delta\delta$ = 61.5, 52.5) and the multiplicity of the ^{13}C NMR signals of the carbon nuclei directly bound to phosphorus atom while the appearance of OH in the normal range (δ = 8 to 9) and the relatively constant signals of C-1 (connected to the OH group) indicate lack of coordination at the oxygen atom. Similar $^1J_{PC\text{-}2}$ coupling constants in **3a,c** and **5c** suggest the *trans*-configuration whereas $^1J_{PC\text{-}2}$ of *cis*-**5a** is larger. **3b**, **3d** and **3f** are less stable and undergo partial deprotonation even in the absence of an auxiliary base, but were detected by characteristic ^{31}P NMR signals (δ^{31}P = 17.8, 13.9 and 34.0), which differ from those of P$^\cap$O$^-$-chelates (see below) in their smaller coordination chemical shift ($\Delta\delta$ = 51.5, 47.3, 51.5). The deprotonation products, the *trans*-monochelates **4b** (δ^{31}P = 12.4, 59.7, $^2J_{PP}$ = 436 Hz), **4d** (δ^{31}P = 13.9, 60.9, $^2J_{PP}$ = 425 Hz) and **4f** (δ^{31}P = 33.5, 56.0, $^2J_{PP}$ = 438 Hz), were detected in the crude product mixtures by phosphorus doublets typically for P-only and P$^\cap$O$^-$-chelate coordination, with two-bond P−Pd−P coupling constants characteristic for *trans*-configuration. Single crystals of **4d** allowed a detailed analysis of the molecular structure (Figure 1, Tables 1, 2). Pd^{II} complexes of type **4** are yet unknown to our knowledge. **4d** forms a distorted square but planar structure (average deviation of Pd, Cl, O1, P1, P2 from the plane



compd.	a	b	c	d	e	f
R^1	Et	*c*Hex	*i*Pr	*c*Hex	*i*Pr	*t*Bu
R^2	Et	*c*Hex	*i*Pr	*c*Hex	*i*Pr	Ph
R^3	H	H	H	*t*Bu	*t*Bu	H
cis-**5** :	100 : 0	(5:95) [a]	0 : 100	0 : 100	0 : 100	95 : 5
trans-**5**		100 : 0				

[a] *Cis* to *trans* in C_6D_6: ≤ 5:95 after 1 h, 70 : 30 after 4 h, 100:0 after 7 d.

0.02 Å) around the palladium(II) atom. The distortions are associated with the rather small P1−Pd−O1 angle (84.06°) of the rigid five-membered ring, which enforces an increase of the angles O1−Pd−P2, Cl−Pd−P2 and Cl−Pd−P1. The chelate ring is planar (average deviation from the best plane 0.03 Å). The arrangement of the phosphinophenol ring (interplanar angle 27° to the chelate ring) is controlled by the hydrogen bond between the hydroxyl group and the phenolate oxygen atom. The two bulky *tert*-butyl groups are in *anti*-positions (dihedral angle C51−P1···P2−C55 −156°) causing *S*-configuration of both P1 and P2 in the molecule shown in Figure 1. The overall structure is however a racemate. Some short C−H···O and C−H···Cl contacts could be interpreted as weak hydrogen bonds (Table 2).

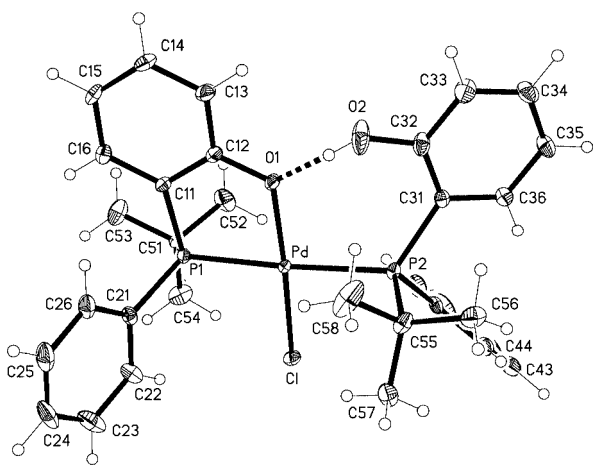


Figure 1 Molecular structure of **4d** (ellipsoids with 50 % probability).

Table 1 Selected bond lengths/Å and angles/°.

Pd-O(1)	1.9972(16)	P(1)-C(51)	1.870(3)
Pd-P(1)	2.2821(6)	P(2)-C(41)	1.828(2)
Pd-Cl	2.2952(6)	P(2)-C(31)	1.848(2)
Pd-P(2)	2.4228(6)	P(2)-C(55)	1.874(3)
P(1)-C(11)	1.805(2)	O(1)-C(12)	1.344(3)
P(1)-C(21)	1.816(3)	O(2)-C(32)	1.354(3)
O(1)-Pd-P(1)	84.06(5)	C(21)-P(1)-Pd	116.36(8)
O(1)-Pd-Cl	176.65(5)	C(51)-P(1)-Pd	114.46(8)
P(1)-Pd-Cl	92.60(2)	C(41)-P(2)-C(31)	101.75(11)
O(1)-Pd-P(2)	91.13(5)	C(41)-P(2)-C(55)	110.26(11)
P(1)-Pd-P(2)	174.82(2)	C(31)-P(2)-C(55)	103.87(12)
Cl-Pd-P(2)	92.21(2)	C(41)-P(2)-Pd	108.76(8)
C(11)-P(1)-C(21)	107.17(12)	C(31)-P(2)-Pd	122.80(8)
C(11)-P(1)-C(51)	106.85(11)	C(55)-P(2)-Pd	108.91(9)
C(21)-P(1)-C(51)	111.10(12)	C(12)-O(1)-Pd	120.69(15)
C(11)-P(1)-Pd	99.51(8)		

Bis(phosphinophenolate) complexes.

^{1}H and ^{13}C NMR and analytical data of **2a,b** and **5a−f** are in accordance with the bis(P$^\cap$O$^-$-chelate) structure, the diamagnetism of the nickel(II) complexes indicating a square-planar configuration around the metal. The chemical equivalence of the two phosphorus atoms prevents the assignment of *cis*- or *trans*-isomers as for **4** simply by their

Table 2 Hydrogen bonds/Å and ° [a]

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(2)-H(02)···O(1)	0.86(4)	1.63(4)	2.490(3)	175(4)
C(58)-H(58C)···O(2)	0.98	2.45	3.319(5)	147.0
C(53)-H(53C)···O(2)#1	0.98	2.65	3.457(4)	140.4
C(14)-H(14)···Cl#2	0.95	2.98	3.678(2)	131.3
C(24)-H(24)···Cl#3	0.95	2.94	3.820(3)	155.0

[a] Symmetry transformations used to generate equivalent atoms: #1 −x, y−1/2, −z+3/2; #2 x−1, y, z; #3 −x+1, −y+1, −z+2.

characteristic two-bond P-M^{II}-P coupling constants. The different nature of linear P-M^{II}-O (*cis*) or P-M^{II}-P and O-M^{II}-O (*trans*) substructures, however, influence the chemical shifts of phosphorus and ^{13}C-1 and the P-C coupling constants of the carbon nuclei C-1, C-2 and C-6 in a way that distinguishes between the two configurations. Characteristic differences are compiled in Table 3.

Typically, the phosphorus coordination chemical shifts $\Delta\delta(^{31}P)$ of the *cis*-isomers are larger than those of the *trans*-isomers ($\Delta\delta_{cis\text{-}trans} = 13-18$) indicating stronger deshielding and donor character of phosphorus. This suggests that the *cis*- differ from the *trans*-isomers by some push(P)-pull(O) bonding character within the nearly linear P-M^{II}-O substructure. In this sense M^{II} acquires more electron density from phosphorus, which in turn reduces the electron withdrawal from O^- and C-1, indicated by the somewhat lower coordination chemical shift $\Delta\delta(^{13}C)$ of C-1 in the *cis*- as compared to the *trans*-isomers ($\Delta\delta_{cis\text{-}trans} = -3$ to -5).

If, as typically, only one isomer is formed, the $\Delta\delta(^{31}P)$ value is less indicative, since it depends apart from the configuration also on the nature of the phosphorus substituents and the metal and is larger for dialkyl- than for alkylphenyl- and diphenylphosphino groups (e.g. $\Delta\delta$ = 85.6, 75.1, 65.0 for *cis*-**2a**, *cis*-[Ni(2-*i*PrPhP-4-$MeC_6H_3O)_2$], *cis*-[Ni(2-Ph_2P-4-$MeC_6H_3O)_2$] [10]) and for palladium than for analogous nickel complexes (cf. **2a,b,e** and **5a,b,e**). However, an unambiguous distinction of *cis*- and *trans*-isomers is possible in terms of the different coupling constants $N = |J+J'|$ of the nuclei ^{13}C-1, ^{13}C-2 and ^{13}C-6 with the two phosphorus nuclei. In most cases three of the expected five lines (X part of ABX; A and B phosphorus adjacent to ^{12}C and ^{13}C) can be observed. *N*, the difference of the outer lines of the pseudotriplet (τ), is larger for C-2 (by 20−30 %) and C-6 (by 60−70 %) in the *cis*- than in the *trans*-configuration while for C-1 the opposite is found ($N_{trans} \approx 2N_{cis}$).

The structure elucidation of the bis(2-dialkylphosphinophenolates) **2a,b** and **5a−e** shows that diethylphosphino groups give rise to *cis*-configuration while diisopropyl groups, like di-*tert*-butyl phosphino groups [15], lead to formation of *trans*-isomers. Dicyclohexylphosphino groups allow both *cis*- and *trans*-configuration. **2b** adopts the *trans*-form in the crystal (as seen by the green color [11, 15]) and in C_6D_6 solution but favors the *cis*-form (90:10 %) in $CDCl_3$ solution. **5b**, as mentioned above, can be obtained as the *trans*-isomer but rearranges into the *cis*-isomer, which is more stable in C_6D_6 and $CDCl_3$. Additional *tert*-butyl groups in 4- and 6-position in **5e** steer the preference to the *trans*-isomer. The preference for the *cis*-configuration not only in Ni^{II} or Pd^{II} bis(2-diphenylphosphinophenolates) [9, 15, 17] but also in **2a** and **5a** and the possible or even preferred *cis*-configuration of **2b** or **5b**, which has even more basic phosphino groups than **2a** and **5a** (for basicity of aryl- and alkylphosphines see [18]) provide evidence that the configuration is not controlled by the basicity of the phosphino groups but only by steric factors as previously suggested, but not proved. The lower stability of the *trans*-configuration in **5b** as compared to **2b** is due to the larger size of Pd^{II} as compared to the Ni^{II} atom, which lowers steric strain by the ligands, while the increased steric stress in **5e** by *tert*-butyl groups in 4- and particularly in 6-position turns the preferred configuration again to *trans*.

Table 3 Selected NMR data of square-planar *cis*- and *trans*-bis-(phosphinophenolate) nickel(II) and palladium(II) complexes **2** and **5** and of *trans*-bis(phosphinophenol)$PdCl_2$ **3** ($\Delta\delta = \delta_{complex}-\delta_{1}$)

compd. (solv.)	$\Delta\delta^{31}$P	$\Delta\delta^{13}$C-1	$N_{P\text{-}C2\text{-}P}$ (Hz)	$N_{P\text{-}C1\text{-}P}$ (Hz)	$N_{P\text{-}C6\text{-}P}$ (Hz)
cis-**2a** [a]	85.6	14.0	55.8	15.6	12.9
cis-**2b** [a]	79.2	12.7	53.0	15.0	11.3
trans-**2b** [b]	61.6	17.5	41.2	32	6.9
trans-**2e** [b] [11]	62.0	17.1	42.6	30.5	7.4
cis-**5a** [a]	95.2	15.3	51.6	11.6	17.1
cis-**5b** [b]	92.5	16.4	48.9	10.7	17.1
cis-**5f** [a]	76.9	15.8	50.5	12	17.3
trans-**5c** [a]	76.2	17.4	38.7	24.7	10.6
trans-**5b** [b]	79.1	19.0	39.2	25.4	10.6
trans-**5e** [b]	80.5	19.6	39.7	24.5	10.5
trans-**5d** [a]	82.1	17.6	38.7	25.0	10.4
trans-**5f** [a,d]	60.3				
trans-**3a** [c]	61.5	−1.6	43.5	0	0
trans-**3c** [c]	52.5	−1.5	40.7	4.4	0

[a] in $CDCl_3$, [b] in C_6D_6, [c] in D_8-THF, [d] minor isomer, ≤ 5 %.

A similar borderline behavior as caused by dicyclohexyl groups was found earlier for *tert*-butylphenylphosphino groups. While *rac*-[Ni(2-*iPr*PhP-4-$MeC_6H_3O)_2$] [10] as well as *meso*-[Ni(2-*i*PrPhP-4,6-*t*$Bu_2C_6H_2O)_2$] [9] crystallize as *cis*-isomers, the somewhat bulkier [Ni(2-*t*BuPhP-4-$MeC_6H_3O)_2$] forms *meso*-*trans*-isomers [10]. [Ni(2-*t*BuPhP-4,6-t$Bu_2C_6H_2O)_2$] (**2f**) displays *trans*-configuration in D_8-THF solution but crystallizes as distorted *rac*-*cis*-isomers [9]. The angle between the best planes of the five-membered rings increases from 11.3° in *meso*-[Ni(2-*i*PrPhP-4,6-*t*$Bu_2C_6H_2O)_2$] to 22.3° in **2f** and thus indicates the labile configuration. **5f**, prepared for comparison, prefers the *cis*-configuration in C_6D_6 and in $CDCl_3$ solution (*cis* to *trans* each 94:6 %) and thus shows the same effect as **5b**, a shift towards the *cis*-configuration by increasing size of the metal ion in borderline cases. Finally, it should be mentioned that 2-bis(2,4,6-trimethoxyphenyl)phosphino-3,5-dimethoxyphenolate ligands, highly P-basic and bulky, also form a *trans*-bis($P^{\cap}O^-$-chelate) complex [19]. In non-anellated

phosphinoenolate complexes the unsaturated C-C-backbone is somewhat less rigid and allows nickel bis(2-diisopropylphosphino-1-phenyl-enolate) to adopt both the *cis*- and *trans*-configuration [20]. Only nickel bis(di-*tert*-butylphosphinoenolates) exist exclusively as *trans*-isomers [21]. The preference for *trans*-bis(P⌒O$^-$-chelates) thus increases in the order Et_2P << *t*BuPhP ≈ *c*Hex_2P < *i*Pr_2P < *t*Bu_2P and matches the order of Tolman angles of dialkylphenylphosphines (Et_2PhP, *i*Pr_2PhP, *c*Hex_2PhP, *t*Bu_2PPh; ϑ 136, 155, 162, 170 [18]) except for diisopropyl and dicyclohexyl groups.

Use of nickel bis(phosphinophenolates) for the polymerization of ethylene

As referred to in the introduction, organonickel 2-phosphinophenolates are efficient catalysts for the poly- or oligomerization of ethylene, and nickel bis(2-phosphinophenolates), shown for **2a** in case of a small ethylene to catalyst ratio, are the spent form of the catalysts [12]. The lability of nickel bis(2-phosphinophenolates), indicated by *cis-trans* isomerizations of **2b** or **2f** on change of the molecular environment, should allow reactivation to improve the productivity of the catalysts or activation to use the air-stable nickel bis(2-phosphinophenolates) themselves as precatalysts. It was shown already that nickel bis(2-diphenylphosphinophenolates) can be activated by heating with $NiBr_2$·DME and excess sodium hydride in toluene in presence of ethylene (50 bar). The polymerization rate (ethylene consumption rate), for [Ni(2-$Ph_2PC_6H_4O)_2$] / 2$NiBr_2$·DME / 3NaH visualized by the pressure-time plot (Figure 2, plot a), is slow as compared to that with the organonickel catalyst formed *in situ* from 2-diphenylphosphinophenol and Ni(1,5-COD)$_2$ under the same conditions, but the selectivity for linear polyethylene is unchanged, and the total conversion of ethylene is improved [12]. Attempts to activate nickel bis(dialkylphosphinophenolates) with excess $NiBr_2$·DME and sodium hydride in toluene as catalyst for the polymerization of ethylene failed, but we observed for **2a** that replacement of toluene by THF, allowing at least partial solution of the salts, enabled slow formation of an oligomerization catalyst. The pressure-time plots (Figure 2, plots b and c) indicate very long induction periods (12 h at 100 °C and 6 h at 130 °C) but the conversions in the subsequent oligomerization come close to those for the catalyst generated *in situ* from **1a** and Ni(COD)$_2$ (84 %) [12], and the selectivity for linear α-olefins is comparable (Table 4). The molecular weights are lower than those of the polyethylene obtained with the catalyst formed from **1a** and Ni(COD)$_2$ in toluene (M_w 21800, M_n ca. 8000 g·mol^{-1} [12]), but this is due to the solvent effect of THF. Attempts to activate the more bulkily substituted **2b** in the same way as **2a** or by heating with $NaBH_4$ in THF / ethylene (50 bar) failed, and little conversion of ethylene to polyethylene was observed upon heating with **2b** and Ni(1,5-COD)$_2$ in THF, even at 130 °C.

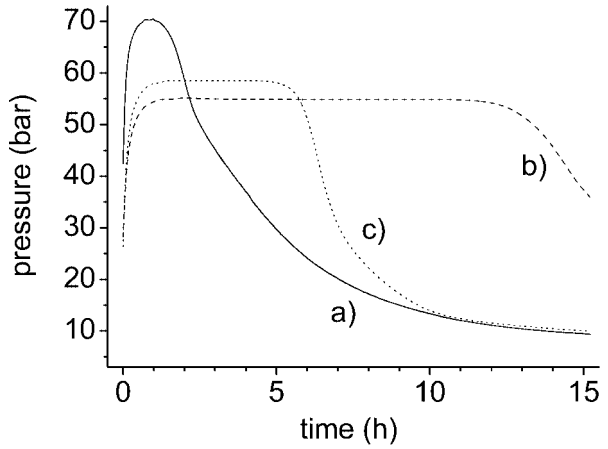


Figure 2 Pressure time plots for batch oligo- or polymerization of ethylene with: a) [Ni(2-$Ph_2PC_6H_4O)_2$] / 2$NiBr_2$·DME / 3NaH (solid), b) **2a** / $NiBr_2$·DME / 4 NaH at 100 °C (dash), c) as b) but at 130 °C (dot). Catalyst each 100 μmol, solvent 20 mL, initial pressure increase by heating from 20 to 100 °C, for further data see Table 4.

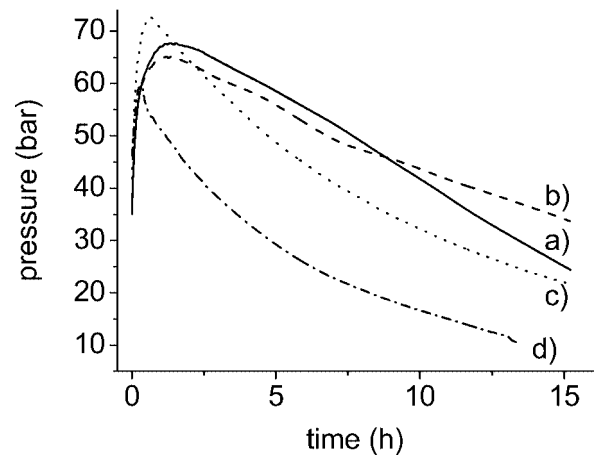
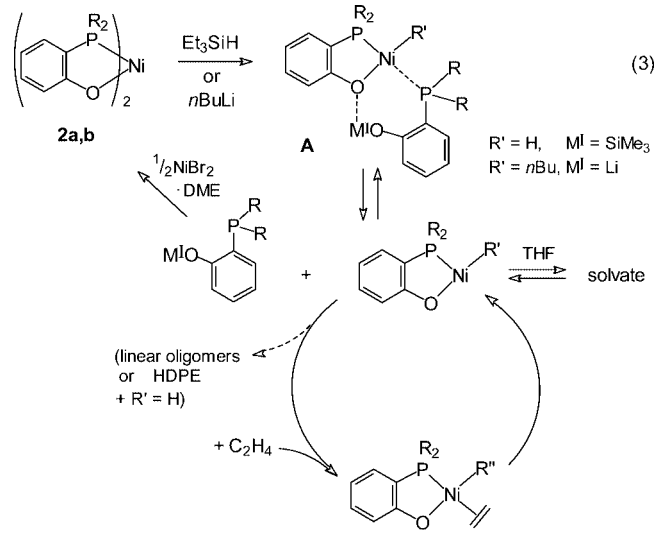


Figure 3 Pressure time plots for batch polymerization of ethylene with: a) **2a** / *n*BuLi in THF at 100 °C (solid), b) **2b** / *n*BuLi in THF at 100 °C (dash), c) **2b** / *n*BuLi in toluene at 100 °C (dot), d) $Ph_2PC_6H_4OH$ / Ph_3P / Ni(1,5-COD)$_2$ in toluene at 100 °C (dash-dot).

To circumvent the disadvantageous low solubility of the inorganic hydrides and low stability of the catalysts at high temperature, attempts were made to cleave off one of the chelate rings of **2a** or **2b** by polar covalent hydride or alkyl sources such as triethylsilane or *n*-butyllithium and to use the P∼O$^-$-ligand for catalyst stabilization, as in diphenylphosphinophenolate-phosphine oligomerization catalysts [22, 23], instead of trapping it by excess nickel(II). Heating ethylene in the presence of **2a** and triethylsilane in THF furnished HDPE with high selectivity for linear α-olefins, but the conversion and reaction rate are low even at high temperature (130 °C). The catalyst formed from **2b** and Et_3SiH in toluene gives similar results (Table 4). Higher

productivities are achieved by the use of *n*-butyllithium. Solutions formed from *n*-butyllithium with **2a** or **2b** in THF or toluene cause oligo- or polymerization of ethylene at 100 °C. The reactions start within 2 h but are then slower than after activation of **2a** with $NiBr_2$·DME and sodium hydride. The pressure-time plots (Figure 3, plots a-c) resemble that of the oligomerization catalyst obtained from 2-diphenylphosphinophenol, Ni(1,5-COD)$_2$ and triphenylphosphine (Figure 3, plot d) [24] and can be understood in terms of competing coordination of the liberated phosphine, ethylene and THF for the catalyst (eq. 3), which slows down the rate of the chain growth reaction. In case of **2a** / *n*BuLi / THF a soft wax consisting of linear α-olefins was isolated after THF and oligomers were removed by flash distillation. The short chain lengths suggest that the rate of the β-olefin elimination is much less decreased by the auxiliary phosphine and THF than that of the chain growth. The catalyst **2b** / *n*BuLi / THF produced linear HDPE (Table 4). The higher molecular weight is due to the higher basicity of the *c*Hex$_2$P as compared to the Et$_2$P group, as observed with catalysts formed from **1a** or **1b** and Ni(COD)$_2$ [12], and to steric hindrance of the coordination of the liberated 2-*c*Hex$_2$PC$_6$H$_4$O$^-$ to the catalyst (cf. [24]). The low effect of THF, which usually causes a strong decrease of the molecular weights, is not clear. As compared to polyethylene obtained with the catalyst **1b** / NiCOD)$_2$ in toluene (M_w 59000, M_n 26500 g/mol) [12], however, the molecular weights are lower. The lower molecular weights



in the polymerization with **2b** / *n*BuLi in toluene may be due to stronger interactions with *c*Hex$_2$PC$_6$H$_4$O$^-$ in absence of THF, and increase if $NiBr_2$·DME is added to trap this ligand (Table 4), but by far not to the value observed with **1b** / Ni(COD)$_2$ in toluene. The slow reaction rate (Figure 4, plot a) shows that this heterogeneous catalyst system is distinct from the homogenous catalyst formed from **1b** and Ni(COD)$_2$ (Figure 4, plot b) and more similar to the catalyst [Ni(2-Ph$_2$PC$_6$H$_4$O)$_2$] / 2$NiBr_2$·DME / 3NaH (cf. Figure

Table 4 Poly- and oligomerization of ethylene by catalysts derived from **2a** or **2b**

exp.	catalyst components (μmol)	solvent, initial pressure (bar), T (°C)	conversion of C_2H_4(g (%)), TON (mol·mol^{-1})	product: α/internal (%); Me/olefin, Me/1000C	PE: mp. (°C), d (g·cm^{-3}), M_{NMR} (g·mol^{-1}) [a]
1	**2a** (113), $NiBr_2$·1.1DME (113), NaH (500)	THF, 34, 100 [b]	5.3 (54), 1580	HDPE, n.d.	132-134, 0.953, n.d.
2	**2a** (113), $NiBr_2$·1.1DME (113), NaH (500)	THF, 32, 130 [c]	6.3 (74), 1785	HDPE, 92:8, 1.4, 5.8	128-130, 0.954, 3400
3	**2a** (100), Et_3SiH (620)	THF, 50, 130	3.2 (28), 1070	HDPE, >97:3, 1.5, 3.7	130-132, 0.956, 6000
4	**2b** (96), Et_3SiH (950)	toluene, 50, 130	2.2 (20), 820	HDPE, 92:8, 1.8, 1.5	129-132, 0.957, 16000
5	**2a** (110), *n*BuLi (150)	THF, 50, 100	11.3 (85), 3660	2.7 g oligomer,[d] 7.6 g soft wax, 95:5, 1.3	55-86, n.d., 430
6	**2b** (88), *n*BuLi (150)	THF, 50, 100	9.0 (79), 3210	HDPE, >97:3, 1.2, 2.2	132-133, 0.975, 6600
7	**2b** (108), *n*BuLi (170)	toluene, 50, 100	11.1 (81), 3660	HDPE, 95:5, 1.2, 13	115-118, 0.961, 1300
8	**2b** (108), *n*BuLi (205), $NiBr_2$·1.1DME (110)	toluene, 50, 100	10.0 (73), 3240 [e]	HDPE, >97:3, 1, 2.6	130-131, 0.962, 5300

[a] M_{NMR} by ^{1}H NMR integration (for low-molecular weight polymers similar to M_n) [12]. [b] Induction period 12 h. [c] Induction period 6 h. [d] Yield rel. to C_2H_4: C4 1.5, C6 4.9, C8 5.7, C10 3.0, C12 0.6 %; isomers < 0.1 % (GC). [e] TON rel. to **2b**.

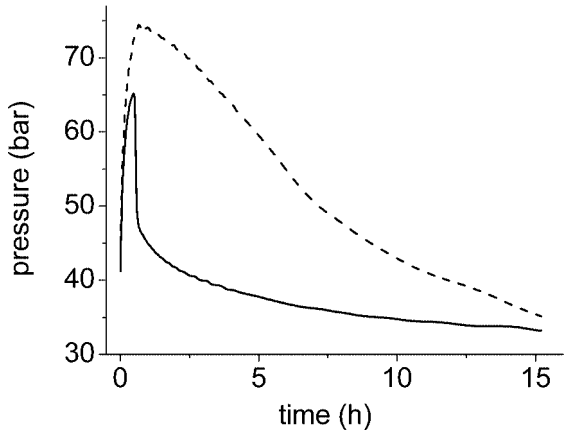


Figure 4 Pressure time plots for batch polymerization of ethylene with: a) **2b** / *n*BuLi / $NiBr_2$·DME in toluene at 100 °C (dash), b) **1b** / Ni(1,5-COD)$_2$ in toluene at 100 °C (solid).

2, plot a), but, as the selectivity is unchanged, it differs probably only by slower but longer lasting catalyst generation and much lower stationary catalyst concentration. The mechanism assumed for the oligo- or polymerization of ethylene by the nickel(II) phosphinophenolate catalysts (eq. (3)), apart from the activation of **2**, corresponds to that proposed by *Keim* for phosphinoenolates [1].

The catalyst systems reported here show principal ways to activate nickel(II) bis(2-dialkylphosphinophenolates) or to reactivate the spent-form of these catalyst systems. Molecular weights of polyethylenes were lower than of those obtained with related 2-Alk$_2$PC$_6$H$_4$OH / Ni(COD)$_2$ catalysts but, except in experiments 5 and 7 by the presence of the P∼OLi-ligand, generally higher than with nickel(II) 2-diphenylphosphinophenolate catalysts. Though MAO seems unsuitable to activate nickel 2-phosphinophenolates, more efficient hydride or alkyl activators / donors may be found to improve these systems in future work. Finally, it should be mentioned that attempts to oligo- or polymerize ethylene with solutions prepared from the analogous palladium bis(P⌒O-chelate) **5b** and *n*BuLi failed under analogous conditions, probably due to the higher stability of organopalladium(II)-2-phosphinophenolates.

Experimental Section

General

All reactions were carried out under argon, using Schlenk techniques and freshly distilled dry solvents. The 2-dialkylphosphinophenols and 2-*tert*-butylphenylphosphinophenol were synthesized as reported earlier [12], other chemicals were purchased. Ethylene (99.5 %, Air Liquide) was used without further treatment. Melting points were performed with a Sanyo Gallenkamp melting point apparatus, elemental analyses with a CHNS-932 analyzer from LECO using standard conditions. NMR spectra were recorded on a multinuclear FT-NMR spectrometer ARX300 (Bruker) at 300.1 (^{1}H), 75.5 (^{13}C), and 121.5 (^{31}P) MHz. Shift references are tetramethylsilane for ^{1}H and ^{13}C and H_3PO_4 (85 %) for ^{31}P. Assignments of hydrogen and carbon nuclei use for the phenolate ring numbers 1 to 6 according to the nomenclature (see eq. (1)), for P-alkyl and cyclohexyl α, β, γ, δ and for P-phenyl groups *i*, *o*, *m*, *p*. Coupling constants refer to J_{HH} in ^{1}H and J_{PC} in ^{13}C NMR data unless stated otherwise. τ means a pseudotriplet appearance of ^{1}H or ^{13}C signals by coupling with two phosphorus nuclei, $N = |J+J'|$.

Nickel complexes

***cis*-Bis[2-(diethylphosphino)phenolato]nickel(II) (2a).** The dark green solution of nickelocene (278 mg, 1.5 mmol) and **1a** (536 mg, 2.9 mmol) in toluene (50 mL) was refluxed for 15 h. After partial evaporation of the solvent and cooling to room temperature the precipitate was filtered, washed with a small amount of cold hexane and dried for some hours at 10^{-4} Torr to yield 480 mg (76 %) of **2a** as yellow powder, mp. > 250 °C, soluble in $CDCl_3$ with orange color.

$C_{20}H_{28}O_2P_2Ni$ (421.08); C 57.12 (calc. 57.05); H 6.68 (6.70) %.

^{1}H NMR ($CDCl_3$): δ = 1.30 (dt, $^3J_{PH}$ = 18.1, ^3J = 7.5 Hz, 12 H, CH_3), 1.70-1.90 (m, 8 H, CH_2), 6.54 (t, $^3J \approx$ 7.2 Hz, 2 H, 4-H), 6.87-6.97 (m, 4 H, 3-H, 6-H), 7.19 (t, $^3J \approx$ 7.6 Hz, 2 H, 5-H). **^{13}C{^{1}H} NMR** ($CDCl_3$): δ = 8.7 (s, CH_3), 19.5 (τ, N = 30.0 Hz, 8 H, PCH_2), 113.5 (τ, N = 55.8 Hz, C-2), 115.3 (τ, N = 7.0 Hz, C-4), 118.8 (τ, N = 12.9 Hz, C-6), 128.3 (s, C-3), 133.8 (s, C-5), 176.0 (τ, N = 15.6 Hz, C-1). **^{31}P{^{1}H} NMR** (C_6D_6): δ = 39.0.

***trans*- and *cis*-Bis[2-(dicyclohexylphosphino)phenolate]nickel(II) (2b).**

Nickelocene (166 mg, 0.9 mmol) and **1b** (510 mg, 1.8 mmol) in toluene (50 mL) were refluxed overnight. On cooling to room temperature green microcrystals of **2b** were collected and dried in vacuum, yield 407 mg (71 %), mp. > 250 °C. The crystals are soluble in C_6D_6 with light green and in $CDCl_3$ with orange color.

$C_{36}H_{52}O_2P_2Ni$ (637.45); C 67.81 (calc. 67.83); H 8.11 (8.22) %.

trans-**2b** in C_6D_6:

^{1}H NMR: δ = 1.00-1.30 (m, 12 H, Cy), 1.53 (br s, 4 H), 1.68-2.05 (m, 20 H, Cy), 2.15-2.25 (m, 4 H, α-H), 2.71 (d, $^3J_{PH}$= 11.4 Hz, 4 H, β-H), 6.50 (t, ^3J = 7.0-7.4 Hz, 2 H, 4-H), 6.87 (d br, ^3J = 8 Hz, 2 H, 6-H), 7.04 (td, $^3J \approx$ 7.6, $^4J \approx$ 1.3 Hz, 2 H, 5-H), 7.12 (ddd, ^3J = 7.7, $^3J_{PH}$= 4.0, ^4J = 1.4-1.6 Hz, 2 H, 3-H). **^{13}C{^{1}H} NMR**: δ = 27.1 (s, C-δ), 27.8 (τ, $N \approx$ 10 Hz, C-γ), 27.9 (τ, $N \approx$ 13 Hz, C-γ′), 29.1 (s, C-β), 29.4 (s, C-β′), 34.1 (τ, N = 22.3 Hz, C-α), 114.3 (τ, N = 41.2 Hz, C-2), 115.2 (τ, N ca. 4 Hz, C-4), 120.1 (τ, N = 6.9 Hz, C-6), 132.4 (s, C-3), 133.3 (s, C-5), 180.5 (τ, N = 32 Hz, C-1). **^{31}P{^{1}H} NMR**: δ = 27.9.

cis- and *trans*-**2b** in $CDCl_3$:

^{1}H NMR (CH-COSY): *cis* δ = 1.15-1.40 (m, 16 H, β′,γ,γ′,δ-H), 1.40-1.60 (m, 4 H, β-H), 1.65-2.00 (m, 16 H, δ,γ,γ′,β-H), 2.05-2.20 (br m, 4 H, α-H), 2.80-2.92 (br m, 4 H, β′-H), 6.45 (t, ^3J = 7.0-7.6 Hz, 2 H, 4-H), 6.89 (d br, ^3J = 8.1 Hz, 2 H, 6-H), 6.96-6.98 (m, 2 H, 3-H), 7.1 (t, ^3J = 7.6 Hz, 2 H, 5-H); *trans* δ = 1.90-2.00 (m, 12 H, β,γ,γ′-H), 2.20 (br m, 4 H, α-H), 2.54 (d br, $^2J \approx$ 12 Hz, β′-H), 6.40 (t, 4-H), other signals superimposed. − **^{13}C NMR** (CH-COSY, DEPT): *cis* δ = 26.0 (s, C-δ), 27.12-27.25 (m, 2 C, C-γ/γ′), 28.0 (s, C-β), 30.0 (s, C-β′), 35.6 (τ, N = 24.4 Hz, C-α), 113.8 (τ, N = 53.0 Hz, C-2), 114.4 (τ, $N \approx$ 6.4 Hz, C-4), 118.7 (τ, N = 11.3 Hz, C-6), 130.3 (s, C-3), 133.2 (s, C-5), 175.7 (τ, N = 15 Hz, C-1); *trans* δ = 21.6 (s, C-δ), 26.9-27.0 (m, 2 C, C-γ/γ′), 27.9 (s, C-β), 32.9 (τ, N = 21.2 Hz, C-α), 113.9 (s, C-4), ca. 118.2 (τ, C-6), 131.4 (s, C-3), 132.0 (s, C-5), (C-1 and C-2 uncertain by low intensity). **^{31}P{^{1}H} NMR**: *cis* δ = 45.5, *trans* δ = 27.1; at 25 °C *cis* / *trans* ca. 10:1, at −40 °C only *cis*-isomer.

Palladium complexes

***trans*-Bis[2-(diethylphosphino)phenol-η^1-P]palladiumdichloride semihydrate(3a**·0.5 H_2O).

Na_2PdCl_4 (279 mg, 0.95 mmol), dissolved in methanol (10 mL), was added to a solution of **1a** (380 mg, 2.09 mmol) in methanol (10 mL) affording a yellow precipitate. To complete the reaction,

the mixture was stirred for 1 h at 40 °C. Then the precipitate was separated, washed with water and dried in vacuum to give 205 mg (40 %) of **3a**·0.5 H_2O as yellow powder, sparingly soluble in C_6D_6, mp. > 220 °C.

$C_{20}H_{30}Cl_2O_2P_2Pd$·0.5 H_2O (550.74); found C 43.77 (calc. 43.62); H 5.81 (5.67) %.

^{1}H NMR (D_8-THF): δ = 1.15 (tτ, $^3J_{HH}$ = 7.7, $N \approx$ 17.9 Hz, 12 H, CH_3), 2.17-2.41 (m, 8 H, CH_2), 6.74 (ddd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 0.6 Hz, $J_{PH} \approx$ 2 Hz, 2 H, 6-H), 6.84 (td, $^3J_{HH}$ = 7.4, 7.5 Hz, $^4J_{HH}$ = 0.6 Hz, 2 H, 4-H), 7.23 (dd, $^3J_{HH}$ = 8.1, 7.4 Hz, $^4J_{HH}$ = 1.6 Hz, 2 H, 5-H), 7.81 (τdd, N = 11.6, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.6 Hz, 2 H, 3-H), 8.80 (s, 2 H, OH); 2.53 (br s, H_2O). **^{13}C{^{1}H} NMR** (D_8-THF): δ = 9.1 (s, CH_3), 16.0 (τ, N = 29.1 Hz, CH_2), 116.3 (s, C-6), 117.0 (τ, N = 43.5 Hz, C-2), 119.9 (τ, N = 10.4 Hz, C-4), 132.5 (s, C-5), 137.0 (τ, N = 12.6 Hz, C-3), 160.4 (s, C-1). **^{31}P{^{1}H} NMR** (D_8-THF): δ = 14.9.

cis-Bis[2-(diethylphosphino)phenolato]palladium(II) (5a).

3a·0.5 H_2O, prepared as described above from **1a** (210 mg, 1.156 mmol) and Na_2PdCl_4 (170 mg, 0.578 mmol), was dissolved in methanol and stirred with Na_2CO_3 (100 mg, 0.94 mmol) for 1 h at 40 °C and overnight at 20 °C. NMR-spectra of the crude product showed broad bands (δ ^{31}P = 51.4). Methanol was evaporated, the residue was washed with water and hexane, and the complex was extracted with $CHCl_3$. Evaporation of the solvents afforded 163 mg (60 %) of yellow **5a**, m.p. > 220 °C.

$C_{20}H_{28}O_2P_2Pd$ (468.81); C 50.95 (calc. 51.24); H 6.12 (6.02) %.

^{1}H NMR ($CDCl_3$): δ = 1.17 (dt, $^3J_{PH}$ = 18.8, 3J = 7.5 Hz, 12 H, CH_3), 1.82-2.15 (m, 8 H, CH_2), 6.56 (ddbr, $^3J \approx$ 7.0, 7.5 Hz, 2 H, 4-H), 6.88-6.97 (m, 4 H, 3-H, 6-H), 7.21 (ddbr, $^3J \approx$ 7.5, 8.2 Hz, 2 H, 5-H). **^{13}C{^{1}H} NMR** ($CDCl_3$): δ = 8.5 (s, CH_3), 20.7 (τ, N = 34.0 Hz, 8 H, PCH_2), 112.2 (τ, N = 51.6 Hz, C-2), 115.4 (τ, N = 8.0 Hz, C-4), 119.4 (τ, N = 17.1 Hz, C-6), 128.9 (s, C-3), 133.9 (s, C-5), 177.3 (τ, N = 11.6 Hz, C-1). **^{31}P{^{1}H} NMR**: δ($CDCl_3$) = 48.6, δ(C_6D_6) = 48.4.

cis- *and trans*-Bis[2-(dicyclohexylphosphino)phenolato]palladium(II) (5b).

a) **1b** (621 mg, 2.14 mmol) was added to a solution of Na_2PdCl_4 (285 mg, 0.97 mmol) in methanol (20 mL) and stirred for 3 h at 40 °C. After cooling the precipitate was filtered, washed with water, dried in vacuum and sublimed at 160 °C / $2 \cdot 10^{-2}$ Torr to give 490 mg (74 %) of spectroscopically pure *cis*-**5b** as pale-yellow microcrystals, mp. >220 °C.

$C_{36}H_{52}O_2P_2Pd$ (685.18); C 60.36 (combustion incomplete, calc. 63.11); H 7.47 (7.65) %.

MS (EI 70 eV, 330 °C): *m/e* = 686 (100 %) [M^+], 604 (48 %), 524 (20 %), 522 (25 %), 520 (44 %), 289.5 (23 %), 55 (34 %). **^{1}H NMR** ($CDCl_3$): δ = 1.10-1.35 (m, 16 H, Cy), 1.35-1.53 („q“, 4 H, Cy), 1.60-1.95 (m, 16 H, Cy), 2.17-2.37 (m, 8 H, Cy), 6.51 (td, $^3J_{HH} \approx$ 7.2 Hz, $^4J_{PH}$ = 0.9 Hz, 2 H, 4-H), 6.92 (dd br, $^3J_{HH} \approx$ 8.5, $^4J_{PH} \approx$ 3 Hz, 2 H, 6-H), 7.02 (τd, N = 16.7, $^4J_{HH}$ = 1.5 Hz, 2 H, 3-H), 7.19 (t br, $^3J_{HH} \approx$ 7.5 Hz, 2 H, 5-H). **^{31}P{^{1}H} NMR** ($CDCl_3$): δ = 59.9.

b) **1b** (86 mg, 0.296 mmol) was stirred with Na_2PdCl_4 (43 mg, 0.146 mmol) in methanol (5 mL) and excess Na_2CO_3 (32 mg, 0.30 mmol) for 2 h at 40 °C to give a precipitate of *trans*-**5b** which was separated, washed with water and dried in vacuum, yield 80 mg (79 %), mp. >220 °C. In C_6D_6 solution *trans*-**5b** isomerizes slowly to *cis*-**5b**.

^{13}C{^{1}H} NMR (C_6D_6): *trans*: δ = 26.0 (s, δ-CH_2), 27.65 (τ, N = 12.4 Hz, γ,γ′-CH_2), 29.2 (s, β-CH_2) , 29.4 (br s, β′-CH_2), 34.9 (τ, N = 24.0 Hz, α-CH_2), 112.6 (τ, N = 39.2 Hz, C-2), 115.6 (τ, N = 6.6 Hz, C-4), 120.5 (τ, N = 10.6 Hz, C-6), 132.9 (s, C-3), 133.7 (s, C-5), 182.0 (τ, N = 25.4 Hz, C-1); *cis*: δ = 26.9 (s, δ-CH_2), 27.8 (τ, N = 10.1 Hz, γ,γ′-CH_2), 28.7 (s, β-CH_2) , 30.4 (s, β′-CH_2), 36.7 (m_{ABX}, N = 27.4 Hz, α-CH_2), 114.1 (m_{ABX}, N = 48.9 Hz, C-2), 115.1 (τ, N = 7.2 Hz, C-4), 120.2 (τ, N = 17.1 Hz, C-6), 131.7 (s, C-3), 135.0 (s, C-5), 179.4 (τ, N = 9.6 Hz, C-1). **^{31}P{^{1}H} NMR** (C_6D_6) δ = 45.4, 58.8 (*trans* / *cis*-intensity after 1 h ≥ 95:5, 4d 30:70, 7d 0:100 %).

trans-Bis[2-(diisopropylphosphino)phenol-η^1-P]palladiumdichloride (3c).

1c (538 mg, 2.56 mmol), dissolved in methanol (10 mL), was added to a solution of Na_2PdCl_4 (342 mg, 1.16 mmol) in methanol (10 mL). After stirring for 1 h at 40 °C the precipitate was collected, washed with water and dried in vacuum to give 506 mg (73 %) of **3c** as yellow powder, slightly soluble in C_6D_6.

$C_{24}H_{38}Cl_2O_2P_2Pd$ (597.84); C 48.62 (calc. 48.22); H 6.35 (6.41) %.

IR (nujol): $\bar{\nu}$ = 3311 cm^{-1} s ν_{OH}. **^{1}H NMR** (D_8-THF): δ = 1.16 (dτ, $^3J_{HH}$ = 7.1, N = 14.2 Hz, 12 H, CH_{3A}), 1.32 (dτ, $^3J_{HH}$ = 7.1, N = 17 Hz, 12 H, CH_{3B}), 2.89-3.00 (m, 4 H, CH), 6.83 (m, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 1, $N \approx$ 4.4 Hz, 2 H, 6-H), 6.89 (t br, $^3J_{HH} \approx$ 7.5 Hz, 2 H, 4-H), 7.26 (dt br, $^3J_{HH}$ = 8.1, 7.1, $^4J_{HH}$ = 1.4 Hz, 2 H, 5-H), 7.49 (ddτ, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.4, N = 9.0 Hz, 2 H, 3-H), 8.41 (s, 2 H, OH). **^{13}C{^{1}H} NMR** (D_8-THF): δ = 18.6 (s, CH_{3A}), 19.8 (s, CH_{3B}), 23.4 (τ, N = 25 Hz, CH), 113.0 (τ, N = 40.7 Hz, C-2), 118.3 (s, C-6), 120.0 (τ, N = 8.1 Hz, C-4), 132.4 (s, C-5 or C-3), 135.9 (s br, C-3 or C-5), 161.2 (τ, N = 4.4 Hz, C-1). **^{31}P{^{1}H} NMR** (D_8-THF): δ = 29.4.

trans-Bis[2-(diisopropylphosphino)phenolato]palladium(II) (5c).

Na_2CO_3 (500 mg) was added to a solution of **3c** (300 mg, 0.50 mmol) in THF (10 mL), and the suspension was stirred for 1 h at 60 °C. After removal of the main part of the solvent and cooling to room temperature the precipitate was collected, washed with water and dried in vacuum to afford 150 mg (57 %) of **5c** as yellow powder, soluble in C_6D_6 or $CDCl_3$.

$C_{24}H_{36}O_2P_2Pd$ (524.92); C 55.21 (calc. 54.92); H 7.13 (6.91) %.

^{1}H NMR ($CDCl_3$): δ = 1.29 (dτ, $^3J_{HH}$ = 7.0, N = 15.6 Hz, 12 H, CH_{3A}), 1.42 (dτ, $^3J_{HH}$ = 7.0, N = 17.5 Hz, 12 H, CH_{3B}), 2.55 (sept τ, $^3J_{HH}$ = 7.0, N = 4.7 Hz, 4 H, CH), 6.49 (tdτ, $^3J_{HH} \approx$ 7.2 Hz, $^4J_{HH}$ = 1 Hz, $N \approx$ 2 Hz, 2 H, 4-H), 6.72 (dm, $^3J_{HH}$ = 8.9, $^4J_{HH}$ = 1, $N \approx$ 4 Hz, 2 H, 6-H), 7.07-7.13 (m, 4 H, 3-H and 5-H). **^{13}C{^{1}H} NMR** ($CDCl_3$): δ = 18.0 (s, CH_{3A}), 18.2 (τ, N = 5.1 Hz, CH_{3B}), 24.6 (τ, N = 24 Hz, CH), 111.6 (τ, N = 38.7 Hz, C-2), 114.7 (τ, N = 6.8 Hz, C-4), 118.9 (τ, N = 10.6 Hz, C-6), 131.6, 132.7 (2 s, C-3 and C-5), 180.1 (τ, N = 24.7 Hz, C-1). **^{31}P{^{1}H} NMR**: δ($CDCl_3$) = 53.1, δ(C_6D_6) = 53.7.

trans-Bis(2-dicyclohexylphosphino-4,6-di-*tert*-butylphenolato)palladium(II) (5d).

A solution of **1d** (610 mg, 1.52 mmol) in methanol (10 mL) and then Na_2CO_3 (106 mg, 1.0 mmol) was added to Na_2PdCl_4 (139 mg, 0.47 mmol) dissolved in methanol (10 mL). The mixture was stirred overnight at 40 °C, cooled to room temperature and filtered. The yellow precipitate was washed with water and dried in vacuum to give 320 mg (74 %) of **5d**.

$C_{52}H_{84}O_2P_2Pd$ (909.60); C 68.90 (calc. 68.66); H 9.55 (9.31) %.

^{1}H NMR (C_6D_6): δ = 1.44 (s, 18 H, tBu$_A$), 1.68 (s, 18 H, tBu$_B$), 1.05-2.0 (m, 36 H, Cy), 2.30-2.56 (m, 8 H, Cy), 7.21 (τd, N = 9.3, $^4J_{HH}$ = 2.3 Hz, 2 H, 3-H), 7.54 (d, $^4J_{HH}$ = 2.3 Hz, 1 H, 5-H). **^{13}C{^{1}H} NMR** ($CDCl_3$): δ = 26.1 (s, δ-CH_2), 26.8 (τ, N = 13.4 Hz, γ-CH_2), 27.0 (τ, N = 11.5 Hz, γ′-CH_2), 28.5 (s, β-CH_2), 29.0 (s, β′-CH_2), 29.3 (s, CMe_3),29.7 (s, β′-CH_2), 31.8 (s, CMe_3), 33.8 (s, CMe$_3$), 34.2 (τ, N = 24.1 Hz, α-CH), 35.2 (s, CMe$_3$), 111.0 (τ, N = 38.7 Hz, C-2), 125.9 and 126.6 (2s, C-3 and C-5), 135.7 (τ, N = 7.0 Hz, C-4), 137.8 (τ, N = 10.4 Hz, C-6), 176.6 (τ, N = 24.5 Hz, C-1). **^{31}P{^{1}H} NMR**: δ(C_6D_6) = 48.6, δ($CDCl_3$) = 48.7.

trans-Bis(2-diisopropylphosphino-4,6-di-*tert*-butylphenolato)palladium(II) (5e).

1e (135 mg, 0.419 mmol) was stirred with Na_2PdCl_4 (63 mg, 0.214 mmol) and excess Na_2CO_3 (30 mg, 0.283 mmol) in methanol (5 mL) for 1 h at 40 °C and overnight at 20 °C to give a yellow precipitate of *trans*-**5e** which was separated, washed with water and dried in vacuum; yield 152 mg (97 %), mp. >220 °C.

$C_{40}H_{68}O_2P_2Pd$ (749.35); C 64.17 (calc. 64.11); H 9.49 (9.15) %.

^{1}H NMR (C_6D_6): δ = 1.18 (dτ, $^3J_{HH}$ = 7.8, N = 15.0 Hz, 12 H, CH_{3A}), 1.41 (s, 18 H, tBu$_A$), 1.44 (dτ, $^3J_{HH}$ = 7.3, N = 21 Hz, 12 H, CH_{3B}), 1.65 (s, 18 H, tBu$_B$), 2.36 (m, 4 H, CH), 7.08 (τd, N = 4.6, $^4J_{HH}$ = 2.3 Hz, 2 H, 3-H), 7.52 (d, $^4J_{HH}$ = 2.3 Hz, 1 H, 5-H). **^{13}C{^{1}H} NMR** (C_6D_6): δ = 19.0 (s, CH_{3A}), 19.9 (τ, N = 6.3 Hz, CH_{3B}), 25.9 (τ, N = 23.9 Hz, CH), 30.5 (s, CMe_3), 32.8

(s, C*Me*$_3$), 34.8 (s, *C*Me$_3$), 36.4 (s, *C*Me$_3$), 112.0 (τ, *N* = 39.7 Hz, C-2), 126.3 (s, C-5), 128.0 (s, C-3), 137.3 (τ, *N* = 7.0 Hz, C-4), 139.4 (τ, *N* = 10.5 Hz, C-6), 177.7 (τ, *N* = 24.5 Hz, C-1). **^{31}P{^{1}H} NMR**: δ(C$_6$D$_6$ or CDCl$_3$) = 56.2.

***trans*-[2-(*tert*-butylphenylphosphino)phenolato-2-(*tert*-butylphenylphosphino)phenol] palladium(II)chloride (4f) and *cis*- and *trans*-Bis[2-(*tert*-butylphenylphosphino)phenolato] palladium(II) (5f).**

A solution of **1f** (610 mg, 2.36 mmol) in methanol (10 mL) was added to Na_2PdCl_4 (315 mg, 1.07 mmol) dissolved in methanol and stirred for 1 h. NMR control revealed formation of two pairs of diastereoisomers of **4f** and a minor amount of *cis*-**5f**. Heating overnight left one pair of diastereoisomers of **4f** [in $CDCl_3$ δ(^{31}P) = 33.5 and 56.0 ($^2J_{PP}$ = 438.1 Hz); δ(^{1}H)$_{tBu}$ = 1.46 (d, $^3J_{PH}$ = 15.9 Hz) and 1.61 (d, $^3J_{PH}$ = 15.0 Hz)] along with increased signals for **5f**. Bis(chelate) formation was completed by addition of Na_2CO_3 (106 mg, 1.0 mmol). Work-up as above gave 530 mg (80 %) **5f** as yellow powder, mp. >220 °C.

$C_{32}H_{36}O_2P_2Pd$ (621.00); C 61.81 (calc. 61.89); H 5.82 (5.84) %.

5f:

^{1}H NMR ($CDCl_3$): *cis* δ = 0.93 (d, $^3J_{PH}$ = 15.7 Hz, 6 H, CH_3), 6.46 („t"br, $^3J_{HH} \approx$ 7 Hz, 2 H, 4-H), 6.76 („t", $^3J_{HH} \approx$ 8.0-8.3 Hz, 2 H, 5-H), 6.99 (dd, $^3J_{HH}$ = 8.3, $^4J_{PH}$ = 4.2 Hz, 2 H, 6-H) 7.15-7.25 (m, 2 H, 3-H), 7.40-7.50 (m, 4 H, Ph), 7.51-7.62 (m, 6 H, Ph); *trans* δ = 1.34 (τ, *N* = 15.9 Hz, CH_3), 6.62 („t"br, $^3J_{HH} \approx$ 7.6 Hz, 4-H), 6.89 (d br, $^3J_{HH} \approx$ 8 Hz, 6-H), 8.18 (m), other signals superimposed. **^{13}C{^{1}H} NMR** ($CDCl_3$): δ = 27.7 (d, *J* = 2.2 Hz, C*Me*$_3$), 37.5 (m$_{ABX}$, *N* = 27.8 Hz, *C*Me$_3$),114.6 (τ, *N* ≈ 7 Hz, C-4), 115.9 (m$_{ABX}$, *N* = 50.5 Hz, C-2), 119.3 (τ, *N* = 17.3 Hz, C-6), 128.6 (τ, *N* = 9.8 Hz, C-*m*), 130.0 (m$_{ABX}$, *N* = 44 Hz, C-*i*) 131.2, 132.1 (2s, C-3 and C-*p*), 133.4 (τ, *N* = 8.9 Hz, C-*o*), 133.9 (s, C-5), 176.7 (τ, *N* ≈ 12 Hz, C-1). **^{31}P{^{1}H} NMR**: δ($CDCl_3$) = 59.4, 42.8; δ(C_6D_6) = 59.3, 43.1; in both solvents intensity ratio of *cis* to *trans* ca. 94:6 %.

4f: The ratio of the originally two pairs of diastereoisomers based on ^{1}H NMR integration is roughly 55:45 % ($_w$ = weaker signal).

^{1}H NMR (C_6D_6): δ = 1.32$_w$, 1.34 (both d, $^3J_{PH}$ = 15.8 Hz, 18 H, *t*Bu$_{chelate}$), 1.52$_w$, 1.65 (both d, $^3J_{PH}$ = 14.9 Hz, 18 H, *t*Bu$_{open}$), 6.45-6.60 (m, 4 H), 6.85-7.35 (m), 7.31 (tm, 2 H), 7.91 (tm, 2 H), 8.10-8.20 (m, 4 H), 11.59, 11.65 (2 s, 2 H, OH). **^{31}P{^{1}H} NMR** (C_6D_6): δ = 33.4$_w$, 36.2, 54.6, 55.2$_w$ (each d, $^2J_{PP}$ = 441.1 Hz).

Single crystals of **4f** were grown from an ethereal solution of the crude product of a separate experiment by slow mixing (overlayering) with hexane; for crystal structure analysis see below.

Crystal Structure Analysis.

Data collection: A crystal of **4d** 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$_\alpha$ radiation and corrected for absorption (program SADABS)

Structure refinement: The structure was refined anisotropically on F^2 using the program SHELXL-97 [25]. Hydrogen atoms were refined either freely (OH), as rigid methyls, or using a riding model. The butyl carbons C52-54 are disordered over two positions in the ratio 9:1.

The crystallographic data are listed in Table 5. For selected bond lengths and angles of **4f** see Tables 1 and 2. Crystallographic data for **4f** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-228472. 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].

Table 5 Crystal data and structure refinement of **4d**.

Empirical formula	$C_{32}H_{36}ClO_2P_2Pd$
Formula weight	656.40
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 10.9610(8) Å b = 18.2488(12) Å β= 110.062(4)° c = 15.9307(11) Å
Volume	2993.2(4) Å^3
Z	4
Density (calculated)	1.457 Mg/m^3
Absorption coefficient	0.844 mm^{-1}
F(000)	1348
Crystal size	0.20 x 0.13 x 0.05 mm^3
Theta range for data collection	1.76 to 28.28°
Index ranges	$-14 \le h \le 14, -24 \le k \le 24, -21 \le l \le 21$
Reflections collected	56564
Independent reflections	7422 [R(int) = 0.0706]
Completeness to theta = 28.25°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.928 and 0.821
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7422 / 6 / 364
Goodness-of-fit on F^2	0.944
Final R indices [I>2sigma(I)]	R1 = 0.0316, wR2 = 0.0635
R indices (all data)	R1 = 0.0578, wR2 = 0.0692
Largest diff. peak and hole	0.588 and −0.430 e. Å^{-3}

Polymerization

a) Catalyst preparation: The catalyst components given in Table 4 were dissolved or suspended in the given solvent (total volume 20 mL) and united at 0 °C or, in preparations using *n*BuLi, at −30 °C. In experiment 8, $NiBr_2$·1.1DME was added to the solution obtained from **2b** and *n*BuLi at −30 °C after stirring for 15 min at 20 °C.

b) Polymerization of ethylene. A 75 mL stainless steal autoclave equipped with gas and catalyst inlet valve, manometer and safety diaphragm was charged with the catalyst solution or suspension and ethylene, placed into a preheated bath (100 °C), and heated for 15-20 h. The pressure was registered online (HEJU pressure sensor 1-100 bar, Juchheim, connected to digital multimeter and PC). (The initial pressure increase in Figures 2-4 is attributed to the increasing temperature. According to internal calibration in absence of catalyst the temperature rises to 80 °C within 12-14 min. and reaches 100 °C after 25-30 min). After cooling the autoclave to 0-5 °C unreacted ethylene was allowed to escape, and the reaction mixture was transferred to a flask. Polyethylene was separated from the liquid, was stirred for 1 d with methanol / hydrochloric acid (1:1), washed with methanol and with CH_2Cl_2, and the residue was dried in vacuum. The solvent and liquid oligomers were distilled off (bath ca. 150 °C, 1.5 Torr) for GC analysis. For further details see in ref. [12].

c) Characterization of poly- and oligomers. ^{1}H NMR spectra of polyethylene were measured at 100 °C using concentrated solutions in C_6D_5Br prepared by swelling for 1 d at 120 °C under argon, acquisition time 4.9-5.4 s, delay 1.0 s. Oligomers were analyzed by GC (HP 57890) using a HP-5 capillary column (30m x 0.32mm x 0.25μm; 5 % phenyl methyl silicone), nitrogen as carrier gas, two isothermal runs at 35 and 100 °C, detection by FID and identification by selected reference samples and the Kovats-Index.

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