

Nickel Chelate Complexes of 2-Alkylphenylphosphanylphenolates: Synthesis, Structural Investigation and Use in Ethylene Polymerization

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2-Diphenylphosphanyl- and 2-alkylphenylphosphanyl-4-methylphenols **1** or their silyl ethers **2** and equimolar amounts of nickelocene react in benzene preferably to give orange-brown diamagnetic cyclopentadienylnickel chelate complexes $[\eta\text{-CpNi(P}^{\text{O}}\text{O)}]$ (**3**). Addition of a second equivalent of **1** or **2** affords (*RR*) and (*SS*) diastereoisomers of *cis*-bis($\text{P}^{\text{O}}\text{O}$ -chelates) **4a–c** (*R* = Ph, Me, *i*Pr) or the unsymmetrical *cis*-bis($\text{P}^{\text{O}}\text{O}$ -chelate) **5**, whereas with bulkier substituted derivatives **1d** or **2d** (*R* = *t*Bu) the second step is

hindered or retarded. The reactivity of **1d** remains high towards nickel salts in polar solvents, but in contrast to **1a–c**, yielding **4**, a sparingly soluble green *trans*-bis($\text{P}^{\text{O}}\text{O}$ -chelate) nickel complex **6d** is formed. Complexes formed in situ from **1** or **2** and Ni(COD)_2 in toluene catalyze the polymerization of ethylene. The cyclopentadienyl ($\text{P}^{\text{O}}\text{O}$) complexes **3**, however, are too stable to be active in this process. The crystal and molecular structure of **3c** and **4c** are described.

Introduction

Functionalized phosphanes containing hard and soft donor centers allow various coordination modes with transition metals in high or low oxidation states and thus have attracted considerable interest in complex chemistry and homogenous catalysis. Tertiary 2-phosphanylphenolates^[1–3] prefer bis($\text{P}^{\text{O}}\text{O}$ -chelate) transition-metal complexes;^[2,4] these are remarkably stabilized, are formed even by dealkylation of 2-phosphanylphenyl-alkyl ether complexes^[5] and are able to undergo *O,O'*-coordination with a second hard metal ion.^[6] Furthermore, monophosphanylphenolate chelate complexes bearing an additional phosphane molecule,^[7] a solely *P*-coordinate 2-phosphanylphenol or a cyclopentadienyl ligand^[2,8,9] are known. Very recently, phenylnickel diphenylphosphanylphenolate phosphane complexes were reported.^[10] In view of the crucial role of mono($\text{P}^{\text{O}}\text{O}$ -chelate) species in the industrially important homogenous nickel-catalyzed oligomerization of ethene (Shell Higher Olefin Process, SHOP),^[11] we investigated complex chemical reactions of various *P*-substituted 2-phenylphosphanyl-4-methylphenols **1a–d** and their *O*-trimethylsilyl ethers **2a–d** with nickelocene in toluene, some nickel salts or complexes in more polar solvents and the polymerization with catalysts obtained from phosphanyl-

phenols and Ni(COD)_2 . The influence of substituents on the polymerization will be reported separately.

Results and Discussion

Reactions

2-Diphenylphosphanyl-4-methylphenol (**1a**) and an equimolar amount of nickelocene in benzene afford the cyclopentadienyl($\text{P}^{\text{O}}\text{O}$ -chelate)nickel complex **3a** ($\delta^{31}\text{P}$ = 37.8; $\Delta\delta$ = 65 ppm) and a small amount of *cis*-($\text{P}^{\text{O}}\text{O}$)₂Ni (**4a**) ($\delta^{31}\text{P}$ = 34.4; $\Delta\delta$ = 61.6 ppm) (Scheme 1). 2-Isopropylphenylphosphanyl-4-methylphenol (**1c**) exhibits a higher selectivity for monosubstitution and is isolated as pure orange-brown **3c** ($\delta^{31}\text{P}$ = 50.5; $\Delta\delta$ = 80.3 ppm) from a benzene solution at 20°C. Contamination by **4c** is observed if the complex is precipitated by ether or, markedly increased, on heating solutions of **1c** or **2c** with nickelocene. The silyl ethers **2** are less reactive than **1** and the higher temperatures required favor contamination by **4**. Reactions of the methyl- (**1b**, **2b**) or *tert*-butyl derivatives (**1d**, **2d**) with nickelocene (1:1) in benzene furnish brown diamagnetic substances, which are highly soluble in benzene, THF, CH_2Cl_2 or chloroform. NMR spectra of the products give evidence of monosubstitution of the *tert*-butyl derivatives, whereas disubstitution to **4b** is preferred for the sterically less demanding methyl species. This is seen in the ¹H-NMR spectra by pseudotriplets for the *P*-methyl protons. A side product with $\delta^{31}\text{P}$ = 26.4 (ca. 15%) in the reaction with **2b**, which could not be isolated, is tentatively assigned to **3b**. Like the other η^5 -cyclopentadienyl($\text{P}^{\text{O}}\text{O}$ -chelate)nickel complexes, it exhibits modest larger values of the typical downfield coordination shift of five-membered chelate complexes^[12] than the *cis*-bis(phosphanylphenolato)nickel com-

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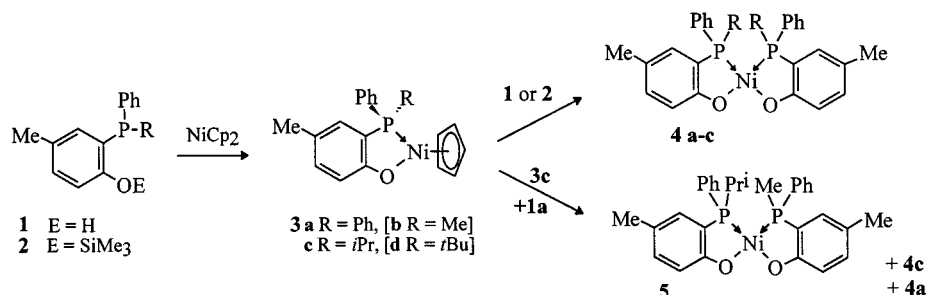
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plexes **4** with O[−] donors *trans* to the phosphorus atoms (Table 1).

2). The bulkier *tert*-butyl derivatives react differently to the others, forming brown solutions of **4a–c**, by precipitation



Scheme 1. Reactions of **1** or **2** with nickelocene

Table 1. ³¹P chemical shifts of **1a–d**, **3a–d**, **4a–c**^[a] and **6d** and coordination chemical shifts Δδ

R	δ (1)	δ (3)	Δδ (3–1)	δ (4a–c) [δ (6d)]	Δδ (4–1) [Δδ (6d–1d)]
a Ph	−27.2	37.8	65	34.4	61.6
b Me	−50.9	26.4 ^[b]	77.3	21.9 ^[c]	72.8
c <i>i</i> Pr	−29.8	50.5	80.3	45.3	75.1
d <i>t</i> Bu	−18.7	57.1 ^[b]	75.8	[24.4] ^[d]	[43.1] ^[d]

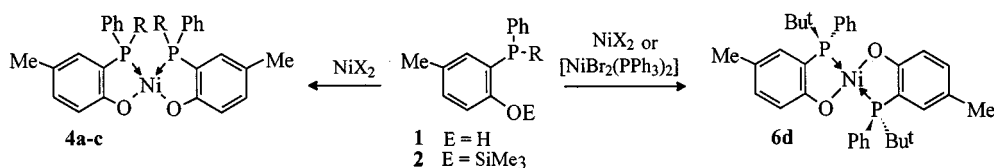
^[a] Spectra in CDCl₃. — ^[b] Substance not isolated, tentative assignment. — ^[c] ³¹P resonance of a minor isomer at δ = 20.0. — ^[d] Solid-state NMR data.^[19]

The reaction of nickelocene with two equivalents of **1a–c** or **2a–c** in benzene smoothly gives *cis*-bis(P–O-chelate)nickel complexes **4a–c**, indicating an easy replacement of the second cyclopentadienyl ligand in the 18-valence-electron complexes **3**. Similarly, addition of **1b** to **3c** yields the unsymmetrical *cis*-[Ni(P[∘]O)(P[∘]O)] chelate complex **5**. Contamination by **4c** and to a smaller amount by **4b** (ratio roughly 60:30:10) provides evidence that ligand substitution is not limited to the cyclopentadienyl anion but involves also the (P[∘]O-chelate) group. The reaction of nickelocene with two equivalents of the *tert*-butyl-substituted 2-phosphanylphenol derivatives **1d** or **2d** in benzene does not proceed completely. Neither **4d** nor **6d** can be detected. It is assumed that the conversion in benzene is hindered or slowed for steric reasons. In polar solvents, however, the ligand exchange is much faster, and bis(P[∘]O)nickel complexes are formed with **1a–c** or **2a–c** as well as with **1d** or **2d**. The reason is the high driving force for the bis(phosphanylphenolato)nickel complexes which are also the usual products in reactions with nickel acetylacetonate, with aqueous nickel salts in methanol, or anhydrous nickel salts in THF if a sufficient amount of base or buffer is added. Similarly, attempts to prepare [(Ph/*t*BuP[∘]O)NiBr(PPh₃)_n] by reacting **1d(Li)** with NiBr₂·2PPh₃ in ether in an equimolar ratio failed in favor of the bis(P[∘]O)nickel complex (Scheme

of a diamagnetic green *trans*-bis(P[∘]O-chelate)nickel complex **6d** which is insoluble or sparingly soluble in all common organic solvents.

Catalysis

The organonickel phosphanylphenolates **3** are structurally related to organonickel phosphanylenolates,^[9,13–15] which form the catalytically active species in the Shell Higher Olefin Process.^[10] Attempts to oligomerize ethylene by using the cyclopentadienylnickel complex **3c** at 40 bar and 140 °C failed, however. The reason is, that despite the easy replacement of the cyclopentadienyl group by **1** or **2**, the semisandwich complexes **3** are thermally very stable and are unable to form catalytically active η¹-CpNi- or NiH-(PO-chelate) complexes. DTA of **3c** indicates loss of cyclopentadiene only at 190–210 °C (endothermic). Complete decomposition of the Ni(P[∘]O-chelate) structure occurs at 280–340 °C. For comparison, the thermal degradation of **4c** proceeds in the same temperature range (280–340 °C) after an exothermic process at 271 °C, whereas **5d** starts to decompose at even higher temperature (310–340 °C). The importance of the loss of the cyclopentadienyl group for catalytic activity was demonstrated for the less stable related



Scheme 2. Reactions of **1** or **2** with nickel salts

phosphanylenolate complex $[\text{Ni}(\eta^5\text{-Cp})\{\text{Ph}_2\text{PCH}=\text{C}(\text{Ph})\text{O}\}]$ (decomp. at 130°C) which like other nickel enolate complexes becomes active at the decomposition temperature and thus gives evidence that the remaining (phosphanylenolato)nickel hydride represents the starting catalyst.^[11,13b] That less stable organonickel complexes obtained from phosphanylphenols and $\text{Ni}(\text{COD})_2$ catalyze the polymerization or oligomerization of ethylene was first claimed by Singleton.^[16] A catalyst prepared from *o*-diphenylphosphanylphenol and $\text{Ni}(\text{COD})_2$ was found to convert ethylene in high yield (95%) to linear polyethylene and a lower amount of linear oligomers whereas a catalyst prepared with 2-diethylphosphanylphenol was found to be much less active (conversion 3.5%) and shows high preference for lower oligomers (C_4 68%, C_6 24%, C_8 4.3%). The recently reported phenylnickel phosphanylphenolate phosphane complexes^[10] and an immobilized $[\text{PhNi}(\text{PPh}_3)(2\text{-Ph}_2\text{P-6-HO-C}_6\text{H}_3\text{O}^-)]$ (P^{O} -chelate) complex^[17] were found to oligomerize ethylene. We observed that complex solutions prepared from the alkylarylphosphanylphenol **1c** or its silyl ether **2c** and equimolar amounts of $\text{Ni}(\text{1,5-COD})_2$ form catalysts for the formation of polymers and smaller amounts of oligomers of ethylene with high selectivity for linear structures (Scheme 3). Toluene was used as the solvent to avoid conversion into the catalytically inactive bis(phosphanylphenolato)nickel complex **4c**, which as seen above, is strongly favored in more polar solvents. Indeed, no catalytic activity was observed if the reaction was run in ethanol. In toluene, at 50 bar/ 160°C , the oligomer-to-polymer ratio was 15%:85%. The oligomer portion consisted of linear olefins, mainly from C_6 to C_{26} with a flat maximum at $\text{C}_{16}/\text{C}_{18}$. The polymer exhibits sharp absorptions for vinyl end groups at 909 and 991 cm^{-1} ($\tilde{\nu}_{\text{C}=\text{C}}$ 1641 cm^{-1}) and a small band for CH_3 at 1368 cm^{-1} but only weak bands for the *trans*- $\text{CH}=\text{CH}$ or $\text{C}=\text{CH}_2$ groups and no indications of branching.^[18] X-ray powder diffraction revealed high crystallinity. A molar mass distribution with $M_w = 9310\text{ g mol}^{-1}$ (corresponding to $n = 330$) and $M_n = 6087\text{ g mol}^{-1}$ was determined. The results with **1c** and **2c** are similar and can be attributed to the easy formation of (P^{O} -chelates) in both cases, as was also found in the reaction with nickelocene.

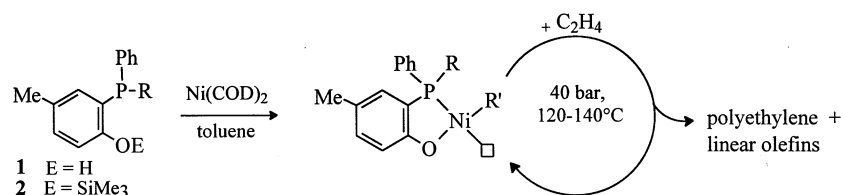
Structure Investigations

Compounds **3–5** are sparingly soluble in hexane or ether but easily soluble in benzene, CH_2Cl_2 , chloroform or THF, allowing structure elucidation by multinuclear NMR spec-

tra. **6d**, obtained as powder or microcrystals, was not sufficiently soluble for solution-NMR studies, and therefore was structurally characterized in comparison with **4c** by a solid-state ^{31}P -NMR investigation which is reported separately.^[19] The solid-state structures of **3c** and **4c** were determined by single-crystal X-ray structure analysis.

^{13}C -NMR data of **3c** indicate unambiguously the semi-sandwich arrangement by a doublet for the cyclopentadienyl group and typical doublet or singlet signals for the phosphanylphenolate ligand with $J(^{31}\text{P}^{13}\text{C})$, depending on the position towards the phosphorus atom. Proton, CH-COSY and phosphorus-NMR data of **3c** support the proposed structure. The assignment of the proton signals of **3a**, **3b** and **3d** was done by comparison with those of **3c**. In the solid state, **3c** crystallizes in the centrosymmetric space group *P*-1 with two independent molecules in the asymmetric unit, which show no significant deviations. The molecular structure of **3c** (Figure 1) shows a perpendicular arrangement of the Cp^- moiety and the planar (P^{O}) chelate ring (89.1 and 88.5°), with the Ni atom only slightly distorted from this plane. The distance from Ni to the cyclopentadienyl carbon atom (C_{21} and C_{39} , respectively) placed in the *trans* position to the oxygen atom, are significantly shorter than are the Ni–C distances to the remaining cyclopentadienyl carbon atoms. This indicates a stabilization of the Ni–C bond by the phenolate *trans* coordination which for related catalytically active organonickel phosphanylphenolate species is important for the chain growth in the polymerization or oligomerization of ethylene. The C–P–C angles are typical for tetracoordination at the phosphorus atom, whereas the small P–Ni–O and $\text{C}_{\text{aroxy}}\text{–P–Ni}$ angles result from geometric factors of the rigid five-membered ring and the bond lengths. The slight increase of the P–Ni–O angle (by $2\text{--}3^\circ$) in comparison to (diphenylphosphanylenolato)-^[13–15] and (diphenylphosphanylalkoxido)nickel complexes^[20,21] is consistent with a shorter P–Ni bond length (ca. 5 pm) within the ring.

In solution ^1H - and ^{13}C -NMR spectra of **4**, various nuclei show “triplets” or other multiplets representing the A_n or A_nA_n' part of A_nXX' or $A_nA_n'XX'$ spin systems by coupling with two ^{31}P nuclei (X, X') and hence, reveal the bis(P^{O} -chelate) nature of **4**. The appearance depends on the relative magnitudes and signs of all coupling constants in the spin system.^[22,23] Whereas the *cis* geometry of **5** is deduced from $^2J_{\text{PP}} = 80\text{ Hz}$, which is much smaller than $^2J_{\text{PP}}$ in *trans*-methylnickel(phosphanylphenolato) PMe_3 complexes (ca. 316 Hz),^[24] the geometry of **4** cannot easily be derived from the NMR data. In the proton spectrum



Scheme 3

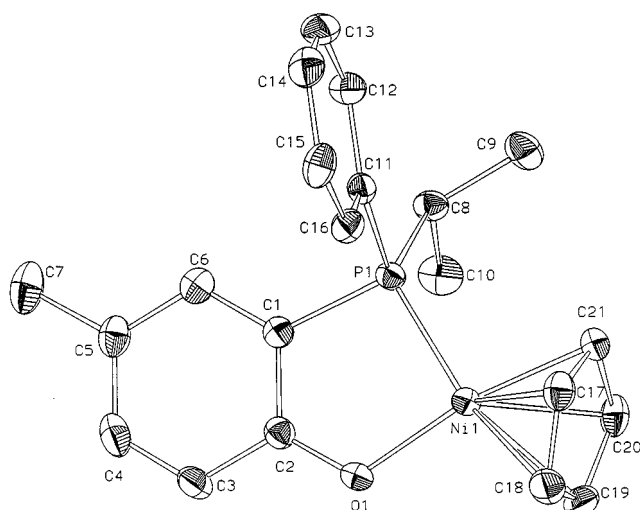


Figure 1. ORTEP plot of **3c**; selected bond lengths [Å] and angles [°], corresponding data for the second independent molecule are given in brackets: Ni1–P1 2.126(2) [2.132(2)], Ni1–O1 1.889 (3) [1.885(3)], Ni1–C21 2.048(4) [2.048(4)], Ni1–(C17–20) 2.144(4)–2.155(4) [2.146–2.162(4)], P1–C1 1.807(4) [1.807(4)], P1–C11 1.819(4) [1.823(4)], P1–C8 1.840(3) [1.850(3)], O1–Ni1–P1 89.49(11) [89.56(12)], Ni1–P1–C1 98.90(13) [98.48(14)], C2–C1–P1 111.9(2) [112.3(2)], C2–O1–Ni1 118.3(1) [118.1(2)], O1–C2–C1 121.5(3) [121.5(3)], C1–P1–C11 105.7 (2) [107.4(2)], C1–P1–C8 107.0(2) [106.2(2)]

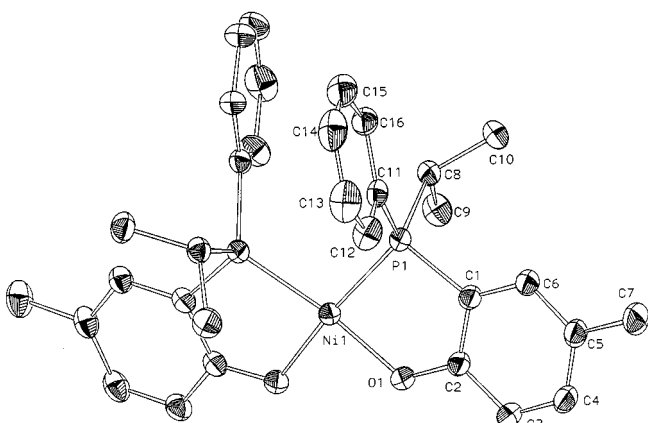


Figure 2. ORTEP plot of **4c**; selected bond lengths [Å] and angles [°]: Ni1–P1 2.1423 (13), Ni1–O1 1.885 (2), P1–C1 1.800 (2), P1–C11 1.814 (3), P1–C8 1.844 (3); P1–Ni1–P1 97.93 (7), O1–Ni1–O1 87.50 (11), O1–Ni1–P1 87.50 (8), Ni1–P1–C1 99.22 (10), C2–C1–P1 110.9 (2), C2–O1–Ni1 118.7 (2), O1–C2–C1 121.6 (2), C1–P1–C11 107.16 (12), C1–P1–C8 109.55 (12); symmetry transformation used to generate equivalent atoms: $\bar{x}, y, -z + 1/2$

of **4c** multiplets are observed for the diastereotopic methyl groups of PCHMe₂ resembling a “doublet of a doublet” and a “filled-in doublet” with doublet splitting of the external lines. Pseudotriplets by coupling with two ³¹P nuclei ($|J_{XX'}| > |J_{AX} - J_{AX'}|$) are observed in the proton spectra of **4b** (PMe) or **6d** (PCMe₃) as well as in the ¹³C-NMR spectra of **4b,c**. The two external lines in the five-line pattern in the A part (¹³C) depend significantly on ²J_{PP} and should allow an assignment of the geometry. However, the intensity of these lines is too low, even for the resonances of C2 or C₄(Ph), which exhibit the largest ³¹P–¹³C coup-

lings and should display the most intensive external lines. As mentioned above, the geometry of **4c** was determined by solid-state investigations.^[19] From the ³¹P-CP/MAS NMR study, a two-bond coupling constant ²J_{PP} of ca. 75 Hz was determined, thus indicating *cis* geometry. Detailed structural information is provided by the single-crystal X-ray structure analysis indicating a slightly distorted square-planar *cis* configuration of **4c** (Figure 2). The molecule has a crystallographic two-fold axis through the Ni atom yielding the (*RR*) or (*SS*) configuration. The P–Ni–O and P'–Ni–O' planes are twisted by 7.1°. The distances and angles within the five-membered rings are similar to those in **3c** (P–Ni–O less by 2°). The O–Ni–O' angle (87.5°) is somewhat smaller than 90° whereas the P–Ni–P' angle is considerably widened in order to reduce steric repulsion of the P substituents. For the sterically less hindered methyl derivative **4a**, we observe characteristic ³¹P- and ¹H-NMR signals of a second nickel atom bis(P⁺O-chelate) (B) (about 15%), which gives evidence of the existence of *rac* and *meso* isomers of **4a**.

The bulkier nickel bis(2-*tert*-butylphenylphosphanyl-4-methylphenolate) (**6d**), resembling *trans*-[Ni(*t*Bu₂P–C₆H₄O)₂]^[2a] and *trans*-[Ni(Ph₂PCH₂R₂O)₂] (R = CF₃)^[20] in its unusual green color and low solubility, prefers an (*RS*)/(*SR*)-*trans* configuration with an inversion center at the nickel atom, as established by the high symmetry found in the solid-state ³¹P-NMR investigation.^[19] The low coordination shift of Δδ(³¹P) = 43 ppm for **6d** as compared to Δδ(³¹P) = 61–75 ppm for **4a–c** may be indicative for the different geometry but the lack of data for comparison needs further investigations to establish such a dependence.

Conclusion

(P⁺O-chelate)nickel(II) complexes **3–6** containing phosphanylphenolato ligands may be obtained by reaction of phosphanylphenols **1** or their silyl ethers **2** with nickelocene or nickel salts. Monochelates are formed with nickelocene in benzene. Small substituents, addition of polar solvents or increased temperature favor formation of bis(P⁺O-chelate)nickel complexes. Complexes formed in situ from **1c** or **2c** and equimolar amounts of Ni(COD)₂ in toluene were found to catalyze the formation of linear polymers and a smaller amount of oligomers of ethylene. From the slower formation of catalytically inactive **6d** from **1d** and nickelocene in benzene or toluene, it may be concluded that bulkier organonickel 2-phosphanylphenolate (P⁺O-chelate) complexes form interesting catalysts for olefin oligomerization or polymerization. The strengthening of the Ni–C bond in the *trans* position to the oxygen atom, as observed in **3c**, suggests a strong influence of donor properties at the O[–] site on the chain length of polyethylene. A more detailed study on the influence of steric and electronic effects of substituents at the phosphorus atom and the aroxy group on polymerization or oligomerization of ethylene is in progress.

Experimental Section

General: All reactions were carried out under argon, using Schlenk techniques and freshly distilled dry solvents. Synthesis, properties and structures of the *P*-tertiary *o*-phosphanylphenols have been described elsewhere.^[3b] Thermal analyses were carried out with a TGDTA92 (SETARAM) instrument. UV-Vis spectra were recorded with a Lambda19 spectrometer (Perkin–Elmer), mass spectra with a single-focussing mass spectrometer AMD40 (Intectra). NMR spectra were measured in CDCl₃ (unless indicated otherwise), using a multinuclear FT-NMR spectrometer ARX300 (Bruker) at 300.13 (¹H), 75.47 (¹³C), and 121.49 (³¹P) MHz. Shift references are tetramethylsilane for ¹H and ¹³C, and H₃PO₄ (85%) for ³¹P. For resonances which are part of a A_{*n*}X₂ spin system (X = ³¹P) *vc* denotes “virtual coupling”, *τ* the usual triplet appearance of the A resonance (*n* = 1) and *N* = |*J* + *J'*|.

Reactions of 1 and 2 with Nickelocene in Equimolar Ratio. – Cyclopentadienyl(2-diphenylphosphanyl-4-methylphenolato)nickel (3a): A solution of **1a** (900 mg, 3.08 mmol) in benzene (10 mL) was added to a solution of nickelocene (580 mg, 3.07 mmol) in benzene (10 mL) and stirred for 2 h. Most of the solvent (ca. 18 mL) was removed in vacuo and ether (5 mL) was added to give 1.15 g of an orange-brown precipitate, consisting of **3a** and **4a** (ca. 70%:30%, d³¹P = 37.8, 34.5). Column chromatography on silica gel yielded 0.7 g (55%) of pure **3a** by elution with CHCl₃/acetone (10:1). – ¹H NMR: δ = 2.13 (s, 3 H, 4-Me), 5.31 (s, 5 H, Cp), 6.63 (d, ³J_{HH} = 7–8, ⁴J_{PH} = 5.5 Hz, 1 H, 6-H), 6.87 (d, ³J_{HH} = 7–8 Hz, 1 H, 5-H), 6.87 (d, ³J_{PH} = 10 Hz, 1 H, 3-H), 7.35–7.55 (m, 6 H, *m,p*-H), 7.65–7.8 (m, 4 H, *o*-H). – C₂₄H₂₁NiOP (415.10): calcd. C 69.44, H 4.80; found C 69.62, H 4.95.

Cyclopentadienyl(2-isopropylphenylphosphanyl-4-methylphenolato)-nickel (3c): (a) A solution of **1c** (274 mg, 1.06 mmol) in benzene (10 mL) was added to nickelocene (200 mg, 1.06 mmol) in benzene (10 mL). After 1 d, about 80% of the solvent was removed. Within 3 d, 216 mg (53%) of orange-brown **3c** crystallized, m.p. 184°C. – UV/Vis [MeOH; λ_{max}/nm (ε/M^{–1}cm^{–1}): 454 (880), 301 (1700), 267 (1500), 226 (sh, 2600). – ¹H NMR and CH COSY (C₆D₆): δ = 0.99 (dd, ³J_{PH} = 18.5, ³J_{HH} = 7.0 Hz, 3 H, Me_A), 1.17 (dd, ³J_{PH} = 16.8, ³J_{HH} = 6.9 Hz, 3 H, Me_B), 2.04 (m, 1 H, CH), 2.07 (s, 3 H, 4-Me), 5.18 (s, 5 H, Cp), 6.81 (d, ³J_{HH} = 8.5, 1 H, 5-H), 6.97 (dd, ³J_{HH} = 8.5, ⁴J_{PH} = 5.5 Hz, 1 H, 6-H), 7.07 (s, 1 H, 3-H), 6.94 (m, 1 H, *p*-H), 7.06 (m, 2 H, *m*-H), 7.66 (m, *o*-H). – ¹³C NMR (C₆D₆): δ (*J*_{PC}) = 18.2 (d, 1.9 Hz, Me_B), 18.8 (d, 5.6 Hz, Me_A), 20.4 (s, Me-4), 27.4 (d, 31.0 Hz, CH), 91.4 (d, 1.8 Hz, Cp), 117.9 (d, 51.1 Hz, C_q-2), 119.3 (d, 9.9 Hz, C-6), 121.9 (d, 7.0 Hz, C_q-4), 128.9 (d, 10.4 Hz, 2 C-*m*), 129.9 (d, 2.6 Hz, C-3), 130.5 (s, C-*p*), 131.9 (d, 10.3 Hz, 2 C-*o*), 134.1 (d, 1.7 Hz, C-5), 134.2 (d, 43.3 Hz, *i*-C), 176.1 (d, Hz, C_q-1). – ³¹P {¹H} NMR: δ = 50.4. – C₂₁H₂₃NiOP (381.1): calcd. C 66.19 H 6.08 P 8.13; found C 66.26 H 6.48 P 7.76. – (b) 965 mg of **2c** (2.9 mmol) in benzene (10 mL) was added to nickelocene (545 mg, 2.9 mmol) in benzene (10 mL). No visible reaction took place within 5 d at 20°C, but on reflux (24 h) a dark brown solution was formed. Work up as above afforded 750 mg (70%) of **3c**, m.p. 185°C. A trace of **4c** was formed besides **3c**. The proportion increased up to 1:3 in larger runs and on precipitation with ether from the benzene solution. Single crystals of **3c** and of **4c** were grown from benzene/nitromethane (ca. 1:1) solution.

Reactions of Nickelocene with Two Equivalents of 1 or 2. – *cis*-Bis(2-isopropylphenylphosphanyl-4-methylphenolato)nickel (4c): (a) Nickelocene (831 mg, 4.4 mmol) in benzene (10 mL) was added to **1c** (2.27 g, 8.8 mmol) in benzene (10 mL). The color turned from green to brown within 1 h, and an orange-brown precipitate was formed after refluxing for 30 min. After removing a part of the

solvent, the suspension was filtered, **4c** was washed with a little benzene and dried at 10^{–2} Torr (8 h) affording 1.65 g (65%) of an orange powder, m.p. 278–280°C. – ¹H NMR and CH COSY: δ = 0.98 (dd, ³J_{PH} = 12.7, ³J_{HH} = 6.8 Hz, 6 H, Me_A), 1.24 (m, 2 H, CHMe₂), 1.41 (vc, ³J_{HH} ≈ 7 Hz, 6 H, Me_B), 2.08 (s, 6 H, 4-Me), 6.42 (vc, 2 H, 3-H), 6.88 (dt, ³J_{HH} = 8.6, *N* = 5.2 Hz, 2 H, 6-H), 7.02 (br. d, ³J_{HH} = 8.6 Hz, 2 H, 5-H), 7.40 (m, 4 H, *o*-H), 7.51 (m, 4 H, *m*-H), 7.60 (m, 2 H, *p*-H). – ¹³C NMR: δ (*N*_{PC}) = 16.6 (τ, *N* = 8.2 Hz, Me_B), 19.4 (τ, *N* = 6.8 Hz, Me_A), 20.0 (s, Me-4), 23.0 (τ, *N* = 28.1 Hz, CH), 112.9 (τ, *N* = 54 Hz, C_q-2), 118.2 (τ, *N* = 13.8 Hz, C-6), 123.5 (τ, *N* = 6.9 Hz, C_q-4), 128.8 (τ, *N* = 10.0 Hz, C-*m*), 129.2 (τ, *N* = 46.3 Hz, C-*i*), 131.0 (s, C-*p*), 131.4 (s, C-3), 132.1 (τ, *N* = 8.3 Hz, C-*o*), 135.2 (s, C-5), 175.1 (τ, *N* = 16.6 Hz, C_q-1). – ³¹P {¹H} NMR: δ = 45.3. – C₃₂H₃₆NiO₂P₂ (573.27): calcd. C 67.05 H 6.33 Ni 10.24 P 10.81; found C 66.76 H 6.66 Ni 10.56 P 10.27. (b) A solution of nickelocene (493 mg, 2.6 mmol) and **2c** (1.73 g, 5.2 mmol) in benzene (30 mL) was refluxed for 3 d to afford a brown solution. Most of the benzene was removed by distillation. From the residual suspension (ca. 3 mL) the solid was separated by filtration and washed with cold benzene (1 mL) yielding 319 mg (21%) of **4c**, m.p. 285°C. – ³¹P NMR: δ = 45.3.

Reaction of 1b with 3c: A solution of **3c** (0.95 g, 2.5 mmol) in benzene (10 mL) was added to **1b** (0.57 g, 8.8 mmol) in benzene. About 12 mL of benzene was distilled off. 1.1 g of a brown precipitate was separated from the resulting viscous solution and analyzed by ³¹P NMR (CDCl₃). The precipitate was found to be a mixture of the unsymmetrical *cis*-bis(P^oO-chelate) **5** and the symmetrical *cis*-bis-(P^oO-chelates) **4c** and **4b** (intensity ratio roughly 60:30:10). – ³¹P {¹H} NMR of **5**: δ = 46.4 (d), 21.7 (d), ²J_{PP} = 80 Hz.

Reactions of 1 or 2 with Nickel Salts or Complexes. – *cis*-Bis(2-diphenylphosphanyl-4-methylphenolato)nickel (4a): NiCl₂·6H₂O (650 mg, 2.74 mmol) was dissolved in hot methanol (20 mL), and a solution of **1a** (1.6 g, 5.48 mmol) in methanol (5 mL) was added. A rapid color change to orange started on addition of Et₃N of which a total of 1.1 g (10.9 mmol, ca. 100% excess) was added. After removing the solvent, the solid residue was crystallized from MeOH/CH₂Cl₂ (1:1) and dried for 2 h at 10^{–2} Torr to yield 1.4 g (80%) of orange-brown **4a** containing a small amount of water. – ¹H NMR: δ = 2.04 (s, 6 H, 4-Me), 3.50 (s, 2 H, H₂O), 6.47 (vc to br. τ, 2 H, 3-H), 6.89 (dt, ³J_{HH} = 8.7, *N* = 5.5 Hz, 2 H, 6-H), 7.02 (br. d, ³J_{HH} = 8.7 Hz, 2 H, 5-H), 7.42 (m, 4 H, *o*-H), 7.10 (τ, ³J ≈ 7.4–7.6 Hz, 4 H, *m*-H), 7.32 (τ, *J* ≈ 7.3–7.5 Hz, 2 H, *p*-H). – ³¹P {¹H} NMR: δ = 34.4. – C₃₈H₃₂NiO₂P₂·H₂O (659.32): calcd. Ni 8.90; found Ni 8.85.

***cis*-Bis(2-methylphenylphosphanyl-4-methylphenolato)nickel (4b):** (a) A solution of **1b** (103 mg, 0.45 mmol) in ethanol (5 mL) was added to a warm solution of nickel acetate · 4 H₂O (57 mg, 0.23 mmol) in ethanol (10 mL), affording a yellow solution which slowly turned brown. The solvent was removed in vacuo (after 3 d), the remainder was extracted with CH₂Cl₂ and dried with Na₂SO₄. Hexane was added and a part of the solvent (mainly CH₂Cl₂) was evaporated in vacuo to yield a brown precipitate which was dried for 2 h at 10^{–2} Torr. 70 mg (59%) of two isomers of **4b** were obtained, isomer ratio (A)/(B) ca. 85%:15% with δ(³¹P) = 21.9, 20.0. – ¹H NMR: (A): δ = 1.09 (τ, *N* = 11.7 Hz, 6 H, PMe), 2.06 (s, 6 H, 4-Me), 6.43 (br. τ, *N* = 8–9 Hz, 2 H, 3-H), 6.87 (m, 2 H), 6.98 (m, 2 H), 7.4–7.6 (m, 10 H, Ph); (B): δ = 1.87 (τ, *N* = 11.1 Hz, PMe), other signals superimposed. – ¹³C NMR: δ (*N*_{PC}) = 9.1 (τ, *N* = 32 Hz, PMe), 20.0 (Me-4), 118.3 (τ, C-6), 124.6 (τ, C-4), 128.9 (C-*p*), 129.1 (τ, *N* = 10.6 Hz, C-*m*), 131.4 (τ, *N* = 10.6 Hz, C-*o*), 135.3 (C-5); weak intensities of C-1, C-2, C-*i* signals. – C₂₈H₂₈NiO₂P₂ (517.17): calcd. Ni 11.35; found Ni 11.08. – (b) An equimolar mixture of

2b (647 mg, 2.14 mmol) and nickel acetylacetonate (550 mg, 2.14 mmol) was refluxed for 8 h in benzene (30 mL) to give, after removal of 2/3 of the solvent, 188 mg (34%) of the bis(phosphanylphenolate) **4b**, m.p. 216–218°C. – UV/Vis [MeOH, λ_{max} /nm ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$): 403(400), 347 (1.300), 293 (sh), 281 (14.000), 220 (sh, 17.000). – $^{31}\text{P}\{^1\text{H}\}$ NMR: δ = 21.8.

cis-Bis(2-isopropylphenylphosphanyl-4-methylphenolato)nickel (4c): **2c** (193 mg, 0.59 mmol) and nickel acetylacetonate (54 mg, 0.21 mmol) were refluxed for 8 h in benzene (20 mL) to give, after removal of the bulk of the solvent, 88 mg (73%) of **4c**, NMR data as above.

trans-Bis(2-isopropylphenylphosphanyl-4-methylphenolato)nickel (6d): (a) 160.8 mg (0.735 mmol) of NiBr_2 and 170 μL of HBr (48%, 1.51 mmol) were dissolved in warm methanol and two equivalents of **1d** (400 mg, 1.47 mmol) in methanol (7 mL) were added. A transient brown color was observed in the mixing area, indicating an equilibrium with dominance of octahedral Ni^{2+} complexes in solution [λ_{max} /nm: 398 (st), 730 (w), 660 (sh)]. On buffering with excess sodium acetate the solution turned brown and 265 mg (60%) of green **6d** precipitated. – (b) A solution of **1d** (588 mg, 2.16 mmol) in THF (15 mL) was added to a suspension of $\text{NiBr}_2 \cdot 1.1\text{DME}$ (337 mg, 1.09 mmol) in 15 mL of THF. On addition of $\text{LiO}i\text{Pr}$ (2.3 mmol) the solution turned brown and a total of 415 mg (63%) of green **6d** precipitated. The reaction of $\text{NiBr}_2 \cdot 1.1\text{DME}$ with **2d** proceeded similarly. – (c) The best variant yielding microcrystalline **6d** was the following: Butyllithium in hexane (9.6 mmol) was added at -5°C to 3.26 g (9.46 mmol) of **2d** in THF (20 mL). A solution of $\text{NiBr}_2 \cdot 2\text{Ph}_3\text{P}$ (3.52 g, 4.73 mmol) in THF (40 mL) was added dropwise, forming a brown solution and, after 5–10 min, a green precipitate. The reaction was complete within 20–30 min and gave 2.06 g (73%) of microcrystalline, diamagnetic **6d**, m.p. 312–317°C (DTA 327.5°C with dec.). Above 120°C **6d** exhibited a reversible gradual color change via olive-green to yellow. The solubility in acetonitrile, nitromethane, methanol, acetone, benzene or hexane was very low and in THF, CHCl_3 or CH_2Cl_2 was just sufficient for UV/Vis spectra. – UV/Vis [THF; λ_{max} /nm, (relative intensities in satd. soln.)]: 611 (10), 434 (100), 391 (500), 320 st, 284 st, 275 st. – Solid-state NMR investigation see ref.^[19] – $\text{C}_{34}\text{H}_{40}\text{NiO}_2\text{P}_2$ (601.3): calcd. C 67.92, H 6.70, Ni 9.76, P 10.30; found C 67.36, H 6.83, Ni 9.63, P 10.26. – X-ray powder diffraction data and density (in ethanol) = $0.89\text{--}0.95\text{ g cm}^{-3}$ fit best with a triclinic crystal system with unit cell dimensions of $a_0 = 10.126\text{ \AA}$, $b_0 = 17.630\text{ \AA}$, $c_0 = 12.184\text{ \AA}$, $\alpha = 89.44^\circ$, $\beta = 90.55^\circ$, $\gamma = 89.98^\circ$, $Z = 2$.

Thermal Analysis: DTA/TG analyses of **3c**, **4c** and **6d** were performed under nitrogen. **3c**: mass lost at 190–210°C, $\Delta m_{210} = 17\%$, corresponding to cleavage of cyclopentadiene (endothermic); further continuously increasing mass lost at 280–340°C, $\Delta m_{350} \approx 70\%$, endothermic peak at 309°C. **4c**: mass lost at 280–340°C, $\Delta m_{350} = 66\text{--}72\%$, exothermic peak at 271°C, endothermic at 290°C. **6d**: mass lost at 310–340°C, $\Delta m_{350} = 72\%$, endothermic peak at 328°C.

Catalysis Experiments: **1c** (56.8 mg, 0.22 mmol) or **2c** (72.6 mg, 0.22 mmol) in toluene (10 mL) were added at 0°C to a solution of $\text{Ni}(\text{COD})_2$ (0.22 mmol) in toluene (10 mL). After stirring for 30 min, the solution was transferred into an autoclave, ethylene added until the pressure was 40 bar and heated for 12 h while stirring with a teflon-coated magnetic stirrer. **2c** was used first. At 60°C no conversion of ethylene occurred, at 120°C the pressure (8.7 g C_2H_4) decreased to 29 bar and polyethylene (3.65 g, 88% of converted ethylene) and a lower portion of linear olefins (C_4 to C_{26}) with a flat maximum at $\text{C}_{16}/\text{C}_{18}$ was isolated. The TON was 666. X-ray powder diffraction and IR revealed high crystallinity and low

branching of the PE. Use of a catalyst prepared from **1c** and $\text{Ni}(\text{COD})_2$ and 8.7 g of C_2H_4 at 140°C led similarly to PE (TON = 698; 3.64 g of HDPE, 85% of converted ethylene), m.p. 121°C; DTA (5 K/min): 131.8°C (up), 117.2°C (down). $M_w = 9310\text{ g mol}^{-1}$, $M_n = 6087\text{ g mol}^{-1}$. Ethylene (40 bar) heated with a solution of **3c** (37.3 mg) in toluene (20 mL) for 12 h at 140°C was not converted. A more detailed study of ethylene polymerization and oligomerization with varied phosphanylphenols is in progress and will be described elsewhere.

Crystal Structure Analysis: Crystal data are presented in Table 2, selected bond angles and bond lengths are given in the captions of Figures 1 and 2. – Data collection: The crystals were mounted on a glass fiber in inert oil and transferred to the cold gas stream (-55°C) of the diffractometer (Siemens-Stoe AED2). Data were collected in the ω -scan mode using monochromated $\text{Mo-K}\alpha$ radiation (0.71073 Å). – Solution and refinement: The structures were solved by direct methods (G.M. Sheldrick, *SHELXS-86*, Univ. Göttingen, 1986) and were refined by the least-squares method based on F^2 with all measured reflections (G. M. Sheldrick, *SHELXL-93*, Univ. Göttingen, 1993) using anisotropic temperature factors for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions or as part of a rigid group (methyl). Only an isotropic temperature factor for each type of hydrogen atom was refined. – Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-114167 (**3c**) and -114168 (**4c**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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