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Ethylene Oligomerisation and Polymerisation with Nickel Phosphanylenolates Bearing Electron-Withdrawing Substituents: Structure–Reactivity Relationships

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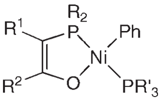
Markus Neuburger,[b] and Antonio Mota[c]

Abstract: Three SHOP-type catalysts, in which the C=C(O) double bond was substituted by electron-withdrawing substituents, $[Ni\{Ph_2PC(R^1)=C(R^2)O\}Ph(PPh_3)]$ (**2**: R^1,R^2 = −C(Me)=NN(Ph)−; **3**: R^1 = CO_2Et, R^2 = Ph; **4**: R^1 = CO_2Et, R^2 = CF_3), were assessed as ethylene-oligomerisation and -polymerisation catalysts and compared to Keim's complex, $[Ni\{Ph_2PCH=C(Ph)O\}Ph(PPh_3)]$ (**1**). A rationale for the influence of the double-bond substituents of the P,O-chelate unit on the catalytic properties is proposed, on the basis of X-ray diffraction studies, spectroscopic data and DFT-B3LYP calculations. Whatever their relative electron-withdrawing strength, the R^1 and R^2 substituents induce an increase in activity with respect to catalyst **1**. For those systems in which the basicity of the oxygen atom is decreased relative to that of the phosphorus atom, the chain-propagation rate increases with respect to that for catalyst **1**. Reduction of the basicity of the P relative to that of the O, however, induces higher chain-termination rates.

Keywords: ethylene · nickel · oligomerization · P,O ligands · polymerization

Introduction

The use of *late* transition-metal complexes as single-site ethylene-oligomerisation and -polymerisation catalysts was first achieved industrially in the early 1970s through employing in situ generated phosphanylenolato–nickel complexes for the selective production of linear α-olefins (SHOP process).[1–4] Since then, the interest in such complexes as catalysts for the production of polyolefins has continually increased.[5–8] Regarding polymerisation reactions, late transition-metal complexes present several advantages over the classical group IV metal catalysts, including easy complex synthesis, low cost for the preparation of the first-series-metal-derivatives, low environmental impact, functional-group tolerance.[9] Nowadays, their development is driven by three main goals: 1) the selective production of C_4–C_{10} α-olefins, for which the demand for copolymerisation purposes is growing rapidly;[10] 2) the production of ethylene/polar-monomer copolymers, which represent one of the most promising areas of development in the polyolefin industry;[11–13] 3) the production of polymer lattices (i.e., stable, colloidal aqueous dispersions of polymer particles) through aqueous-emulsion polymerisation under mild conditions.[14]



A

The SHOP catalysts (**A**), which contain anionic, phosphanylenolato chelates, proved to be suited for all these purposes. Although such complexes, if used without any additive, usually function as ethylene-oligomerisation catalysts, their combination with a phosphine scavenger (e.g., $[Ni(cod)_2]$ (cod = 1,5-bis(cyclooctadiene))), allowing removal of the neutral phosphine ligand (PR'_3 in **A**) results in a polymerisation cat-

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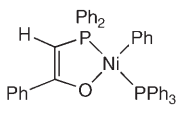
alyst.[15,16] The original SHOP catalysts, once deprived of the unidentate phosphine ligand, displayed only modest activities in ethylene polymerisation. In fact, highly efficient systems may be obtained through modification of the P,O chelator. It appears that introduction of *electron-withdrawing* substituents on the P,O backbone (which here are referred to as “Z” substituents) significantly increases the rate of ethylene polymerisation.[15–17] For example, complex **B**, which contains a sulfonato substituent on the P$-C_{\alpha}$ carbon atom, shows an activity, which under optimised conditions, is two orders of magnitude higher than that of prototype **1**.[15,16] Interestingly, the $-SO_3Na$ substituent of **B** further induces the formation of polymer chains longer than those formed with **1** (if operating as a polymerisation catalyst). Careful examination of the literature reveals that the presence of Z substituents does not systematically result in higher polyolefins. In a recent paper, we showed that the strongly electron-withdrawing pyrazole ring of complex **2** causes a dramatic shift in the polyolefin distribution towards the formation of shorter olefins.[18] In fact, **2** is the only phosphanylenolato–nickel complex that, under typical polymerisation conditions (i.e., after removal of the neutral phosphine ligand), is able to produce significant amounts of short oligomers with good activities.[19,20] Note that the phosphanylacetato complex **C** was found to behave similarly.[21,22] Intuitively, these observations suggest that the properties of SHOP catalysts containing electron-poor P,O chelates are strongly dependent on the way the Z group modifies the relative donor properties of the P and O atoms of the chelate, that is, to what extent the basicity of the donor atoms is modified. To gain greater insight into the intimate factors that govern the properties of such complexes, we compared the structural and catalytic properties of three phosphanylenolato–nickel complexes, namely **2**–**4**, in which the two carbon atoms of the P,O chelates are substituted by Z groups of unequal strength (Scheme 1). Their catalytic properties were assessed with respect to both ethylene oligomerisation and polymerisation, and compared with those of **1**. It is worth mentioning that the chelating P,O ligands of **3** and **4** were recently assessed by other authors, but only for polymerisation through using in situ generated complexes.[17] We recently reported a synthesis of **2**, together with some preliminary catalytic results.[18]



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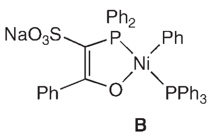

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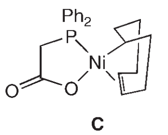

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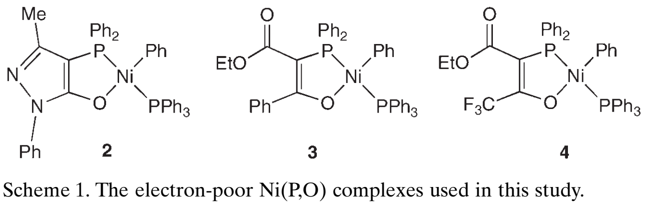
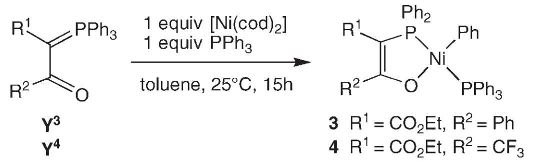


Scheme 1. The electron-poor Ni(P,O) complexes used in this study.

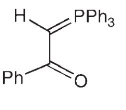
Results

Synthesis of the complexes: The new complexes **3** and **4** were synthesised in good yields by reaction of [Ni(cod)$_2$] with the appropriate phosphorus ylide in the presence of PPh$_3$ (Scheme 2).

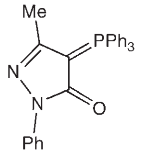


Scheme 2. Preparation of complexes **3** and **4** by using phosphorus ylides.

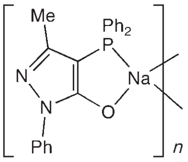
We found that this methodology, originally applied by Keim for the preparation of **1** (starting from **Y^1**, in which R^1= H, R^2 = Ph),[4] could also be applied to the synthesis of complex **2** by using the phosphorus ylide **Y^2**. Nevertheless, the previously reported preparation of **2**, which relies on the sodium phosphanylpyrazolonate **5**, requires fewer synthetic steps and, in practice, gives readier access to **2**.[18]



Y^1



Y^2



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Complexes **3** and **4** could be isolated as dark-yellow crystals upon slow diffusion of hexane into a toluene solution of the complex. Addition of hexane to a concentrated toluene solution of **4** precipitated a powder that spontaneously converted to monocrystals upon standing. The two complexes were characterised by elemental analysis, ^{1}H, ^{31}P and ^{13}C NMR and X-ray analysis (see below). Both ^{31}P NMR spectra exhibit an AB system, with $J(AB)$ values (276 Hz (**3**) and 277 Hz (**4**)) in accord with *trans*-positioned phosphorus atoms (cf. 284 and 280 Hz for **1** and **2**, respectively). On going from **3** to **4**, that is, upon replacement of Ph by a CF$_3$ group, the charge distribution on the C=C double bond is strongly perturbed, as can be seen from the chemical-shift variations of the corresponding carbon atoms, $\Delta\delta(C_{\beta-P}) = -17.6$ ppm, $\Delta\delta(C_{\alpha-P}) = +3.3$ ppm. Owing to the conjugation of the C=O$_{ester}$ bond with the C=C bond of the chelating unit, the $\nu(C{=}O)_{ester}$ frequency (1670 cm^{-1}) of complex **3** is lowered with respect to that of conventional, nonconjugated esters. However, in keeping with the strong inductive effect of the CF_3 group, which lowers the conjugation between the C=C bond and the CO_2 group, the carbonyl band of **4** appears at a higher wavenumber than in **3**, namely 1699 cm^{-1}. The two IR spectra exhibit further strong, characteristic ν(C=C)+ν(C–O) combination bands, at 1459 cm^{-1} for **3** and 1517 cm^{-1} for **4**. That of **3** is somewhat lower than expected (cf. 1506 cm^{-1} for **1**[23]), suggesting a structural distortion within the PCCO arm (see below). The solid-state structures of **3** and **4** were determined by single-crystal X-ray diffraction studies (Figures 1 and 2; for structural data see Table 1). Together with that of **2**, they constitute the only reported structures of SHOP-type catalysts having an electron-deficient P,O chelate. Notably, the natural bond orbital (NBO) charge analysis at the DFT-B3LYP/6-31G* level (see Supporting Information) shows that the positive global charge of the NiPCCO ring (+0.755 (**3**); +0.681 (**4**)) in both complexes is considerably higher than in **1** (+0.478). For comparison, the corresponding charge in **2** is +0.808.

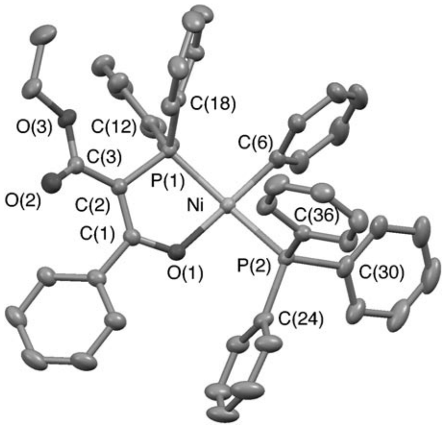


Figure 1. Molecular structure of **3**.

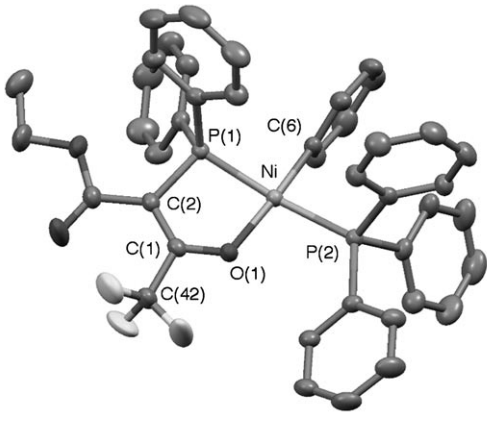


Figure 2. Molecular structure of **4**.

As previously observed for **2**,[18] the coordination environment of **3** deviates slightly from an ideal square-planar geometry. Thus, P(1) and P(2) lie on the same side of the mean square-coordination plane, whereas C(12) and O(1) are turned towards the other side of this plane (P(1)-Ni-P(2) = 161.7°; C(6)-Ni-O(1) = −177.9°). A similar "Td-oriented" distortion was also found in **4** (P(1)-Ni-P(2) = 170.3°; C(6)-Ni-O(1) = −170.6°). Comparison of the structural data of **1**[4,24] and **3** shows that substitution of the enolate hydrogen atom of **1** by an ethoxycarbonyl group has only a minor impact on the four bond lengths involving the nickel centre. On the other hand, in keeping with the IR data discussed above, the carbonyl group of **3** induces a lengthening of the conjugated C(1)=C(2) bond with respect to **1** (Table 1). An interesting feature of this complex is that the metallacyclic unit deviates significantly from planarity (distance of P(1) to the plane defined by Ni, O(1), C(1), C(2): 0.277(2) Å). In fact, the observed distortion results from an important steric interaction between the carbonyl group and the neighbouring phenyl ring, as revealed by the C(6)-C(1)-C(2)-C(3) torsion angle of 22.7° (Figure 3).

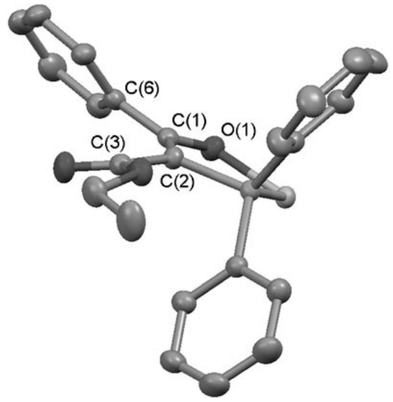


Figure 3. Partial view of **3** showing the distortion about the C(1)=C(2) double bond.

Surprisingly, the presence of the CF_3 group in **4** induces only a slight lengthening of the Ni–P_{chel} and Ni–O bonds with respect to those of **3** (Table 1). Nevertheless, the NBO charge analysis shows that the negative charge on the oxygen atom of the metallacycle undergoes a significant variation, namely from −0.730 in **3** to −0.705 in **4** (cf. −0.781 in **1**). Moreover, the whole charge of the nickel-bonded phenyl group also decreases, going from −0.391 to −0.377, whereas the charge on each phosphorus atom remains practically un-

Table 1. Selected structural data for complexes **1**–**4** (bond lengths [Å], angles [°]).

Compound	P–$C_{chelate}$	C–O	C=$C_{chelate}$	Ni–PPh_2	Ni–PPh_3	Ni–O	Ni–C	P-Ni-O
1(DAGBES)[a]	1.76(2)	1.30(2)	1.34(2)	2.154(4)	2.275(6)	1.89(1)	1.90(2)	88.0(4)
1(PBZMNI)[a]	1.768	1.313	1.365	2.167	2.230	1.913	1.892	86.49
2	1.770(2)	1.296(2)	1.393(2)	2.210(1)	2.224(1)	1.955(1)	1.885(2)	89.33(6)
3	1.792(2)	1.295(2)	1.395(2)	2.168(1)	2.232(1)	1.907(1)	1.891(2)	85.99(4)
4	1.810(2)	1.286(2)	1.374(2)	2.1754(5)	2.2565(5)	1.921(1)	1.894(2)	85.56(4)

[a] DAGBES and PBZMNI differ in their space groups. Standard deviations are not available for PBZMNI.

changed. Thus, should **3** and **4** display important differences in their catalytic behaviour, this could then be due to the charge differences along the O-Ni-C(Ph) axis. As far as the X-ray structure is concerned, the strong $-I$ effect of the CF_3 group is best exhibited in the C=C bond length of **4** (1.374(2) Å), which is significantly shorter than the corresponding bond length in **3** (1.395(2) Å).

As reported in a preliminary work, the presence of the electron-withdrawing pyrazolyl ring in **2** induces a marked lengthening of both the Ni−P and Ni−O bonds. In this case, the Ni−O and Ni−P bonds are 0.056 and 0.065 Å longer, respectively, than the corresponding bonds in **1**, which indicates that the electron-withdrawing effect of the pyrazolyl ring of **2** is not only strong, but also nearly symmetrically distributed over the P,O chelate. Interestingly, the charge of the oxygen atom in **2**, as well as that of the P_{chel} atom, are almost identical to those of **1**, as inferred from DFT calculations. We note, however, that the charge of the metallated aryl ring has changed from −0.399 in **1** to −0.375 in **2**, which reflects the strong inductive effect of the pyrazolyl ring.

We have shown previously that the pyrozolonato complex **2** may undergo reductive elimination, both in solution and in the solid state, resulting in formation of ylide $\mathbf{Y^2}$.[18] A similar transformation was also observed for **4**, but at a considerably lower rate. Overall, the rate of reductive elimination varies in the order $\mathbf{2}>\mathbf{4}>\mathbf{3}\approx\mathbf{1}$, that is, it follows the same variation as the length of the $Ni{-}P_{chelate}$ bond.

Ethylene oligomerisation: The catalytic tests were carried out in toluene at 70 °C, at constant pressures, by using a 200-mL glass reactor. For comparison, complex **1** was also tested under these conditions. As expected, the complexes **2–4** catalyse the oligomerisation of ethylene, producing, as with **1**, oligomers that are linear to 99 %. The selectivity for α-olefins, determined on the C_4–C_{16} fraction (5-bar experiments), is higher than 96 % for complexes **1–3** and decreases, owing to isomerisation, to 81 % for complex **4** (Table 2, entries 1, 4, 7 and 10). The olefins are present in a Schulz–Flory distribution.[25] The α values decrease significantly on going from **1** and **3** ($\alpha=0.92$ and 0.93, respectively) to **2** and **4** ($\alpha=0.73$ and 0.78, respectively), that is, strongly electron-withdrawing Z groups favour the formation of shorter oligomers. The shift towards shorter oligomers is remarkable in the case of complex **2** (Figure 4). Thus, upon operating at 5 bar, the C_4–C_{16} fraction obtained with this complex represents approximately 73 wt % of the total amount of olefins produced (Table 2, entry 4), whereas it represents only 15 wt % upon using **1** under similar conditions. Interestingly, the ability of complexes **2** and **4** to shift the product distribution towards shorter olefins does not correlate with the observed reaction rates. Indeed, these vary in the order $\mathbf{2}<\mathbf{1}<\mathbf{4}<\mathbf{3}$, with complex **3** operating seven times faster than **2** (Table 2, compare entries 1, 4, 7, 10).

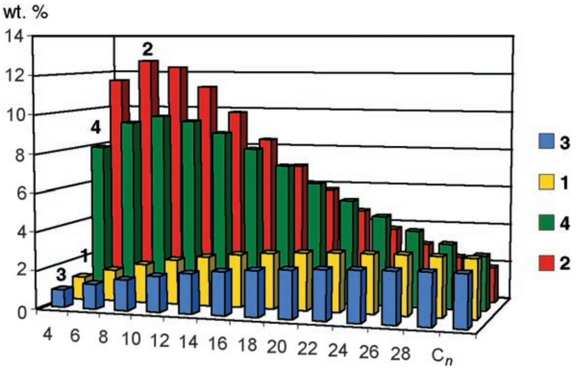


Figure 4. Ethylene oligomerisation. Product distribution by using catalysts **1–4** (5 bar, 1 h).

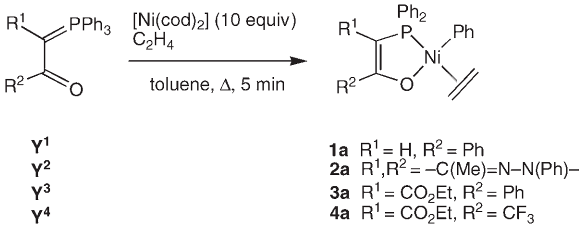
Table 2. Ethylene oligomerisation by using complexes **1–4** under a constant ethylene pressure.[a]

Run	Cat.	P [bar]	t [h]	TOF[b]	α[c]	C_2H_4 consum. [g]	C_4–C_{16} [wt %]	α-olefin[d] [wt %]
1	**1**	5	1	15 500	0.92	3.25	15.3	98.6
2	**1**	5	2	7500	0.92	3.15	15.3	98.3
3	**1**	5	0.5	29 600	0.89	3.11	25.1	97.3
4	**2**	5	1	9700	0.73	2.04	72.5	95.9
5	**2**	5	2	6600	0.83	2.77	45.2	95.2
6	**2**	5	0.5	14 400	0.69	1.51	80.2	96.2
7	**3**	5	1	68 000	0.93	14.32	12.3	95.8
8	**3**	2.5	2	14 800	0.87	6.23	31.9	92.3
9	**3**	2.5	1	27 600	0.86	5.81	37.0	92.6
10	**4**	5	1	32 600	0.78	6.87	60.2	81.5
11	**4**	2.5	1	26 500	0.72	5.58	75.2	75.8

[a] 200-mL glass reactor filled with 7.5 μmol catalyst in 30 mL PhMe, 70 °C (external oil-bath temperature). [b] Turnover frequency, mol(C_2H_4) per mol(Ni) per h. [c] Schulz–Flory parameter $\alpha=$mol(C_{n+2}) per mol(C_n). [d] For the C_4–C_{16} fraction.

Thus, the factors that govern the activity and the product distribution of SHOP-type catalysts containing electron-poor chelators cannot be attributed solely to the electron-withdrawing strength of the Z substituents. Recent work has already shown that the outcome of ethylene oligomerisation by SHOP catalysts markedly depends on the relative electronic (and steric) properties of the two P^{III} centres.[26–35] Logically, an understanding of the intrinsic properties of the Ni(P,O) metallacycles described in this work is required to assess the catalytic systems lacking the PPh_3 ligand. Therefore, we decided to generate catalytic systems of the types **1a–4a** (see next section). In keeping with a number of polymerisation studies on SHOP-type catalysts, we anticipated that this approach would result in the formation of polyolefins of higher molecular weight.[16]

Ethylene polymerisation: Two methods were, a priori, available to generate in situ complexes of the types **1a–4a**: a) treatment of one of the complexes described above with a phosphine scavenger, such as [Ni(cod)$_2$] or [Rh(acac)(C_2H_4)$_2$] (acac = acetylacetone); or b) reaction of the appropriate phosphorus ylide with [Ni(cod)$_2$] in toluene. To get catalytic systems that were rigorously PPh_3-free, the latter method was preferred (Scheme 3). The runs were carried



Scheme 3. In situ generation of the catalytic systems **1a**–**4a**.

out under constant pressure and stopped after 0.5 h. The temperature of the reaction was kept constant. The results are summarised in Table 3.

Table 3. Ethylene polymerisation by using in situ generated catalysts **1a**–**4a**.[a]

Run	Cat.	Cat. [μmol]	P [bar]	T[b] [°C]	PE[c] [g]	Activity[d]	M_w[e] [g mol^{-1}]	PDI[f]	T_m[g] [°C]
1	**1a**	4	5	70	1.12	560	6600	2.5	127.0
2	**1a**	4	5	80	1.87	940	–	–	126.7
3	**1a**	4	5	90	2.27	1140	3900	1.8	124.0
4	**1a**	2	10	80	2.83	2830	4100	1.8	127.4
5	**2a**	4	5	70	3.37	1690	1100	1.6	97.9
					4.5[h]	2200			
6	**2a**	4	5	80	3.46	1730	–	–	96.2
					4.4[h]	2200			
7	**2a**	4	5	90	2.59	1300	1200	1.3	95.7
					3.8[h]	1900			
8	**2a**	2	10	80	3.81	3810	1500	1.5	98.1
					4.3[h]	4300			
9	**3a**	4	5	70	0.61	300	9500	2.0	129.7
10	**3a**	4	5	80	2.75	1370	–	–	128.7
11	**3a**	4	5	90	2.37	1190	7100	1.9	127.8
12	**3a**	2	10	80	4.42	4420	8200	1.9	128.0
13	**4a**	4	5	70	2.96	1480	5200	1.9	124.5
14	**4a**	4	5	80	4.29	2150	–	–	121.5
15	**4a**	4	5	90	4.27	2140	4300	1.8	119.6
16	**4a**	2	10	80	4.11	4110	4600	1.7	124.3

[a] Conditions: 100-mL stainless-steel autoclave, 20 mL PhMe, 0.5 h reaction time, 10 equiv [Ni(cod)$_2$]. [b] Temperature inside the autoclave. [c] Polyethylene, after precipitation of the reaction mixture with 200 mL MeOH/HCl. [d] Units, g per mmol$_{\text{cat.}}$ per h. [e] Determined by HT-SEC versus polystyrene standard, uncorrected. [f] PDI (polydispersity index) = M_w/M_n. [g] Measured by differential scanning calorimetry (DSC). [h] Total amount of products, including soluble oligomers.

These experiments revealed that the pyrazolone derivative **2a** is the most-active catalyst, its performance slightly surpassing that of **4a**, which was previously regarded as the most-active neutral, SHOP-derived polymerisation catalyst. Overall, the activity of the complexes follows the order: **1a** < **3a** < **4a** < **2a**. In other words, the higher the electron deficiency of the P,O chelate, the higher the reaction rate. For the three electron-poor systems **2a**–**4a**, the maximum activity was found for a reaction temperature of around 80 °C upon conducting the runs at 5 bar. The optimised activity of **1a** was not determined, but clearly requires temperatures greater than 90 °C. As expected, increasing the pressure from 5 to 10 bar increases the activity of the catalysts (Table 3, entries 4, 8, 12, 16).

The influence of the electron-withdrawing Z group(s) on the chain length of the polyethylene is remarkable. Compound **3a** produces polyethylene characterised by a M_w higher than that obtained with **1a** (Table 3, entries 1 and 9), whereas the chains produced with **2a** and **4a** are shorter. Analysis by GC of the reaction solutions revealed that the outcome of the **2a** catalysis differs from all others, this catalyst being the only one producing significant amounts of light oligomers. Approximately 25 wt % of the oligomers formed are soluble in methanol. In keeping with this observation, the polydispersity of the polymeric material obtained after precipitation was lower than that of the polymer formed with the three other catalysts (Table 3, entries 5–8). The low values of the corresponding melting temperatures (T_m) are also consistent with these findings.

Discussion

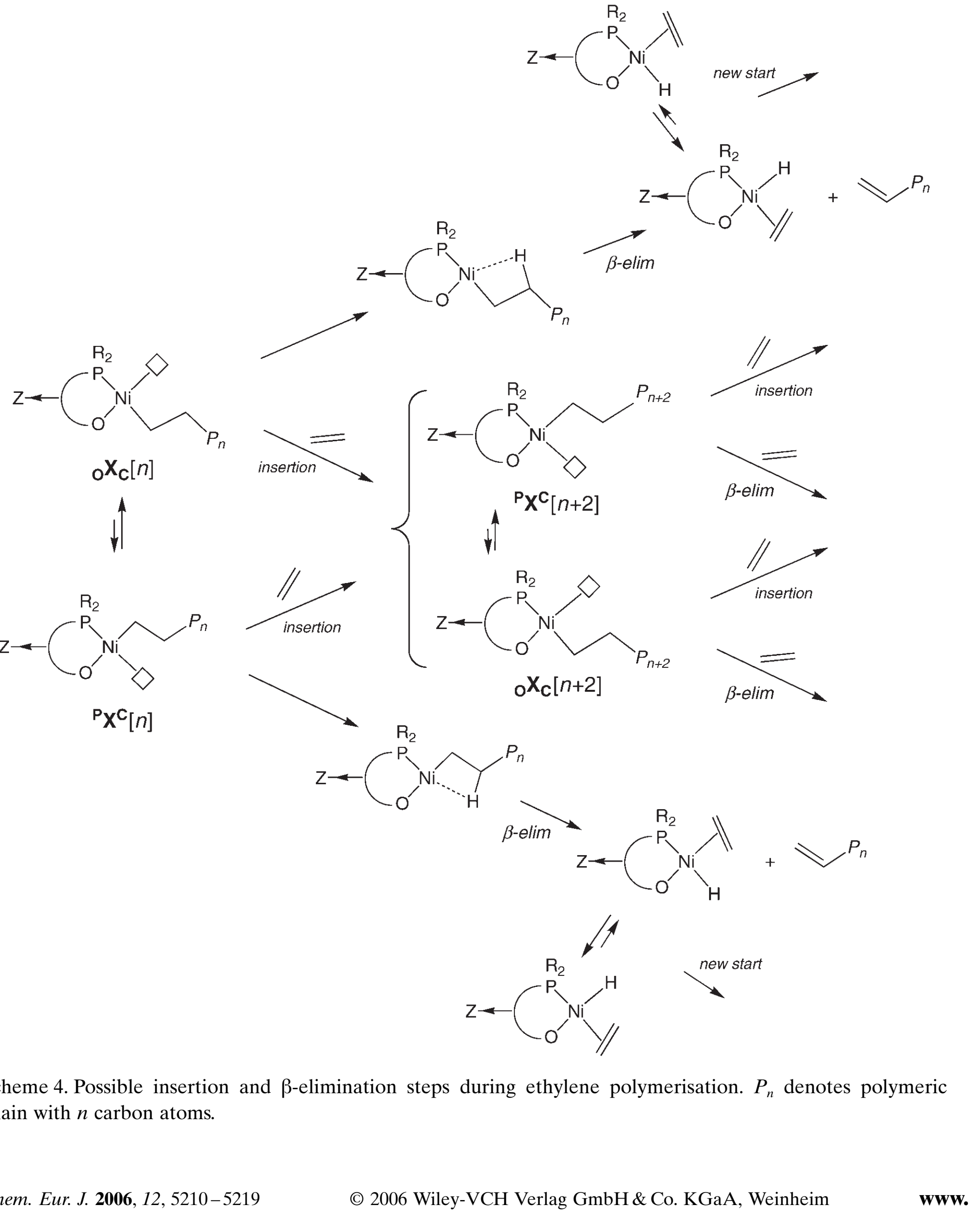
The results presented above clearly show that under "polymerisation conditions", that is, in the absence of PPh$_3$, the P,O chelators substituted by electron-withdrawing groups (**2a**–**4a**) gave catalysts that were all more active than system **1a**. These findings do not correspond to the observations made under oligomerisation conditions. Thus, complex **2** was found to be a little less active than **1**, and **4** less active than **3**. Taking again **1** (or **1a**) as a reference compound, whatever the conditions used, the pyrazolonato ligand of **2**/**2a** and the CF$_3$/CO$_2$Et-substituted enolate of **4**/**4a** shift the product distribution towards compounds with lower molecular weights. In contrast, system **3a**, in which the P,O chelate is Ph/CO$_2$Et-substituted, gave compounds with increased molecular weight. Note, polymers with much higher molecular weights were obtained with the related Ph/SO$_3$Na-substituted complex **B** reported by Klabunde et al.[16]

To understand the effects exerted by Z substituents, one must consider the recent studies by Heinicke and Keim, which showed that a selective increase in the basicity of the P$_{\text{chel}}$ atom increases the activity of the catalyst under polymerisation conditions.[32] This strongly suggests that the systematic activity increase observed with SHOP-catalysts having Z-substituted P,O arms must arise from a decrease in the basicity of the oxygen atom. The latter was shown, by theoretical calculations, to induce an electron-density decrease along the ONiC(Ph) axis. This is also in line with the recent calculations made by Ziegler for N,O-chelated Ni catalysts, which showed that an electron-density decrease on the O atom reduces the ethylene-insertion barrier.[36] Notably, the Ni−O bonds in **2** (1.955(1) Å) and **4** (1.921(1) Å), which are the two complexes with the strongest electron-withdrawing substituents and the highest activities, are significantly longer than those of **3** (1.907(1) Å) and **1** (1.89(1) Å).

Furthermore, the electronic properties of the P$_{\text{chel}}$ atom markedly influence the product distribution.[32] By using phosphanylphenolato complexes, Heinicke et al. found that replacement of the PPh_2 moiety by $P(alkyl)_2$ groups favors the formation of longer chains under polymerisation conditions. The authors proposed that, with more-basic PR_2 groups, the nickel becomes less electropositive and, accordingly, the barrier for the β-*elimination* step is increased. This suggests that, generally, the C–H activation occurs preferentially in an intermediate having a *cis*-P,alkyl structure (abbreviated ${}^{\mathrm{P}}\mathbf{X}^{\mathrm{C}}[n+2]$ in Scheme 4) rather than a *trans*-P,alkyl structure (noted ${}_{\mathrm{O}}\mathbf{X}_{\mathrm{C}}[n+2]$), that is, the hydride is formed on the coordination site *trans* to the phosphorus atom. On the other hand, in keeping with calculations made by Ziegler for N,O-chelated complexes,[36] it seems reasonable to consider that the *ethylene-insertion barrier* is lower for a complex of the ${}_{\mathrm{O}}\mathbf{X}_{\mathrm{C}}[n]$ type than for a ${}^{\mathrm{P}}\mathbf{X}^{\mathrm{C}}[n]$ complex (Scheme 4). Therefore, isomerisation of ${}^{\mathrm{P}}\mathbf{X}^{\mathrm{C}}[n]$ alkyl complexes into ${}_{\mathrm{O}}\mathbf{X}_{\mathrm{C}}[n]$ complexes occurs, in general, before the insertion step. Z groups that decrease the donor properties of the P atom only should logically facilitate the β-elimination step in the intermediates of the ${}^{\mathrm{P}}\mathbf{X}^{\mathrm{C}}[n+2]$ type (originating from a ${}_{\mathrm{O}}\mathbf{X}_{\mathrm{C}}[n]$-type complex). If the Z group is also able to decrease the basicity of the oxygen atom, then β-elimination should also be favoured in ${}_{\mathrm{O}}\mathbf{X}_{\mathrm{C}}[n+2]$ structures. One may envisage that in complexes in which the basicities of both the P and O atoms have been considerably decreased, the β-CH activation process becomes favoured on both coordination sites, *trans* to P and *trans* to O, and not just *trans* to P. Overall, the role of Z groups exerting a *strong* withdrawing effect on both coordinating atoms, as in **2**, is to allow CH activation on two sites, which in turn increases the probability of chain termination.

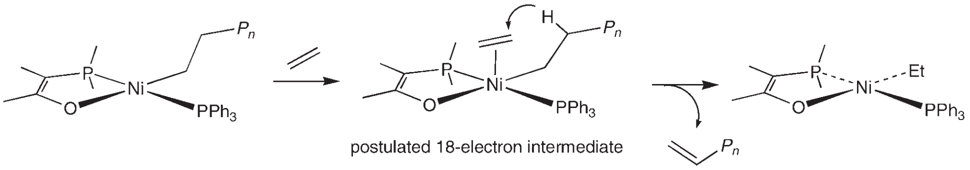
Complex **4a** is an interesting case in which the CF_3/CO_2Et couple exerts a larger influence on the oxygen atom than on the P_{chel} atom (see above, structure of **4**). Here, the distribution shift towards lower olefins is less pronounced than with **2a**, as a consequence of the higher electron density on the P_{chel} atom, which makes β-elimination in intermediates of the ${}^{\mathrm{P}}\mathbf{X}^{\mathrm{C}}[n+2]$ type somewhat less favorable. Nevertheless, the rate of β-elimination remains high, possibly because it is strongly favored in the ${}_{\mathrm{O}}\mathbf{X}_{\mathrm{C}}[n+2]$-type intermediates (the position *trans* to the electron-deficient O atom having a high activation efficiency). One may ask why catalyst **3a**, whose activity is comparable with that of **1a**, results in polymers that are longer than those obtained with **1a**. It is likely that this relates directly to the observed metallocycle puckering (see above) induced by the steric interaction between the neighbouring phenyl and CO_2Et groups. Electron delocalisation within the PCCO arm of **3** becomes less efficient than in **1**, and accordingly, the phosphorus becomes a better donor, thus, disfavoring β-elimination. Note that one of the two ^{31}P-phosphorus signals of **3** has undergone a significant low-field shift, of more than 10 ppm, with respect to its counterpart in **1** (for details, see Experimental Section).

Are these interpretations consistent with the observations made under oligomerisation conditions, that is, in the presence of the PPh_3 ligand? The effect of PR_3 ligands was investigated by several authors.[27,33] It is well established that strongly coordinating PR_3 li-



Scheme 4. Possible insertion and β-elimination steps during ethylene polymerisation. P_n denotes polymeric chain with n carbon atoms.

gands decrease the activity of the complex, as displacement of this phosphine by the incoming ethylene molecule is more difficult. Interestingly, PR_3 ligands also have an impact on the product distribution. An increase in the phosphine basicity usually induces a decrease in the molecular weight of the oligomers formed. A rationale for this observation, in mechanistic terms, has not yet been given. Monteiro et al. suggested that, besides the conventional β-elimination from a $^{\mathbf{P}}\mathbf{X}^{\mathbf{C}}[n+2]$-type intermediate (Scheme 4), a second termination mechanism must occur, in this case involving a PR_3 complex.[37] Chauvin and Braunstein came recently to a similar conclusion.[38] However, the intimate mechanism leading to olefin release was not elucidated. Such an elimination could, for example, occur within an 18-electron ethylene/phosphine complex by transfer of a β-hydrogen atom to the coordinated ethylene (Scheme 5). Of course, an electron-poor P,O chelate that makes the Ni atom electron-deficient should favor coordination of ethylene, resulting in the 18-electron species shown in Scheme 5. Note, the idea that 18-electron Ni–ethylene intermediates are also likely to play an important role in ethylene polymerisation was recently proposed for Ni(α-diimine) catalysts.[39]



Scheme 5. One of the possible chain-termination steps during oligomerisation, taking into account the presence of a PR_3 ligand.

The most-active oligomerisation catalyst is complex **3**. This implies the presence of a PPh_2 moiety with a relatively high *trans* influence that facilitates the labilisation of the PPh_3 ligand, and is further consistent with the rather long chains formed under polymerisation conditions (see above). Thus, although the CO_2Et group of this complex acts as an electron-attracting group through conjugation, it reduces, through steric interactions with the neighbouring Ph substituent, the electron delocalisation of P electrons within the chelating unit. In contrast, the pyrazolonato complex **2** is the least-active of the four complexes studied. This is in accord with the strong electron-withdrawing effect exerted by the pyrazole ring on the P_{chel} atom, which, incidentally, strengthens the Ni–PPh_3 coordination, thereby making phosphine substitution by ethylene more difficult. On the other hand, complex **4** is, as under polymerisation conditions, more active than **1**, confirming that the P_{chel} atom is only weakly affected by the presence of the CF_3 group.

Finally, it should be emphasised that an enforced PPh_3 binding is not the only criterion for shifting the olefin distribution towards shorter oligomers. This is clearly shown by considering the fact that **4**, in which the PPh_3 ligand is expected to be more labile than in **2**, also induces a significant shift in distribution towards lower olefins ($\alpha = 0.78$). This observation strongly suggests that the basicity of the O atom may also play a key role with respect to the production of such short olefins. A possible mechanism consistent with this finding involves the 18-electron intermediate shown in Scheme 5, although chain termination through a β-agostic interaction at an apical site of a $[Ni(P,O)(alkyl)PPh_3]$ intermediate cannot formally be excluded.

Conclusion

We have examined the impact of electron-withdrawing substituents anchored at the C=C double bond of nickel phosphanylenolates on their structural and catalytic properties. From results of the structural and theoretical studies, it appears that such groups induce a significant lengthening of both the Ni–O and Ni–P_{chel} bonds, the amplitude of the lengthening being a good indication of the attracting power of the backbone substituents. Replacement of the *H*(C=C) atom of **1** by a CO_2Et group (leading to **3**) does not induce important bond changes in the first coordination sphere (the CO_2Et group perturbs mainly the electron delocalisation within the PCCO moiety), whereas the CF_3 group of **4** exerts its electron-withdrawing influence primarily on the O-Ni-C(Ph) rod. On the other hand, the pyrazol ring, which is by far the best acceptor, exerts a strong, but balanced influence on the Ni–P_{chel} and Ni–O bond lengths. Our catalytic studies clearly show that, under polymerisation conditions: 1) Z substituents increase the insertion rate, whatever the relative acceptor strength of the two enolate substituents, this effect probably being propagated through the oxygen atom; and 2) Z substituents shift the product distribution towards short chains, this effect being propagated essentially through the P atom, although a less-basic oxygen atom may also facilitate the β-CH activation process *trans* to the oxygen atom. Under oligomerisation conditions, the introduction of Z substituents on the C=C double bond necessarily increases the reaction rate, provided the Z groups exert a global effect directed more towards the oxygen atom than towards the phosphorus atom. Should the donor properties of the P_{chel} atom also be significantly lowered (as in **2**), then the binding of the *trans*-bonded PPh_3 ligand increases and, accordingly, makes olefin coordination more difficult. The factors that govern the product distribution are more subtle. Possibly, *strong* electron-withdrawing substituents, whatever their directional properties, favor the formation of a pentacoordinated $[Ni(P,O)(alkyl)PPh_3(C_2H_4)]$ intermediate, from which termination occurs. This termination route would then occur concomitantly with the conventional β-elimination route involving a 14-electron [Ni(P,O)(alkyl)] intermediate. Further mechanistic studies to confirm these conclusions are currently underway.

Experimental Section

General considerations: All syntheses were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and were distilled immediately prior to use. Routine ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} spectra were recorded by using an AC-200 Bruker FT instrument. ^{1}H NMR spectra were referenced to residual protonated solvents (7.16 ppm for C_6D_6), ^{13}C chemical shifts are reported relative to deuterated solvents (128.0 ppm for C_6D_6) and the ^{31}P NMR data are given relative to external H_3PO_4. The ^{19}F spectrum of complex **4** was measured relative to neat $CFCl_3$. The catalytic solutions were analysed by using a Varian 3900 gas chromatograph equipped with a WCOT fused-silica column (25 m, 0.32 mm inside diameter, 0.25 mm film thickness). High-temperature size-exclusion chromatography (HT-SEC) measurements were performed at 150 °C by using a PL220 apparatus (Column set HT-Mixed B-TCB-01) in 1,2,4-trichlorobenzene (with 0.2 % Irganox). Calibration was made by using linear PS samples. $\mathbf{Y^1}$,[40] $\mathbf{Y^2}$,[41] $\mathbf{Y^3}$,[42] $\mathbf{Y^4}$,[43] and the complexes [Ni(cod)$_2$],[23] **1**[4] and **2**[18] were prepared according to literature procedures. The chemical shifts of the phosphorus atoms of **1** and **2** are as follows: $\delta(C_6D_6) = 21.5$ and 19.9 ppm for **1** and 20.2 and −8.6 ppm for **2**.

Syntheses

*[Ni{Ph$_2$PC(Me)=NN(Ph)C(O)}(Ph)PPh$_3$] (**2**)*: A cold solution (0 °C) of [Ni(cod)$_2$] (0.316 g, 1.15 mmol) in toluene (20 mL) was added to a cold suspension (0 °C) of 3-methyl-1-phenyl-4-triphenylphosphoranylidene-2-pyrazolin-5-one ($\mathbf{Y^2}$) (0.500 g, 1.15 mmol) and PPh_3 (0.303 g, 1.15 mmol) in toluene (20 mL). The mixture was stirred for 15 h, after which the solution was concentrated to approximately 5 mL. Slow diffusion of hexane into this solution afforded yellow crystals of **2** (0.591 g, 68 %). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 8.25$–6.44 (35 H; arom. H), 2.02 ppm (s, 3 H; CH_3); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): $\delta = 140.76$–118.06 (arom. C), 89.83 (d, J(P,C) = 63 Hz, PC_{pyrazo}), 14.77 ppm (s, CH_3); ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): $\delta = 20.2$, −8.6 ppm (AB spin system, $J(PP') = 280$ Hz); IR (KBr): $\tilde{\nu} = 1592.6$ (m), 1515.5 (s), 1495.0 (s), 1425.8 cm^{-1} (s); elemental analysis calcd (%) for $C_{46}H_{38}N_2NiOP_2$ (755.46): C 75.10, H 5.47, N 3.34; found: C 74.6, H 5.39, N 3.34.

*[Ni{Ph$_2$PC(CO$_2$Et)=C(Ph)O}(Ph)PPh$_3$] (**3**)*: A cold solution (0 °C) of [Ni(cod)$_2$] (0.330 g, 1.20 mmol) in toluene (20 mL) was added to a cold suspension (0 °C) of ethyl-(2-benzoyl-2-triphenylphosphoranylidene)acetate ($\mathbf{Y^3}$) (0.500 g, 1.19 mmol) and PPh_3 (0.315 g, 1.2 mmol) in toluene (20 mL). The mixture was stirred for 15 h and then concentrated to approximately 5 mL. Slow diffusion of hexane into this solution afforded yellow crystals (0.630 g, 74 %). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 7.83$–7.78 (4 H; arom. H), 7.50–7.44 (m, 8 H; arom. H), 7.15–6.88 (m, 20 H; arom. H), 6.58 (t, $J = 7.0$ Hz, 1 H; arom. H), 6.48 (t, $J = 7.3$ Hz, 2 H; arom. H), 3.74 (q, $^{3}J = 7.1$ Hz, 2 H; CH_2), 0.54 ppm (t, $^{3}J = 7.1$ Hz, 3 H; CH_3); ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): $\delta = 195.01$ (d, ^{2}J(PC) = 24 Hz, C(O)Ph), 165.53 (s, CO_2Et), 137.77–121.34 (arom. C), 90.73 (d, J(PC) = 50 Hz, $C_\alpha PPh_2$), 58.45 (s, CH_2), 13.91 ppm (s, CH_3); ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): $\delta = 31.60$, 20.08 ppm (AB spin system, $J(PP') = 276$ Hz); attempts to assign the ^{31}P signals through selective ^{13}C[28] experiments failed, probably because the ^{31}P signals relax too fast; IR (KBr): $\tilde{\nu}$(C=O) = 1670 cm^{-1} (s), $\tilde{\nu}$(C=C)+$\tilde{\nu}$(C−O) = 1459 cm^{-1} (s); elemental analysis calcd (%) for $C_{47}H_{40}NiO_3P_2$ (773.46): C 72.98, H 5.21; found: C 73.25, H 5.43.

*[Ni{Ph$_2$PC(CO$_2$Et)=C(CF$_3$)O}(Ph)PPh$_3$] (**4**)*: A solution of [Ni(cod)$_2$] (0.124 g, 0.45 mmol) in toluene (10 mL) was added to a cold (0 °C) solution of ethyl-(2-trifluoroacetyl-2-triphenylphosphoranylidene)acetate ($\mathbf{Y^4}$) (0.200 g, 0.45 mmol) and PPh_3 (0.118 g, 0.45 mmol) in toluene (20 mL). The mixture was stirred at RT for 15 h. The solution was then concentrated to approximately 0.5 mL and hexane (20 mL) was added, affording a yellow precipitate. Upon standing, the yellow powder slowly transformed into dark-yellow crystals (0.23 g, 67 %). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 7.66$–7.60 (m, 4 H; arom. H), 7.44 (t, $J = 8.4$ Hz, 6 H; arom. H), 7.03–6.95 (15 H; arom. H), 6.76 (d, $J = 7.4$ Hz, 2 H; arom. H), 6.52 (t, $J = 7.0$ Hz, 1 H; arom. H), 6.40 (t, $J = 7.3$ Hz, 2 H; arom. H), 3.78 (q, $^{3}J = 7.1$ Hz, 2 H; CH_2), 0.65 ppm (t, $^{3}J = 7.1$ Hz, 3 H; CH_3); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): $\delta = 177.45$ (dq, ^{2}J(PC) = 27 Hz, ^{4}J(FC) = 35 Hz, C(O)CF$_3$), 163.07 (s, CO_2Et), 137.42–121.30 (arom. C), 93.82 (d, J(PC) = 45 Hz, $C_\alpha PPh_2$), 59.13 (s, CH_2), 13.51 ppm (s, CH_3); ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): $\delta = 30.58$, 18.84 ppm (AB spin system, $J(PP') = 277$ Hz); ^{19}F{^{1}H} NMR (282 MHz, C_6D_6): $\delta = -67.76$ ppm; IR (KBr): $\tilde{\nu}$(C=) = 1699 cm^{-1} (s), $\tilde{\nu}$(C=C)+$\tilde{\nu}$(C−O) = 1517 cm^{-1} (s); elemental analysis calcd (%) for $C_{42}H_{35}F_3NiO_3P_2$ (765.362): C 65.91, H 4.61; found: C 65.73; H 4.63.

X-ray crystal-structure determination of 3 and 4: Single crystals of **3** and **4** (dark-orange prisms) suitable for X-ray diffraction analysis were obtained from slow diffusion of hexane into a toluene solution of the corresponding complex. Crystals of the compounds were mounted on a Nonius Kappa CCD. Data collection was carried out by using the Nonius collect suite.[44] The structures were solved by direct methods with the program SIR92.[45] Least-squares refinements were carried out by using the program CRYSTALS.[46,47] Hydrogen atoms are in calculated positions. Complex **3** crystallised with 0.5 molecule of toluene. Final results are given in Table 4. CCDC 299905 (**4**) and 299906 (**3**) contain the supplementary crystallographic data for this paper. These data can be ob-

Table 4. Crystallographic data for **3** and **4**.

	3	**4**
formula	$C_{47}H_{40}NiO_3P_2 \cdot 0.5\,C_7H_8$	$C_{42}H_{35}F_3NiO_3P_2$
M_r	819.56	765.39
crystal system	monoclinic	monoclinic
space group	$P2/a$	$P2_1/n$
a [Å]	18.0407(2)	14.3693(2)
b [Å]	11.3007(1)	13.3818(1)
c [Å]	20.6002(2)	18.8392(2)
α [°]	90	90
β [°]	97.5760(5)	90.3555(6)
γ [°]	90	90
V [Å^3]	4163.16(7)	3622.47(7)
Z	4	4
ρ_{calcd} [g cm^{-3}]	1.308	1.403
μ (Mo$_{K\alpha}$) [mm^{-1}]	0.586	0.679
F(000)	1716	1584
crystal size [mm]	0.13 × 0.22 × 0.40	0.10 × 0.10 × 0.30
T [K]	173	173
λ (Mo$_{K\alpha}$) [Å]	0.71073	0.71073
θ min/max [°]	2.0/28.7	1.8/30.1
data set (h; k; l)	−24/24; −15/15; −27/27	−20/19; −18/18; −26/26
total/unique data/R_{int}	42232/10735/0.117	36903/7160/0.064
obsd data with [$I > 2.0\sigma(I)$]	6676	7134
reflns/parameters	6676/535	7134/460
$R1/wR2/S$	0.0336/0.0604/1.09	0.0324/0.0461/0.99
min/max resid. electron density [e Å^{-3}]	−0.62/0.61	−0.49/0.41

tained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Catalytic runs

Ethylene oligomerisation: Low-pressure catalytic runs were carried out in a Büchi miniclave (200 mL) equipped with a Teflon-coated magnetic stirrer, at constant ethylene pressure. The reactor was dried under vacuum at 100 °C for 1 h before use. In a typical procedure, a Schlenk flask was charged with the complex (7.5 μmol) and toluene (10 mL). The resulting solution was injected into the autoclave together with additional toluene (20 mL). The autoclave was then pressurised with ethylene and heated at the desired temperature. The temperature refers to the external oil bath. After completion of the reaction, the autoclave was cooled by using an ice bath and depressurised over 1 h. The solution was analysed by GC. Heptane was used as an internal reference.

Ethylene polymerisation: Polymerisations were carried out at constant ethylene pressure in a Parr stainless-steel autoclave (100 mL), equipped with a mechanical stirrer, a heating device and an internal-temperature probe. The autoclave was heated at 100 °C under vacuum for 1 h before use and purged with ethylene. In a typical run, the reactor was charged at ambient temperature under an ethylene atmosphere, with a solution of the ylide in toluene (10 mL), followed by a solution of $[Ni(cod)_2]$ (10 equiv) in toluene (10 mL). The autoclave was then pressurised, and heated to the desired temperature. The reaction exothermicity was controlled by means of an ice bath. Venting the autoclave quenched the reaction and the mixture was subsequently poured into a stirred solution of acidified methanol (200 mL of 10 % HCl) to precipitate the polymer. The white powder was isolated by filtration, washed with methanol and dried in vacuo at 50 °C.

Computational details: The calculations were carried out at the DFT-B3LYP level[48–50] by using the Gaussian 03 program.[51] As starting geometries, we used those provided by the X-ray structures. The geometries were fully optimised by using the gradient technique with the following basis: the LANL2DZ basis set for Ni, the standard 6-31G basis set for C, H, N and O,[52] and the corresponding polarised 6-31G* basis set for P and F.[53]

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[1] R. Bauer, H. Chung, K. W. Barnett, P. W. Glockner, W. Keim (Shell Oil Co.), US-3686159, **1972**.

[2] R. S. Bauer, H. Chung, P. W. Glockner, W. Keim (Shell Oil Co.), US-3635937, **1972**.

[3] D. M. Singleton, P. W. Glockner, W. Keim (Shell Int. Res.), GB-1364870, **1974**.

[4] W. Keim, F. H. Kowaldt, R. Goddard, C. Krüger, *Angew. Chem.* **1978**, *90*, 493; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 466–467.

[5] G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem.* **1999**, *111*, 448–468; *Angew. Chem. Int. Ed.* **1999**, *38*, 428–447.

[6] S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169–1204.

[7] R. Spitz, C. Boisson, *Actual. Chim.* **2002**, 54–58.

[8] V. C. Gibson, S. K. Spitzmesser, *Chem. Rev.* **2003**, *103*, 283–315.

[9] S. Mecking, A. Held, F. M. Bauers, *Angew. Chem.* **2002**, *114*, 564–582; *Angew. Chem. Int. Ed.* **2002**, *41*, 544–561.

[10] F. Speiser, P. Braunstein, L. Saussine, *Acc. Chem. Res.* **2005**, *38*, 784–793.

[11] S. Y. Desjardins, K. J. Cavell, J. L. Hoare, B. W. Skelton, A. N. Sobolev, A. H. White, W. Keim, *J. Organomet. Chem.* **1997**, *544*, 163–174.

[12] L. S. Boffa, B. M. Novak, *Chem. Rev.* **2000**, *100*, 1479–1494.

[13] M. J. Yanjarappa, S. Sivaram, *Prog. Polym. Sci.* **2002**, *27*, 1347–1398.

[14] L. Kolb, V. Monteil, R. Thomann, S. Mecking, *Angew. Chem.* **2005**, *117*, 433–436; *Angew. Chem. Int. Ed.* **2005**, *44*, 429–432.

[15] U. Klabunde, S. D. Ittel, *J. Mol. Catal.* **1987**, *41*, 123–134.

[16] U. Klabunde, R. Mulhaupt, T. Herskovitz, A. H. Janovicz, J. Calabrese, S. D. Ittel, *J. Polym. Sci. Part A* **1987**, *25*, 1989–2003.

[17] R. Soula, J. P. Broyer, M. F. Llauro, A. Tomov, R. Spitz, J. Claverie, X. Drujon, J. Malinge, T. Saudemont, *Macromolecules* **2001**, *34*, 2438–2442.

[18] P. Kuhn, D. Sémeril, C. Jeunesse, D. Matt, P. Lutz, R. Welter, *Eur. J. Inorg. Chem.* **2005**, 1477–1481.

[19] M. Huhn, M. Burgard, D. Matt, J. Steiner (EEHEICS), DE-4415725, **1994**.

[20] D. Matt, M. Huhn, M. Bonnet, I. Tkatchenko, U. Englert, W. Kläui, *Inorg. Chem.* **1995**, *34*, 1288–1291.

[21] W. Keim, R. P. Schulz, *J. Mol. Catal.* **1994**, *92*, 21–33.

[22] M. Peuckert, W. Keim, *Organometallics* **1983**, *2*, 594–597.

[23] T. M. Gomes Carneiro, J. Dupont, M. Luke, D. Matt, *Quim. Nova* **1988**, *11*, 215–217.

[24] H. Qichen, X. Minzhi, Q. Yanlong, X. Weihua, S. Meicheng, T. Youqi, *J. Organomet. Chem.* **1985**, *287*, 419–426.

[25] P. J. Flory, *J. Am. Chem. Soc.* **1940**, *62*, 1561–1565.

[26] K. Hirose, W. Keim, *J. Mol. Catal.* **1992**, *73*, 271–276.

[27] J. Pietsch, P. Braunstein, Y. Chauvin, *New J. Chem.* **1998**, *22*, 467–472.

[28] 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.

[29] J. Heinicke, M. Koesling, R. Brüll, W. Keim, H. Pritzkow, *Eur. J. Inorg. Chem.* **2000**, 299–305.

[30] O. Kristen, J. Heinicke, W. Keim, M. Köhler, M. He (BASF AG), DE-19947519, **2001**.

[31] J. M. Malinoski, M. Brookhart, *Organometallics* **2003**, *22*, 5324–5335.

[32] J. Heinicke, M. Köhler, N. Peulecke, M. He, M. K. Kindermann, W. Keim, G. Fink, *Chem. Eur. J.* **2003**, *9*, 6093–6107.

[33] J. Heinicke, M. Köhler, N. Peulecke, W. Keim, *J. Catal.* **2004**, *225*, 16–23.

[34] J. Heinicke, M. Köhler, N. Peulecke, M. K. Kindermann, W. Keim, M. Köckerling, *Organometallics* **2005**, *24*, 344–352.

[35] J. Heinicke, N. Peulecke, M. Köhler, M. He, W. Keim, *J. Organomet. Chem.* **2005**, *690*, 2449–2457.

[36] M. S. W. Chan, L. Deng, T. Ziegler, *Organometallics* **2000**, *19*, 2741–2750.

[37] A. L. Monteiro, M. O. de Souza, R. F. de Souza, *Polym. Bull.* **1996**, *36*, 331–336.

[38] P. Braunstein, Y. Chauvin, S. Mercier, L. Saussine, *C. R. Chim.* **2005**, *8*, 31–38.

[39] R. F. de Souza, L. C. Simon, M. C. M. Alves, *J. Catal.* **2005**, *214*, 165–168.

[40] F. Ramirez, S. Dershowitz, *J. Org. Chem.* **1957**, *22*, 41–45.

[41] A. J. Mota, A. Dedieu, P. Kuhn, D. Matt, R. Welter, M. Neuburger, *Dalton Trans.* **2005**, 3155–3160.

[42] P. A. Chopard, R. J. G. Searle, F. H. Devitt, *J. Org. Chem.* **1965**, *30*, 1015–1019.

[43] B. C. Hamper, *J. Org. Chem.* **1988**, *53*, 5558–5562.

[44] COLLECT Software, Nonius BV, **1997–2001**.

[45] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435–436.

[46] D. J. Watkin, C. K. Prout, P. W. Carruthers, P. W. Betteridge, R. I. Cooper, *CRYSTALS,* Issue 11, Chemical Crystallography Laboratory, Oxford, UK, **2001**.

[47] J. R. Carruthers, D. J. Watkin, *Acta Crystallogr. Sect. A* **1979**, *35*, 698–699.

[48] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100.

[49] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.

[50] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.

[51] Gaussian 03 (Revision C.02), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyen-

gar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian Inc., Wallingford, CT, **2004**.

[52] W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257.

[53] P. C. Hariharan, J. A. Pople, *Mol. Phys.* **1974**, *27*, 209.

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