

The impact of P substituents on the oligomerization of ethylene with nickel 2-diphenyl and 2-dicyclohexylphosphinophenolate phosphine catalysts

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Dedicated to Professor Gerd-Volker Röschenhaler on the occasion of his 60th birthday

Abstract

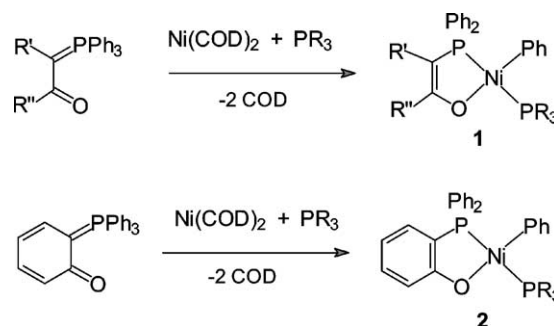
Solutions of 2-diphenyl- or 2-dicyclohexylphosphinophenol, nickel bis(1,5-cyclooctadiene), and a tertiary phosphine R₃P in toluene oligomerize ethylene in most cases with high selectivity to linear α -olefins. The molecular weights can be tuned by the catalyst composition. Molecular weights are generally lower with Ph₂P[^]ONi than with *c*Hex₂P[^]ONi catalysts and in the presence of R₃P additives, but basicity-dependent effects of various triarylphosphine additives on the molecular weights and relative reaction rates, displayed by pressure-time plots, are rather different or opposite for Ph₂P[^]ONi and *c*Hex₂P[^]ONi catalysts.

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1. Introduction

The oligomerization of ethylene to linear α -olefins by the Shell Higher Olefins Process (SHOP) is of industrial as well as of academic interest and has stimulated intensive research on nickel catalysts with P[^]O- and related chelating ligands [1–6]. It was shown that catalytically active and selective 2-phosphinoenolate and 2-phosphinophenolate nickel complexes are chelates with square-planar geometry [7–12]. In the single-component catalysts the activation temperature depends strongly on the nature of the ligand *trans* to oxygen [1,13,14] while the molecular weights are particularly influenced by substituents at phosphorus [12–16] and by solvents or ligands interacting or bound in *trans* position to phosphorus, e.g., donor solvents or pyridine [13,16–20], phosphines [19,21], or ylides [22,23]. A study of the influence of various phosphines R₃P in diphenylphosphinoenolate and -phenolate phenylnickel phosphine single-component oligomerization catalysts **1** and **2**, accessible from α -keto- or *o*-chinone-triphenylphosphorus ylides, Ni(COD)₂, and the



Scheme 1.

respective phosphine (Scheme 1) [7,8], demonstrated widely varying activities and mass distributions of the resulting ethylene oligomers, somewhat higher molecular weights, and different response toward PMe₃ and P*c*Hex₃ ligands on the use of the phosphinophenolate as compared to the phosphinoenolate catalysts (**1** C₄–C₃₀; **2** C₄–C₉₀) [21].

In investigations of phosphinophenolate methylnickel trimethylphosphine complexes bearing varying R₂P groups we observed a strong influence of the P substituents in addition to the PMe₃ content on the catalytic activity toward ethylene and the molecular weights of the oligomers [12].

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To learn more on the interplay of the phosphino groups of the P[⊖]O chelate and the PR₃ ligand in the *trans* position, we studied the oligomerization of ethylene with catalysts prepared in situ from 2-diphenyl- or 2-dicyclohexylphosphinophenol **3a** or **3b**, respectively, Ni(COD)₂ (COD 1,5-cyclooctadiene), and a phosphine additive and report here on the results.

2. Experimental

2.1. General

All operations with phosphines and catalyst solutions were carried out under carefully dried, oxygen-free argon, using Schlenk techniques. Toluene was ketyl-dried and distilled before use. Ni(COD)₂ [24] and the phosphinophenols **3a** [25] and **3b** [13] were synthesized as reported, and other chemicals were purchased. Ethylene (99.5%, Air Liquide) was used without further treatment. GC analyses were carried out using a Siemens SICHRMAT 1-4, column SE54-CS(25m), 50–280 °C, 5 min isotherm, 8 or 12 °C/min, reference *n*-nonane, or a gas chromatograph Hewlett Packard 5890, column HP-5(30m) (crosslinked 5% PhMe silicone), 40–150 °C, 10 min isotherm, 4 °C/min. ¹H NMR spectra of polymers were measured on a multinuclear FT-NMR spectrometer ARX300 (Bruker) (300.1 MHz) at 100 °C, acquisition time 4.9–5.4 s, delay 1.0 s, using concentrated solutions of the polyethylene samples prepared by swelling for 1 day at 120 °C under argon in C₆D₅Br (*p*-CH₃, δ = 7.23 as reference). Melting points were determined with a Sanyo Gallenkamp melting-point apparatus. The maximum turnover frequency (TOF_{max}) was determined in experiments carried out with online pressure registration (HEJU pressure sensor 1–100 bar from Juchheim connected to digital multimeter and PC) from the slope of the steepest (nearly) linear pressure decrease (pressure vs ethylene amount in 20 mL of toluene calibrated at 100 °C after heating for 1 h; effects of products on the solubility of ethylene neglected).

2.2. Oligomerization: general procedure

3a (27.8 mg, 100 μmol) or **3b** (29.0 mg, 100 μmol) and Ni(COD)₂ (27.5 mg, 100 μmol) were dissolved in toluene (each 8 mL) at 0 °C, combined, and stirred for 5 min at 0 °C and for 10 min at 20 °C to give orange or yellow solutions. Then, the corresponding amount of the phosphine (Table 1) dissolved in toluene (4 mL) was added. Me₃P (as 1 M solution in toluene), *c*Hex₃P, and TMOP did not induce significant color changes while addition of *o*Tol₃P or *m*Tol₃P furnished light (**3a**/Ni/R₃P) or dark red (**3b**/Ni/R₃P), *p*Tol₃P darker and Ph₃P deep red solutions for both **3a**- and **3b**-based catalysts. The precatalyst solution was stirred for 2 min and transferred by a syringe (Teflon canula) to a stainless-steel autoclave (75 mL), equipped with a Teflon-coated magnetic stirrer, gas inlet and sample inlet valves,

mechanic or electronic pressure gauge, and a safety diaphragm. Ethylene was added (see Table 1, *p*_{start} ca. 50 bar), and the autoclave was placed into a preheated bath (100 °C) and heated overnight (ca. 15 h). After cooling unreacted ethylene was allowed to escape, butenes were condensed in a cooling trap (−78 °C). The remaining product, cooled to −25 °C, was transferred to a flask, and volatiles were flash-distilled (80–100 °C/1–10^{−2} Torr) into a cooling trap (−196 °C). Residual waxes or polymers were stirred for 1 day with methanol/hydrochloric acid (1/1), washed with methanol, and dried. The mp and ¹H NMR data were determined after extraction of lower oligomers with 50 mL of CH₂Cl₂; mass loss was usually < 2%. Conversion, isolated products, and characteristic data of polymers are given in Table 1, and the oligomer composition in Table 2 so far analyzed by GC and exceeding 5% of the flash distillate. (Differences between the amount of converted ethylene and the amount of isolated products are due mainly to loss of butenes, and in the case of polyethylene also to loss of soluble oligomers.)

3. Results and discussion

3.1. Introductory remarks to the catalyst system

Recently we have shown that catalysts generated in situ from equimolar amounts of 2-diphenyl- or 2-dicyclohexylphosphinophenol (**3a** or **3b**) and Ni(COD)₂ polymerize ethylene like methallylnickel 2-diphenyl- or 2-dicyclohexylphosphinophenolate single-component catalysts with high selectivity for linear α-olefins. The similarity is due to the formation of allyl-type precursor complexes detected in solution by ¹H, ¹³C, and ³¹P NMR spectroscopy [13] and related activation pathways (Scheme 2). Both catalyst types derived from **3a** furnish low molecular weight polyethylenes (*M*_w ca. 3000–5000 g mol^{−1}) while catalysts based on **3b** give much higher chain lengths (*M*_w ca. 60,000 g mol^{−1}) under comparable conditions. Replacement of the solvent toluene by a variety of O-donor solvents improves the catalyst lifetime and productivity but diminishes the molecular weights and slightly the reaction rate while the selectivity is not influenced. Additions of tetrahydrothiophene (THT) or pyridine (pyr) to the precatalyst solution in toluene have a much stronger impact on the molecular weight and the reaction rate and improve the catalyst lifetime as expressed by the pressure time plot (Fig. 1) [13]. The effects of phosphine additives which are soft Lewis bases like THT are diverse and dependent on the P substituents, and are reported here in more detail.

3.2. Influence of the molar ratio of 2-phosphinophenolate, nickel, and triphenylphosphine

The molar ratio of 2-phosphinophenol and Ni(COD)₂ (in the following abbreviated as **3**/Ni) influences strongly the

Table 1
Oligomerization of ethylene with catalysts formed from **3**, Ni(COD)₂, and R₃P^a

Exp.	Ligands (μmol)	C ₂ H ₄ (g), conversion (%), TON (mol mol ⁻¹)	TOF _{max} (mol mol ⁻¹ h ⁻¹), <i>t</i> _{start} (min)	Products ^c (g)	Solid polymer: mp (°C), molar mass ^f (g mol ⁻¹)
1	3a (100) [13]	12.6 (50–66) 2250–2960	8000–23,000 (22–16)	Oligomers (< 0.1) HDPE (6.0–8.1) ^d	mp 124–126 <i>M</i> _{NMR} 1300–2000
2	3a (120)	12.6 (76) 3420	26,000 (15)	Wax (0.5) HDPE (9.1) ^d	mp 119–120 <i>M</i> _{NMR} 1600–1700
3	3a (100) Ph ₃ P (100)	14.6 (95) 4950	28,000 (13)	C ₄ and C ₆ (2.5) Oligomers (2.8) Wax (8.6)	
4	3a (100) Ph ₃ P (200)	13.6 (> 99) 4850	10,000 (13)	Butenes (1.0) Oligomers (8.4) Wax (3.2)	mp < 50
5	3a (100) Ph ₃ P (300)	11.9 (> 99) 4240		Butenes Oligomers (2.4) Wax	
6	3a (100) Ph ₃ P (400)	18.0 (97) 6240		Butenes (> 3.1) Oligomers (7.7)	
7	3a (100) Ph ₃ P (500)	20.8 (96) 7130	6000 (12)	Butenes (> 2.3) Oligomers (11.7)	
8	3a (100) Ph ₃ P (700)	18.7 (87) 5810		Butenes (> 4.6) Oligomers (8.6)	
9	3a (100) Ph ₃ P (800)	13.4 (95) 4530		Cond. butenes (1.8) Oligomers (10.4)	
10	3a (100) Ph ₃ P (900)	13.3 (89) 4210		Cond. butenes (1.5) Oligomers (10.0)	
11	3a (100) Ph ₃ P (1000)	18.6 (71) 4700	2000 (12)	Butenes (> 4.4) Oligomers (5.4)	
12	3a (100) Ph ₃ P (1500)	14.0 (70) 3500		Cond. butenes (2.9) Oligomers (6.9)	
13	3a (100) <i>p</i> Tol ₃ P (100)	10.1 (> 99) 3600	8000 (10)	Butenes (> 1.1) Oligomers (5.8)	
14	3a (100) <i>m</i> Tol ₃ P (100)	13.0 (99) 4600	4000 (13)	Butenes (1.8) Oligomers (4.7) Wax (6.4)	
15	3a (100) <i>m</i> Tol ₃ P (300)	14.0 (99) 4950		Butenes (7.4) Oligomers (6.4) Trace wax	
16	3a (100) <i>m</i> Tol ₃ P (500)	13.2 (92) 4310	4500 (10)	Butenes (8.8) Oligomers (4.0)	
17	3a (100) <i>o</i> Tol ₃ P (100)	13.7 (51) 2500	12,000 (23)	Oligomers (0.1) HDPE (6.5) ^d	mp 124–125 <i>M</i> _{NMR} 1900–2100
18	3a (100) Mes ₃ P (100)	9.5 (99) 3350	6000 (23)	Oligomers (0.1) HDPE (9.2) (Me/Vin 2.6–3.0, α-olefins 90%)	mp 120–122 <i>M</i> _{NMR} 4000–4300 <i>M</i> _w 4600 <i>M</i> _n 1950
19	3a (100) TMOP ^b (100)	11.5 (88) 3600	16,000 (23)	Oligomers (0.3) HDPE 9.8 (Me/Vin 1.9–2.3, α-olefins 92%)	mp 122–124 <i>M</i> _{NMR} 2300–2700 <i>M</i> _w 3400 <i>M</i> _n 1300
20	3a (100) Me ₃ P (100)	11.3 (70) 2800	300 (39)	Butenes (> 3.8) Oligomers (1.5)	
21	3a (115) Et ₃ P (115)	16.0 (72) 3600	1600 (22)	Butenes (> 4.8) Oligomers (6.8)	
22	3a (110) Et ₃ P (330)	15.0 (44) 2150	500 (36)	Butenes (> 4.4) Oligomers (2.3)	
23	3a (100) Cy ₃ P (100)	6.8 (57) 1390	2000 (15)	Oligomers (0.1) Wax	

(continued on next page)

Table 1 (Continued)

Exp.	Ligands (μmol)	C_2H_4 (g), conversion (%), TON (mol mol^{-1})	TOF _{max} ($\text{mol mol}^{-1} \text{h}^{-1}$), t_{start} (min)	Products ^c (g)	Solid polymer: mp ($^{\circ}\text{C}$), molar mass ^f (g mol^{-1})
24	3a (120) Cy ₃ P (120)	15.0 (77) 3560	16,000 (16)	Oligomers (0.5) Wax (11.1) (Me/Vin 1.3, α -olefins 94%)	mp 112–115 M_{NMR} 840
25	3b (100) [13]	11.1–15.3 (62–72) 2460–3920	15,000 (29)	Oligomers (< 0.1) HDPE ^d	mp 133–134 M_{w} 58,900 M_{n} 26,500
26	3b (100) Ph ₃ P (100)	12.9–15.0 (60–70) 3200	6000–8000 (20 ^h –24)	Butenes (\leq 0.3) Oligomers (0.2–0.7 ^h) HDPE (8.8–8.0) ^d	mp 96–98 ^h mp 124–126 M_{NMR} 800 ^h –2500
27	3b (100) Ph ₃ P (500)	12.8 (99) 4530	8000 (17)	Butenes (0.1) Oligomers (0.8) HDPE (11.8) ^d	mp 110–112 M_{NMR} 1100
28	3b (100) Ph ₃ P (1000)	13.0 (0)			
29	3b (100) <i>p</i> Tol ₃ P (100)	12.3 (81) 3565	11,000 (20)	Oligomers (< 0.1) HDPE (9.8) ^d	mp 128–130 M_{NMR} 2300
30	3b (100) <i>m</i> Tol ₃ P (100)	13.8 (73) 3600	8000 (19)	Oligomers (< 0.1) HDPE (9.9) ^d	mp 126–128 M_{NMR} 2550
31	3b (100) <i>m</i> Tol ₃ P (500)	12.0 (0)			
32	3b (100) <i>o</i> Tol ₃ P (100)	13.1 (70) 3280	9000 (21)	Butenes (0.6) Oligomers (< 0.1) HDPE (8.5) ^d	mp 131–132 M_{NMR} 6800
33	3b (100) TMOP ^b (300)	13.0 (53) 2460	6000	Oligomers (0.2) HDPE (6.7) (Me/Vin 2.5, α -olefins 66%) ^d	mp 126–128 M_{NMR} 2300
34	3b (100) TMOP ^b (700)	12.6 (38) 1710	7000 (33)	Oligomers (0.1) HDPE (4.7) ^e (Me/Vin 2.3, α -olefins 88%)	mp 132–133 M_{NMR} 4700
35	3b (100) Me ₃ P (100)	12.6 (58) 2600	500 (32)	Butenes ^g Oligomers (0.7) Wax	mp 89–93
36	3b (100) Me ₃ P (300)	12.7 (44) 2000	100 (48)	Butenes ^g Oligomers (2.6) Wax	

^a Ni(COD)₂ 100 μmol , solvent toluene.

^b **TMOP** is [2,4,6-(MeO)₃C₆H₂]₃P.

^c Butenes: amount of condensed gaseous products (cooling trap -78°C) and of butenes in the flash-distilled oligomer solution; oligomers: amount of dist. oligomers except butenes in the distilled oligomer solution analyzed by GC.

^d Content of α -olefins \geq 96%, Me/Vin ratio 1.2–2.0 (based on ¹H NMR integration).

^e Mass loss on extraction with CH₂Cl₂ 7%, crude polymer mp 123–126 $^{\circ}\text{C}$.

^f M_{NMR} based on ¹H NMR integration; M_{w} and M_{n} based on GPC (HDPE not extracted with CH₂Cl₂).

^g Uncertain, low content.

^h Shorter formation time caused lower molecular weights.

properties of the resulting catalysts. Excess Ni(COD)₂ with respect to a 1/1 molar ratio of **3**/Ni is decomposed and diminishes the productivity of the catalyst. A small excess of 2-phosphinophenol, e.g., **3a**/Ni (1.2/1), is tolerated and even increases the ethylene conversion (Table 1, Fig. 2) without marked effects on the molecular weights of the oligomers and the selectivity while a molar ratio of 2/1 **3a**/Ni leads to inactivity. The phosphorus/nickel ratio is not the crucial point in the suppression of catalytic activity. Triphenylphosphine, lacking the 2-hydroxyl group of **3a**, can be added in

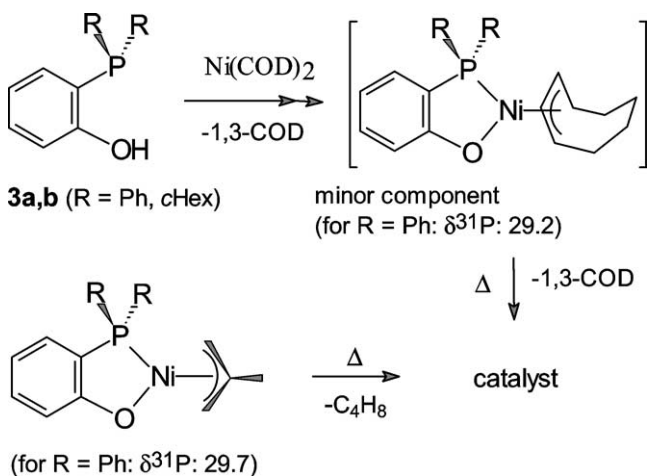
a 10–15 molar excess to the **3a**/Ni (1/1) precatalyst without cessation of the catalytic conversion of ethylene. The deactivation is thus caused by formation of a stable bis(P[∩]O-chelate) complex (cf. [25,26]). However, the conversion of ethylene in the presence of triphenylphosphine is considerably different from that in its absence. Using catalysts formed from **3a**, Ni(COD)₂, and Ph₃P in toluene in molar ratios of 1/1/1 up to 1/1/15, the turnover numbers and catalyst lifetime rise with the Ph₃P content until a maximum at a molar ratio of roughly 1/1/5, then they decrease, but even

Table 2
Oligomer composition C_{4–20}

Exp.	∑ oligomers in distillate ^a , % (g)	C _n , % (linear α-olefins, %)								
		C ₄	C ₆	C ₈	C ₁₀	C ₁₂	C ₁₄	C ₁₆	C ₁₈	C ₂₀
3	14.1 (2.8)	–	11.3 (95)	30.4 (96)	29.7 (94)	20.2 (94)	6.6 (95)	1.4	0.3	0.05
4 ^b	32.7 (9.4)	11.4 (90)	10.9 (78)	6.1 (80)	2.7 (78)	1.0 (80)	0.2			
5	13.4 (2.4)	0.7 (68)	29.1 (56)	30.3 (60)	24.3 (54)	11.7 (57)	2.9 (59)	0.7 (65)	0.2	0.1
6	38.5 (10.6)	27.0 (90)	24.0 (80)	16.9 (81)	11.5 (74)	7.6 (74)	4.9 (72)	3.2 (69)	1.9 (70)	1.1 (73)
7	43.8 (13.4)	12.5	30.4 (91)	22.0 (91)	14.2 (85)	8.6 (85)	5.2 (81)	3.1 (78)	1.8 (78)	1.0 (80)
8	40.7 (11.7)	26.6 (> 99)	33.0 (95)	19.7 (93)	10.6 (88)	5.4 (88)	2.6 (90)	1.1 (96)	0.5	0.2
11	32.4 (8.0)	32.0 (> 99)	39.1 (96)	17.9 (95)	7.2 (88)	2.5 (92)	0.9 (96)	0.3	0.08	0.02
13	27.0 (6.8)	15.4 (70)	22.6 (46)	18.6 (44)	13.8 (44)	9.9 (44)	6.3 (44)	4.2 (41)	2.9 (40)	2.1 (40)
14	20.3 (4.8)	1.7	22.5 (58)	22.7 (61)	20.2 (59)	17.6 (58)	13.9 (56)	1.3 (54)	0.1	0.02
15	24.7 (6.5)	0.6	32.8 (38)	31.0 (45)	18.8 (35)	11.0 (38)	4.6 (36)	0.9 (34)	0.2 (40)	0.1 (75)
16	17.2 (4.0)	1.7	44.6 (88)	32.4 (89)	13.9 (78)	5.5 (79)	1.7 (76)	0.2		
20	18.7 (4.1)	63.9 (91)	26.2 (94)	7.5 (89)	1.9 (84)	0.4	0.1			
21	36.2 (9.8)	> 41 (99)	30.0 (94)	14.1 (96)	4.7 (93)	1.8	1.1			
22	20.2 (4.5)	> 70 (99)	15.5 (90)	2.9 (82)	0.2	< 0.01				
26	4.2 (0.7)	17.6 (72)	27.2 (83)	24.1 (99)	19.2 (97)	10.0 (96)	1.9			
27	5.9 (1.2)	3.9 (98)	18.8 (94)	23.3 (94)	23.3 (93)	19.5 (94)	9.1 (93)	1.9	0.2	
35	3.3 (0.6)	0.4	9.7 (94)	19.5 (91)	20.9	21.9	19.7	7.0	0.8	0.1
36	12.4 (2.6)	4	32 (98)	28.3 (98)	21.1 (98)	10.0 (97)	3.2	1.0	0.3	

^a Solvent and volatile oligomers flash distilled at 80–100 °C/1–10^{–2} Torr.

^b Higher boiling components not distilled (waxy residue, 3.2 g).



Scheme 2.

for a 15-fold molar excess of Ph₃P the conversion of ethylene exceeds or reaches that in absence of Ph₃P (Table 1). The reaction rate, illustrated by the pressure–time plot (Fig. 2), is increased in the presence of a small amount of triphenylphosphine (1/1/1) and likewise in the case of a small excess of **3a** (1.2 **3a**/Ni), probably by prevention or retardation of catalyst deactivation. Larger portions of Ph₃P compete with ethylene for coordination and result in an increasing decrease of the reaction rate while the heating/induction period¹ is slightly shortened. The chain lengths of the resulting α-olefins decrease with growing Ph₃P/**3a** ratio. The cat-

¹ The reaction starts around 70 °C, reached 12–14 min after the beginning of heating. If the precatalyst solution is added to a preheated solution of ethylene in toluene (80 °C) the induction period is very short but the lifetime of the catalyst is low.

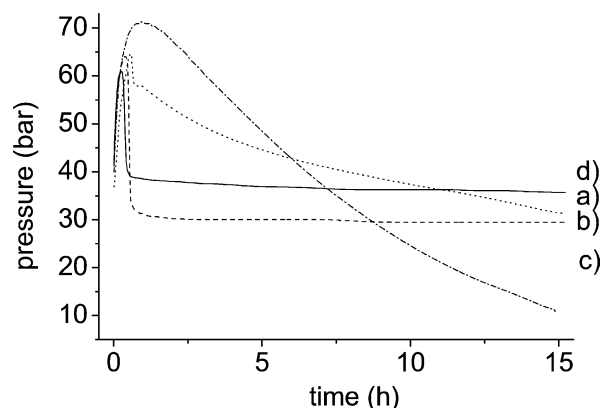


Fig. 1. Pressure–time plots for batch polymerization of ethylene with catalysts formed in situ from **3a** and Ni(COD)₂: (a, solid line) in toluene, (b) in thf, (c) in toluene/pyr (9/1), (d, dotted line) in toluene/tht (9/1) (each 0.1 mmol **3a** and Ni(COD)₂, solvents 20 mL, p_{start} 50 bar, bath temperature 100 °C) [13].

alyst **3a**/Ni/Ph₃P (1/1/1) converts ethylene mainly to waxy oligomers while catalysts with higher portions of Ph₃P give rise to lower liquid oligomers and butenes (Table 2). For catalysts **3a**/Ni/Ph₃P (1/1/ n) $n \geq 5$ the oligomer distribution fits approximately with a Schulz–Flory distribution [27–29]. The β value, the ratio of the rates of elimination and chain growth reactions, is about 0.6, 0.9, 1.4 for $n = 5, 7, 10$. The selectivity for linear α-olefins is lower than in the polymerization of ethylene by **3a**/Ni [13] and ranges from 60 to > 95% with a minimum for the catalyst **3a**/Ni/Ph₃P (1/1/3).

3.3. Influence of basicity and steric demand of the phosphine additive

Studies with other phosphine additives reveal that the effects on the conversion of ethylene in the presence of

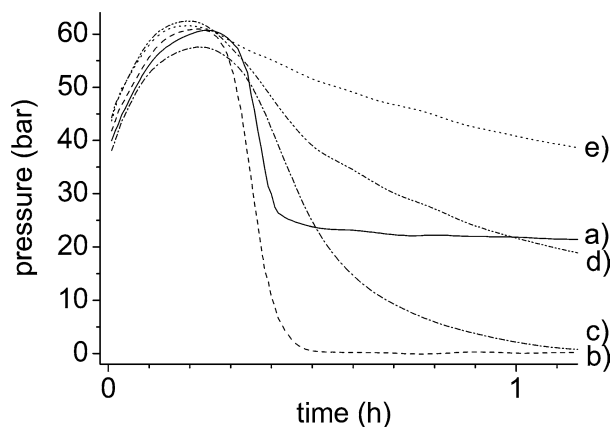


Fig. 2. Pressure–time plots for batch oligomerization of ethylene, catalysts formed from **3a**, Ni(COD)₂, and Ph₃P in toluene: (a) 1/1.2/0, (b) 1/1/1, (c) 1/1/2, (d) 1/1/5, (e) 1/1/10.

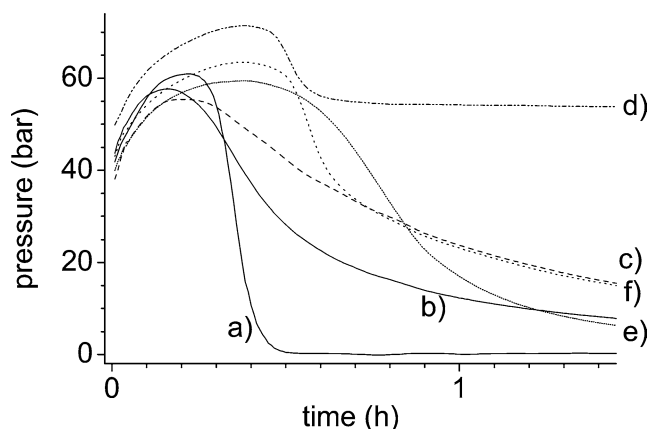


Fig. 3. Pressure–time plots for batch oligomerization of ethylene with catalysts **3a**/Ni/triarylphosphine (1/1/1); R₃P: (a) Ph₃P, (b) *p*Tol₃P, (c) *m*Tol₃P, (d) *o*Tol₃P, (e) Me₃P, (f) [2,4,6-(MeO)₃C₆H₂]₃P.

3a/Ni/R₃P (1/1/1) catalysts depend strongly on the basicity and bulkiness of the added phosphine R₃P (Tables 1 and 2). Replacement of triphenylphosphine (pK_a 2.73, θ 145° [30,31]) by the more basic tris(*p*-tolyl)phosphine (pK_a 3.84, θ 145°) leads to a strong decrease of the oligomerization rate (Fig. 3) and a strong drop of the molecular weights and the selectivity for linear α -olefins from about 95 to 45%. Replacement by tris(*m*-tolyl)phosphine (pK_a 3.3, θ 165°) which is less basic but bulkier than *p*Tol₃P causes a slower conversion, similar low molecular weights, and somewhat lower loss in selectivity (60–70% α -olefins). An increase of the amount of *m*Tol₃P (to 1/1/3 and 1/1/5) has no marked effect on the reaction rate but similar to Ph₃P the selectivity is lowest for the 1/1/3 molar ratio. The slowest reaction rates are exhibited in those cases where small trialkylphosphines (Me₃P, Et₃P; pK_a 8.65, 8.69; θ 118°, 132° [30,31]) are added (Fig. 4, Table 1). The small space demand along with the high basicity and soft character allows rather strong coordination (for PMe₃ stronger than PEt₃) on account of the interactions with ethylene and other donors but does not block the catalytic conversion and fur-

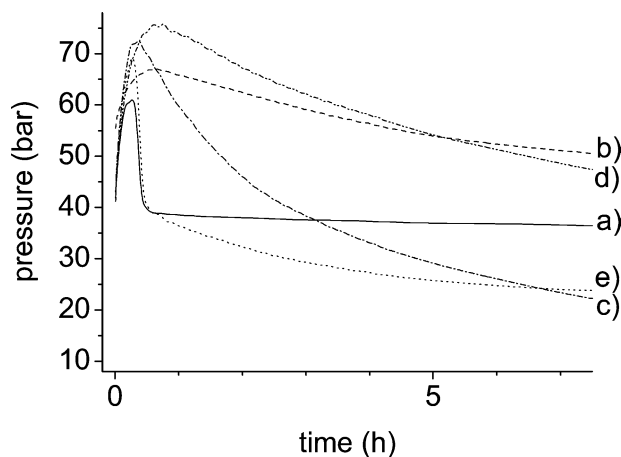


Fig. 4. Pressure–time plots for batch oligomerization of ethylene with: (a) **3a**/Ni (reference) and with **3a**/Ni/trialkylphosphine, (b) Me₃P (1/1/1), (c) Et₃P (1/1/1), (d) Et₃P (1/1/3), (e) *c*Hex₃P (1/1/1).

nishes low molecular weight oligomers (Table 2). Increasing concentration of the small trialkylphosphine increases the effect on the reaction rate and molecular weights but diminishes the conversion of ethylene by deactivation at a higher residual ethylene concentration (pressure). The rather more basic but much bulkier tricyclohexylphosphine (pK_a 9.7, θ 170° [30,31]) behaves like more bulky triarylphosphines as tris(*o*-tolyl)phosphine (θ 194°), trimesitylphosphine (θ 212°), or tris(2,4,6-trimethoxyphenyl)phosphine (PTMOP) and allows maximum turnover frequencies and formation of polymer chain lengths similar to those in the absence of a phosphine additive. The formation time, however, is extended and the more basic *c*Hex₃P, Me₃P, and PTMOP additives stabilize the catalyst and cause higher productivity than in its absence (Figs. 3 and 4, Table 1). A lower ethylene to catalyst ratio, e.g., conversion of ethylene by **3a**/Ni/*c*Hex₃P (1/1/1) at p_{start} 30 bar, leads to slower reaction rates and conversions. The R₃P additives diminish the selectivity for linear α -olefins in oligomers with short chain lengths, but not to a significant extend in the polymers ($\geq 90\%$ α -olefins). Finally, it should be noted that an addition of triethylphosphite, possessing low P basicity but good π -acceptor properties, causes inactivity already at a molar ratio **3a**/Ni/(EtO)₃P (1/1/1).

3.4. Influence of the P basicity of the 2-phosphinophenol

The nickel catalyst formed from the more P-basic 2-dicyclohexylphosphinophenol **3b** and Ni(COD)₂ gives rise, as noted above, to much higher molecular weights in the polymerization of ethylene than the **3a**/Ni catalyst. This feature is maintained, though in much lower measure, in the presence of phosphine additives. The catalyst systems **3b**/Ni/ar₃P (1/1/1) (ar₃P = Ph₃P, *p*Tol₃P, *m*Tol₃P, *o*Tol₃P, Me₃P, TMOP) convert ethylene mainly to low molecular weight high-density polyethylenes (HDPE), and the molecular weights of the HDPE formed with catalysts from **3b**/Ni and bulky arylphosphines, *o*Tol₃P or TMOP, are higher than

those of HDPE obtained with related catalysts based on **3a**. Excess of triarylphosphines increases the productivity, e.g., in **3b**/Ni/Ph₃P (1/1/5), or stops the catalytic activity of **3b**/Ni catalysts, e.g., **3b**/Ni/Ph₃P (1/1/10) or **3b**/Ni/*m*Tol₃P (1/1/5), rather than to shift the conversion toward markedly lower oligomers as observed for **3a**/Ni/Ph₃P (1/1/*n*) (*n* = 1 to 15) or **3a**/Ni/*m*Tol₃P (1/1/*n*) (*n* = 1, 3, 5). Finally, even the addition of the small and highly P-basic trimethylphosphine causes mainly formation of waxy polymers. However, in this case the amount of lower oligomers is higher for the catalyst **3b**/Ni/Me₃P (1/1/3) as compared to **3b**/Ni/Me₃P (1/1/1) (Tables 1 and 2).

The catalyst systems **3b**/Ni/R₃P distinguish themselves from **3a**/Ni/R₃P not only by different effects on the molecular weights and catalyst deactivation, but also by the impact of triarylphosphines on the reaction rate. Under comparable conditions, Ph₃P and *m*Tol₃P cause similar drops of the maximum reaction rates (TOF_{max} 6000–9000 mol mol⁻¹ h⁻¹) while the bulkier phosphine *o*Tol₃P displays a weaker influence (TOF_{max} 11,000 mol mol⁻¹ h⁻¹). Addition of the highly basic but even more bulky triarylphosphine TMOP (three and seven molar excess) cause only slightly diminished reaction rates (6000–7000 mol mol⁻¹ h⁻¹). In all cases, the reaction rates decrease strongly after a more or less short period of a steep pressure drop in the beginning (Fig. 5). As the rate of the polymerization of ethylene by **3**/Ni in toluene is diminished by addition of olefins [13] or by use of liquid α -olefins in place of toluene, in case of **3b**/Ni much stronger than by **3a**/Ni [32], this is attributed to interactions of the catalyst **3b**/Ni/R₃P (R = aryl) with the α -olefins formed. Excess of triphenylphosphine suppresses this influence as shown by the rapid conversion of ethylene (99% within 1.1 h) to HDPE by **3b**/Ni/Ph₃P (1/1/5) (Table 1).

In contrast to the different response of **3a**/Ni and **3b**/Ni to triarylphosphine additives, the influence of the small and highly basic trimethylphosphine on the oligomerization rate is similar and strong in both **3a**- and **3b**-based nickel catalysts.

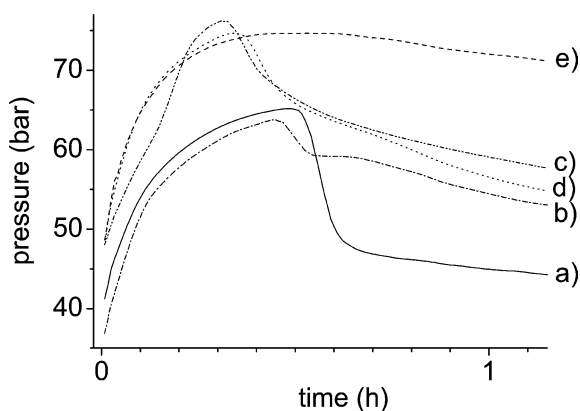
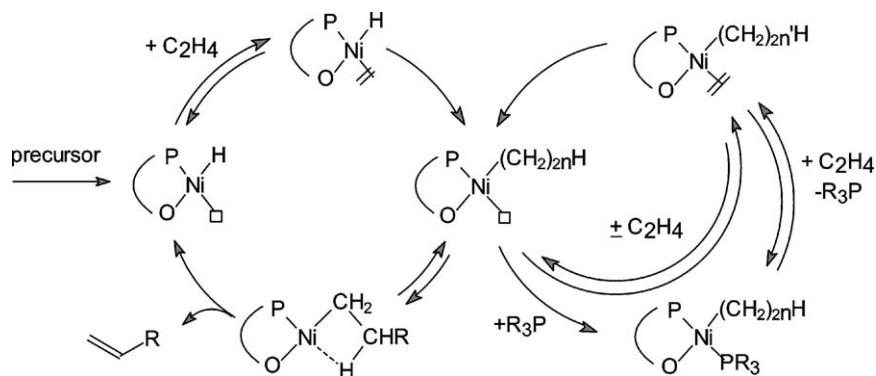


Fig. 5. Pressure–time plots for batch oligomerization of ethylene with **3b**/Ni and (a) no additive (reference), (b) Ph₃P, (c) *m*Tol₃P, (d) *o*Tol₃P, (e) Me₃P, each in 1/1/1 molar ratio.

4. Discussion

The above results show that the two types of phosphine ligands in in situ-formed nickel phosphinophenol(ate) phosphine catalysts, 2-R₂PC₆H₄OH and R₃P, have different functions in the oligomerization of ethylene. The necessity of one and the inactivity of systems with two phosphinophenol per nickel give evidence that the P, O ligand forms the essential structural feature, the stabilizing backbone of the nickel catalyst as seen in the known square-planar single-component organonickel phosphinophenolate phosphine oligomerization catalysts. The strong *trans* effect of the phosphino group allows rapid exchange of the *trans*-ligand by the nucleophiles present in the solution, ethylene, phosphine additives, and solvent, deactivation by a free phosphinophenolate ligand, or interactions with a β -hydrogen atom of the Ni-alkyl chain to start the olefin elimination step. The different properties of the catalyst systems based on **3a** and **3b**, respectively, indicate a distinct influence of the 2-diphenylphosphino and the 2-dicyclohexylphosphino group on the P–Ni bond in the P[⊖]ONi chelate and the interplay with the nucleophiles, controlled by σ -bonding, π -bonding, and steric factors. Such differences were also observed for defined variously P-substituted methylnickel 2-phosphinophenolate trimethylphosphine single component oligomerization catalysts [12], and a comparison may help to understand the behavior of the in situ catalysts.

Diisopropylphosphino derivatives were found to be more fluxional (sharp ³¹P NMR doublets only at –70 °C, diphenylphosphino derivatives –40 to –30 °C), to be catalytically more active (higher TON), and to give higher molecular weight oligomers than diphenylphosphino derivatives [12]. It is supposed that the more rapid replacement of PMe₃ in the complex by solvent (in absence of ethylene) and the longer oligomer chain lengths on use in ethylene oligomerization (smaller relative rate of olefin elimination versus chain growth) are due to weaker bonding or interactions of σ -donors (PMe₃, β -hydrogen atom of Ni-alkyl in transition state) opposite to the basic *i*Pr₂P ligand, and that the higher catalytic productivity is due to stronger fixation of the π -acidic ethylene (higher equilibrium concentrations of intermediate ethylene complexes) and subsequent insertion of ethylene into the Ni–C bond. The behavior of the in situ-formed catalysts **3a**/Ni/R₃P or **3b**/Ni/R₃P fits similarly with the assumption of higher equilibrium concentrations of intermediates with balanced charge at nickel as a main controlling factor (Scheme 3). Thus, the decreasing rate of ethylene conversion by **3a**/Ni/triarylphosphine with increasing concentration or basicity of triarylphosphines (so far as they are not too bulky) can be ascribed to favored coordination of phosphines (σ -donors, weak π -acceptors) opposite to the Ph₂P donor site, while the lower effect of triarylphosphines and stronger impact of olefins on the reaction rate in catalyses with **3b**/Ni/triarylphosphine (P basicity of **3b** higher than of **3a**) points to a shift in favor of *trans* interactions to ethylene or olefins (π -donors, π -acceptors).



Scheme 3.

The effect of small donors like trimethylphosphine remains strong, however, and suggests that the steric situation is also an important factor in the subtle balance of intermediates controlling the conversion of ethylene. The lowered selectivity of **3a**/Ni/R₃P catalysts containing *p*Tol₃P or *m*Tol₃P additives might be induced by a competing *trans* effect of the relatively basic triarylphosphine ligands which lower the stability of the P[⊖]O chelate.

5. Conclusions

Catalysts for the oligomerization of ethylene to α -olefins of defined molecular weight ranges and selectivity can be obtained from 2-diphenyl- or 2-dicyclohexylphosphinophenol, nickel bis(1,5-cyclooctadiene) and an appropriate amount of a suitable tertiary phosphine additive in toluene. The 2-phosphinophenols form the backbone of the nickel catalyst while the phosphine additives, competing with ethylene and olefins for coordination in the *trans* position to the 2-phosphino group, allow tuning of the catalyst properties. A rough estimation of the effects of other substituents or additives and of the scope and limits for application of such catalysts in the ethylene oligomerization should be feasible based on the above results and assumptions made to understand the in part controversial behavior of **3a**/Ni/PR₃ and **3b**/Ni/PR₃ catalysts.

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